Reinhold Environmental Ltd.

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Measurement of SO_3 Emissions

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Principle Methods used for Measuring SO3 Concentrations

Acid Dew Point

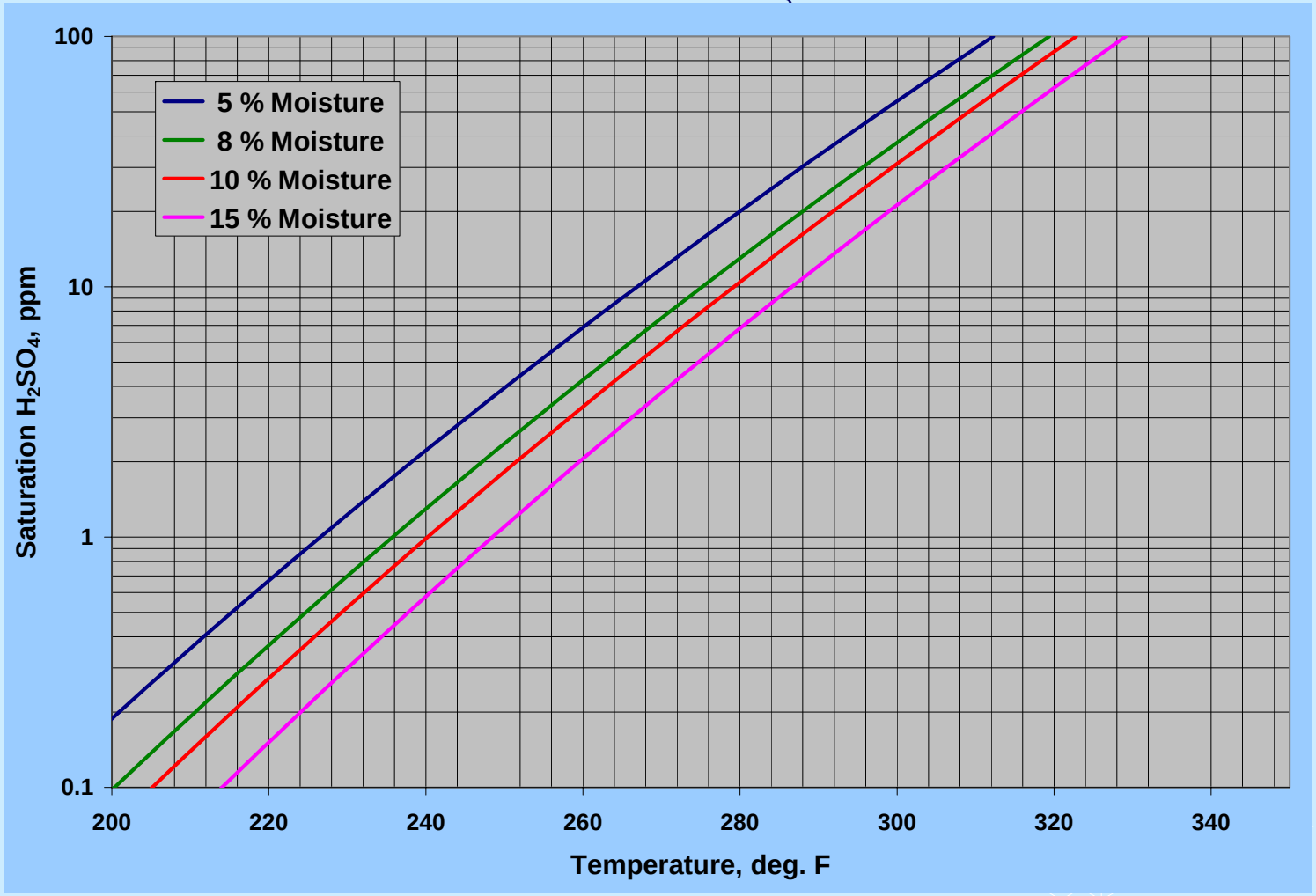
EPA Method 8

Controlled Condensation

Dew point meters detect formation of condensed acid film on a substrate.

Detection is typically by either electrical conduction across the surface of an insulator or by light scattering from the substrate surface.

Primary problem with the method is that the dew point depends on the moisture concentration in addition to the SO_3 concentration.



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Removal of SO_3 or H_2SO_4 from the flue gas can take place through a number of mechanisms:

- **Reaction with reagents injected for control of vapor phase SO_3/H_2SO_4**
- **Condensation on the heat exchanger surfaces in air preheaters**
- **Condensation and subsequent collection in the form of particles.**
- **Uptake by fly ash**

Significant removal can result from uptake on fly ash particles but the mechanisms are not fully understood and at present cannot be well predicted.

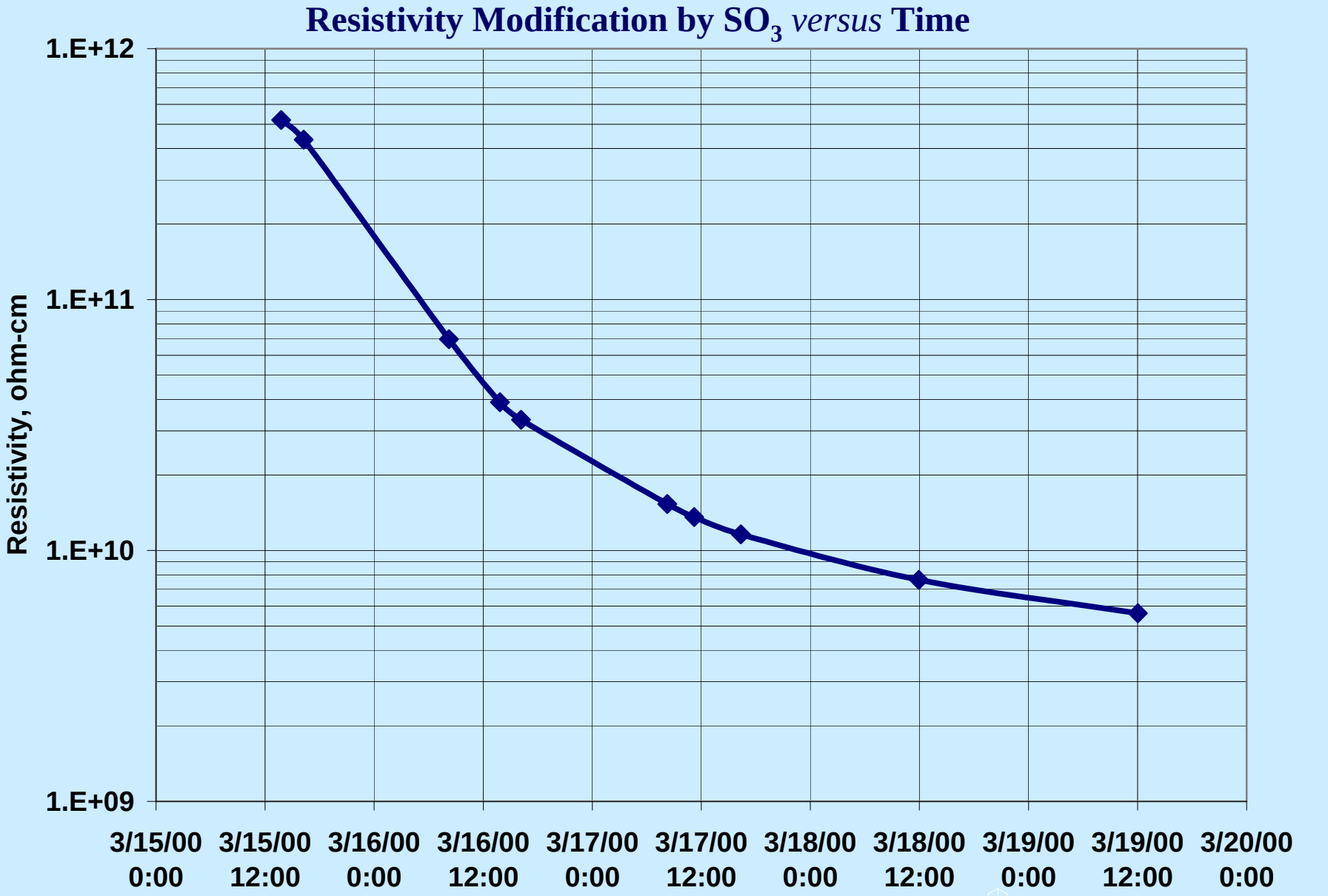
A study was undertaken to provide data which might be used to aid in the development of a predictive model for uptake of SO_3/H_2SO_4 by fly ash from coal-fired utility boilers. The results of the study also have implications with regard to measuring SO3/H2SO4 emissions.

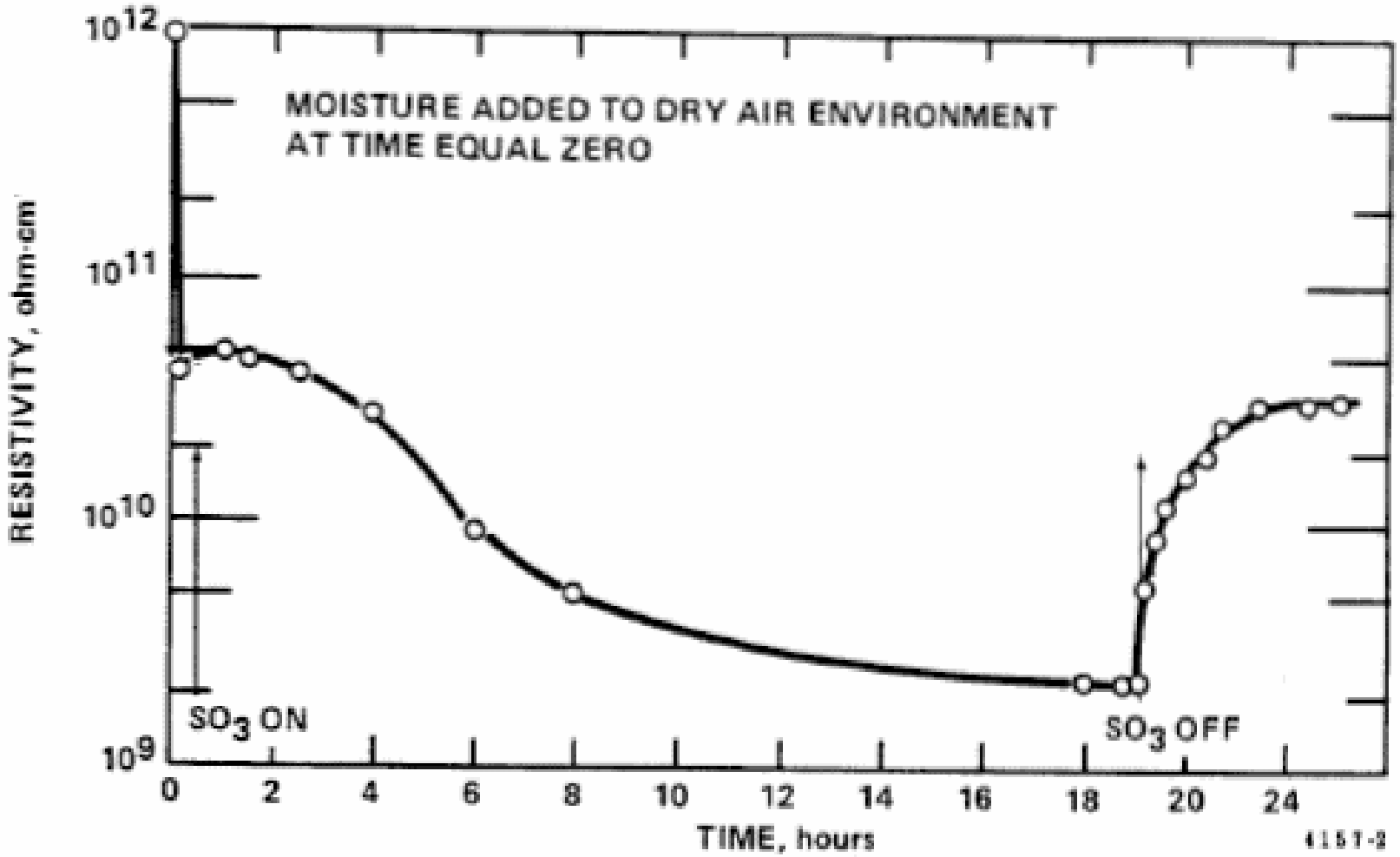
Nine ashes having a wide range of compositions were selected.

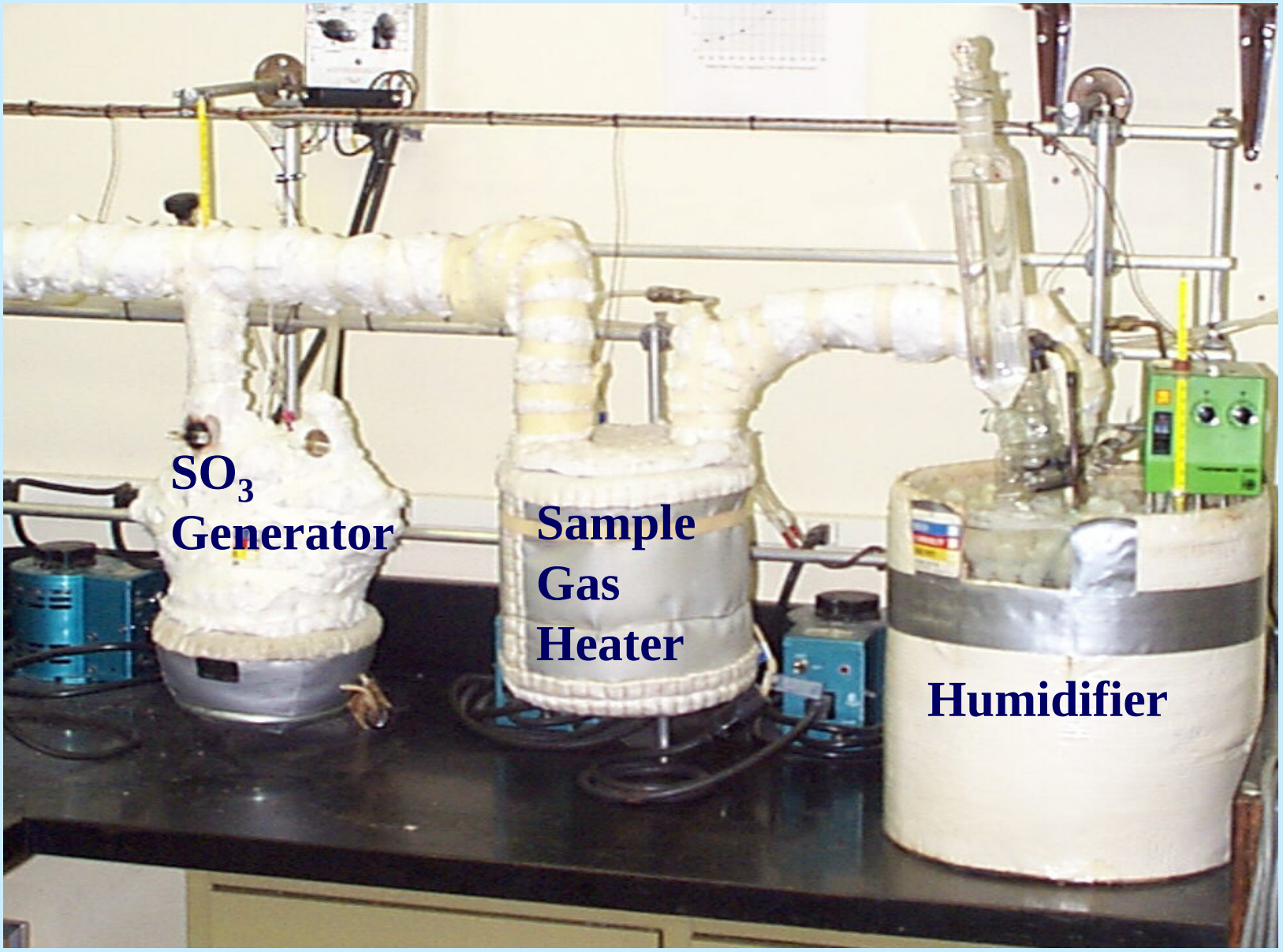
Samples of these nine ashes (with three duplicates) were exposed to two concentrations of SO_3/H_2SO_4 vapor at five temperatures.

Exposures were done in parallel for periods of 72 to 96 hours.

Layer thickness of 1 mm was selected based on previous SO_3 ash resistivity conditioning.







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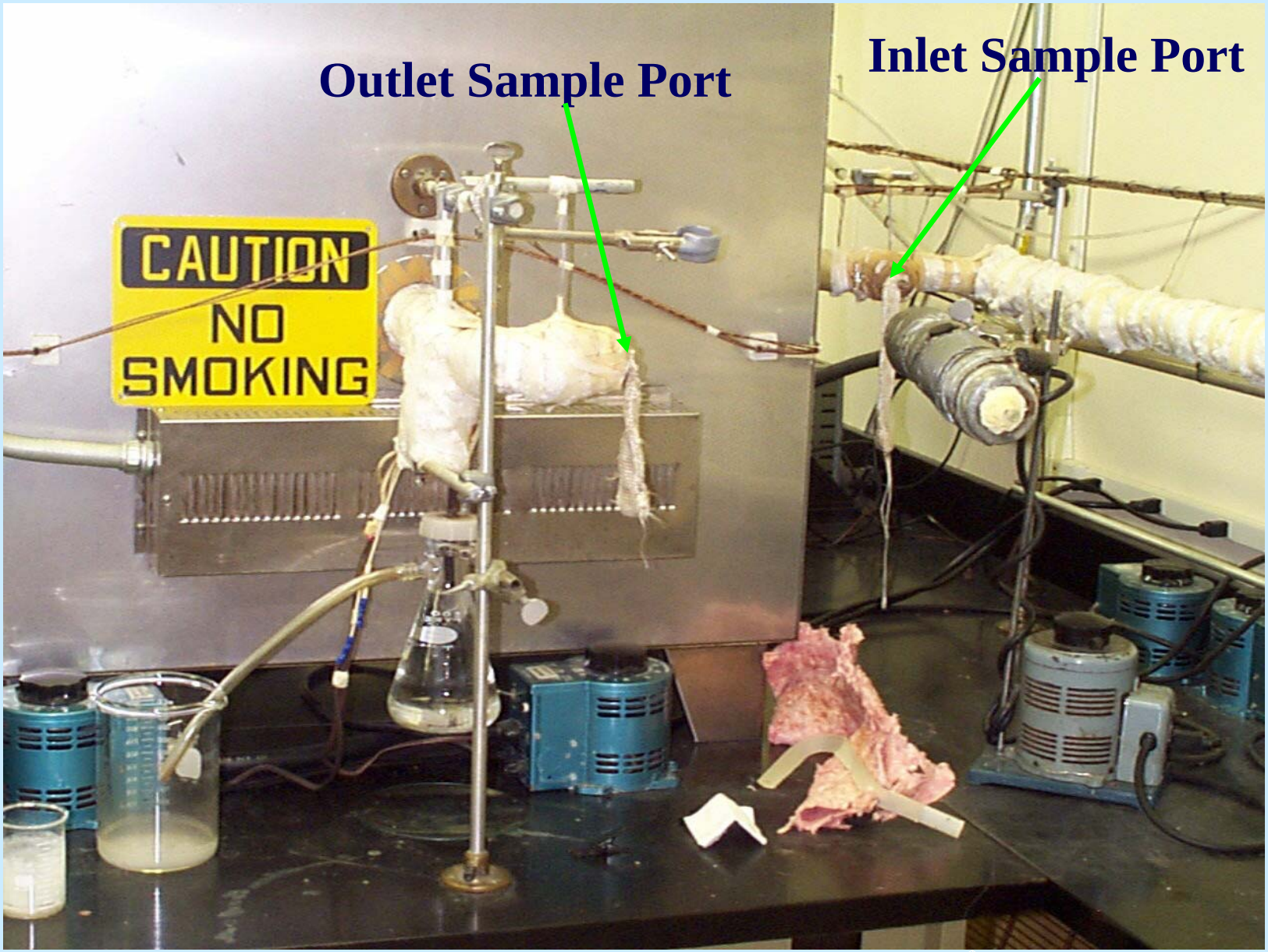

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Layout of Exposure Chamber

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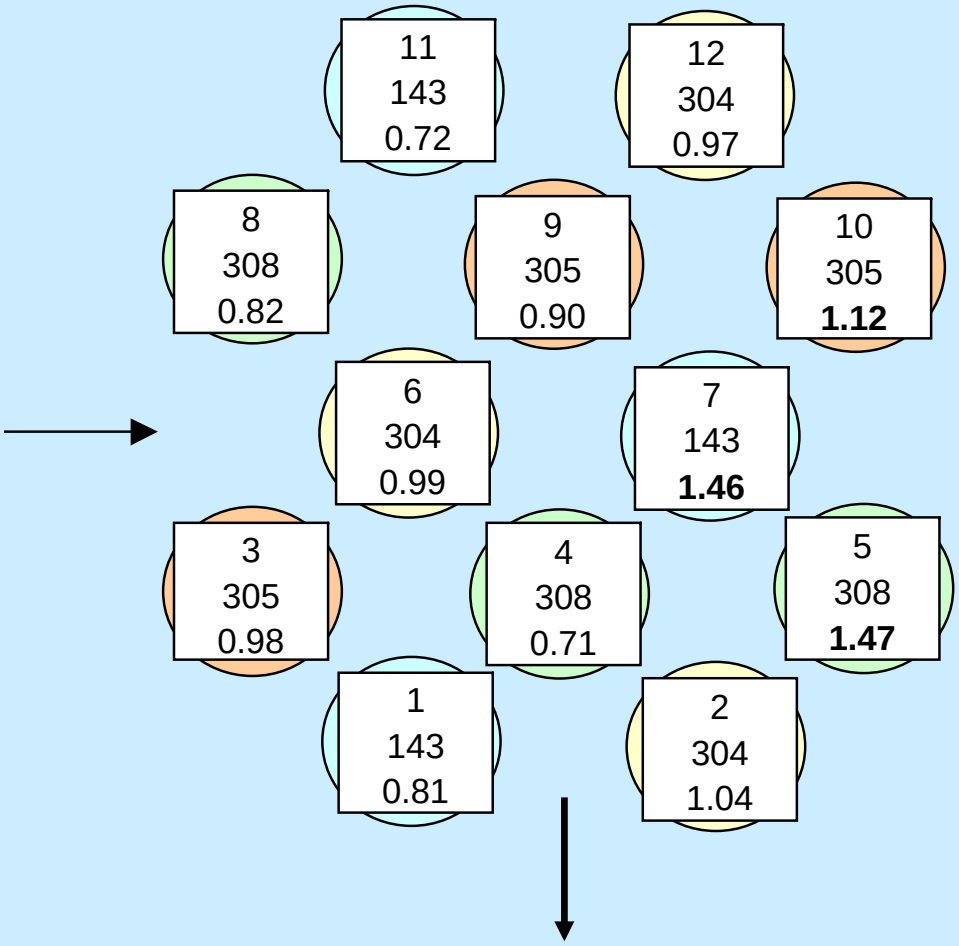

Ash Source	Base/Acid Ratio
Low sulfur eastern bituminous coal	0.092
Low sulfur western sub-bituminous coal	0.149
High sulfur eastern bituminous coal	0.242
Eastern bituminous coal	0.354
Low sulfur western sub-bituminous coal	0.462
Low sulfur western sub-bituminous coal	0.535
Western sub-bituminous coal	0.698
Power River Basin coal	0.901
North Dakota lignite	1.558

Base/Acid ratio = $(Na_2O+K_2O+MgO+CaO+Fe_2O_3)/(Al_2O_3+SiO_2+TiO_2)$

Li_2O	0.01 - 0.05
Na_2O	**0.19 - 4.0**
K_2O	0.20 - 3.1
MgO	**0.85 - 8.9**
CaO	**0.56 - 32.2**
Fe_2O_3	**4.10 - 13.1**
Al_2O_3	12.3 - 32.2
SiO_2	22.6 - 59
TiO_2	0.92 - 2.6
P_2O_5	0.15 - 1.4
SO_3	**0.18 - 7.9**

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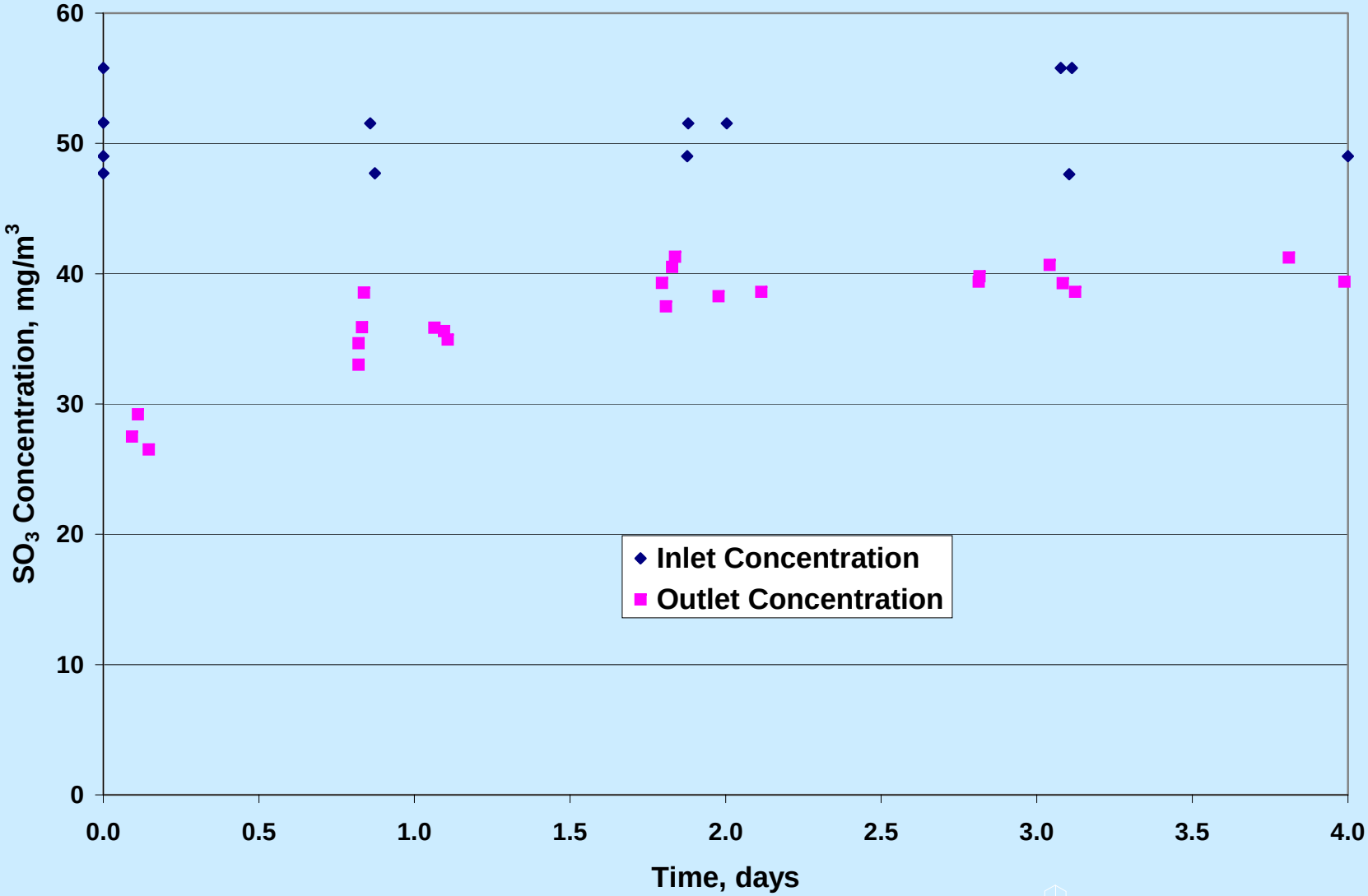

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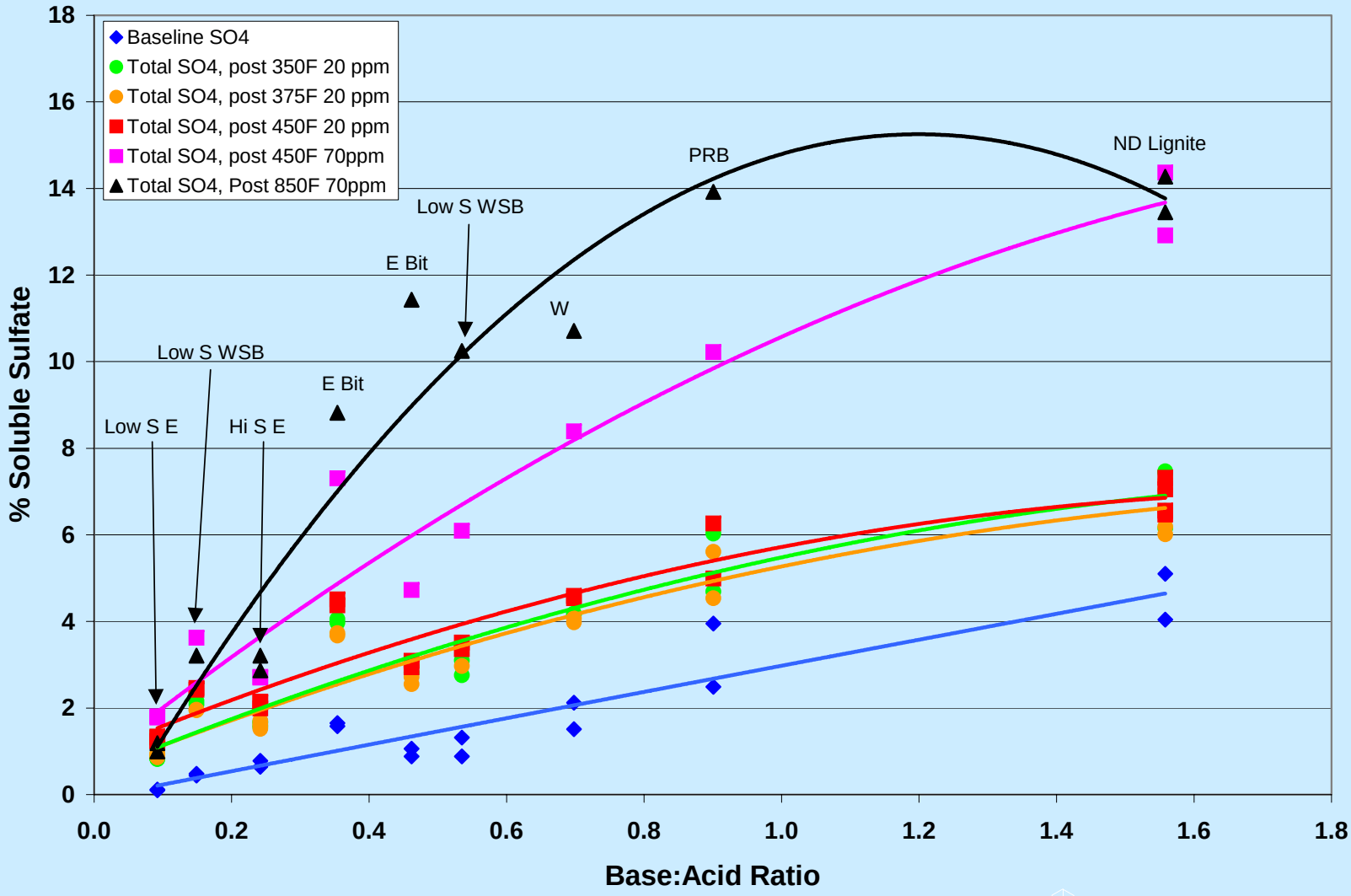
Duration, hours	96	75	75	93	96
Oven Temperature, °C	177	190	232	232	454
Oven Temperature,°F	351	374	450	450	850
SO_3 Conc., ppm	20	20	20	70	70
Percent Capture by Ash	21.5	26.7	26.3	19.2	25.8
Mass Balance, %	96.7	96.1	94.4	100.9	99.5



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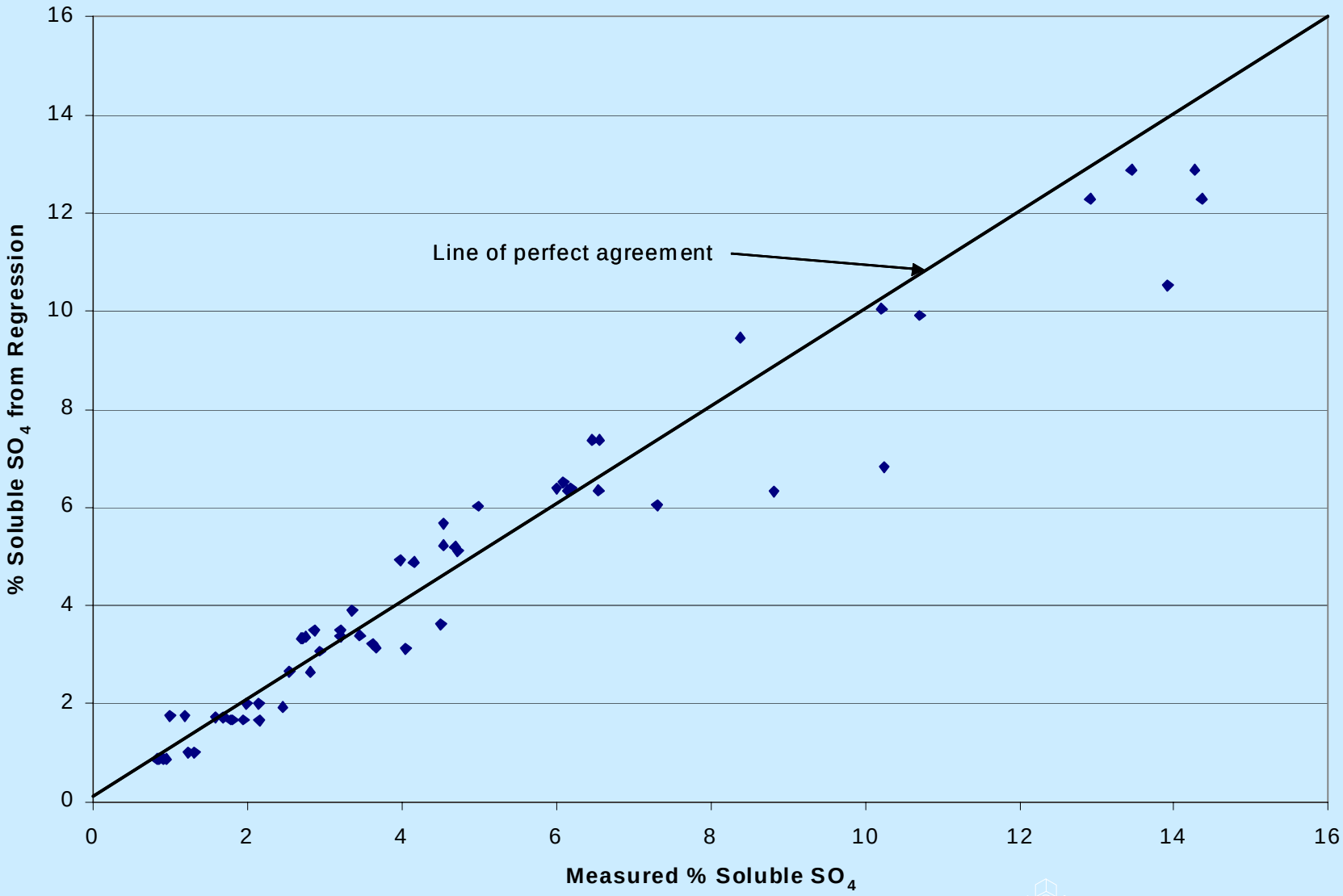

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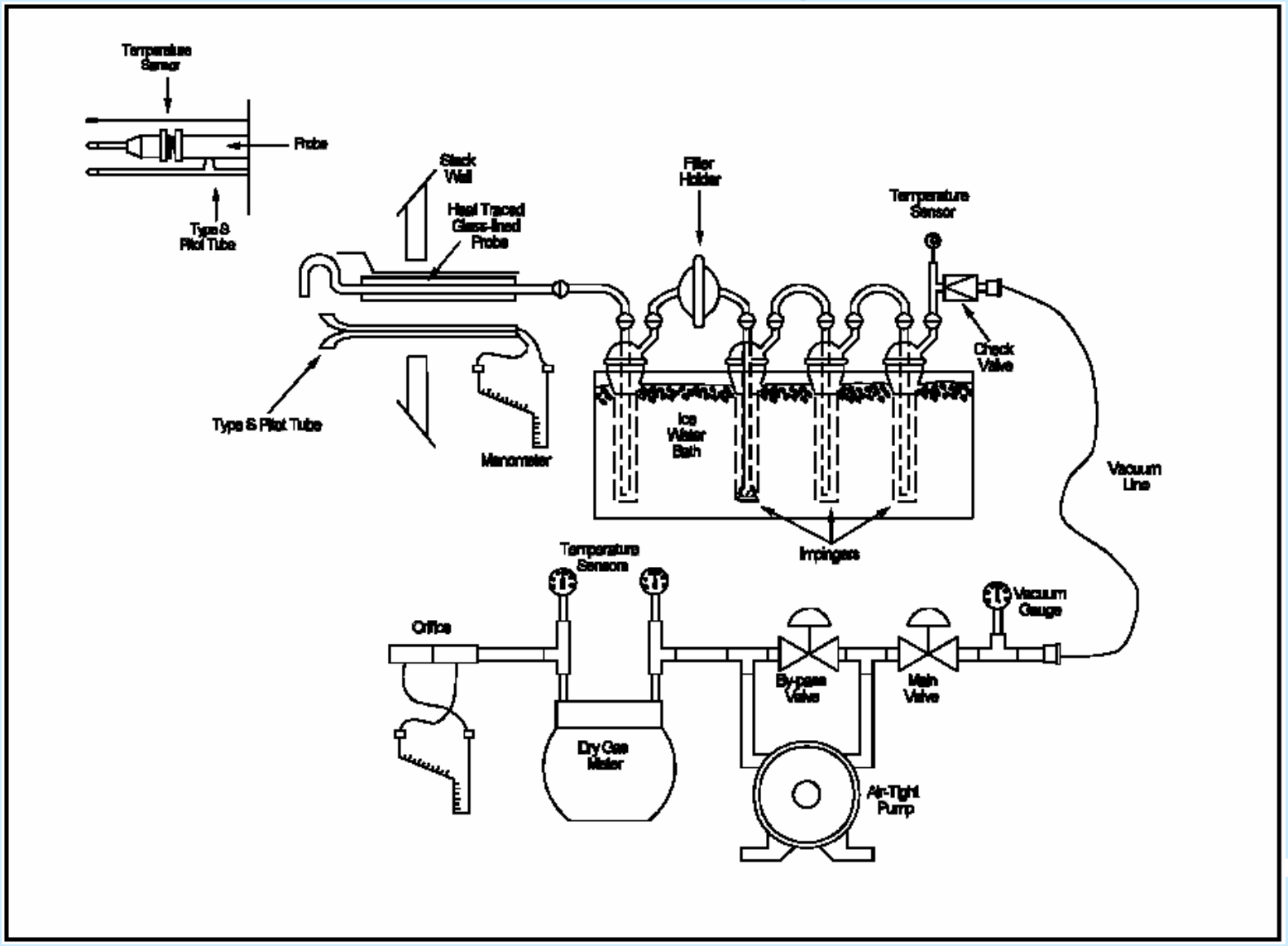
EPA Method 8 is the only Officially Promulgated Method

In Method 8 particulate matter and SO_3/H_2SO_4 are co-collected in impingers



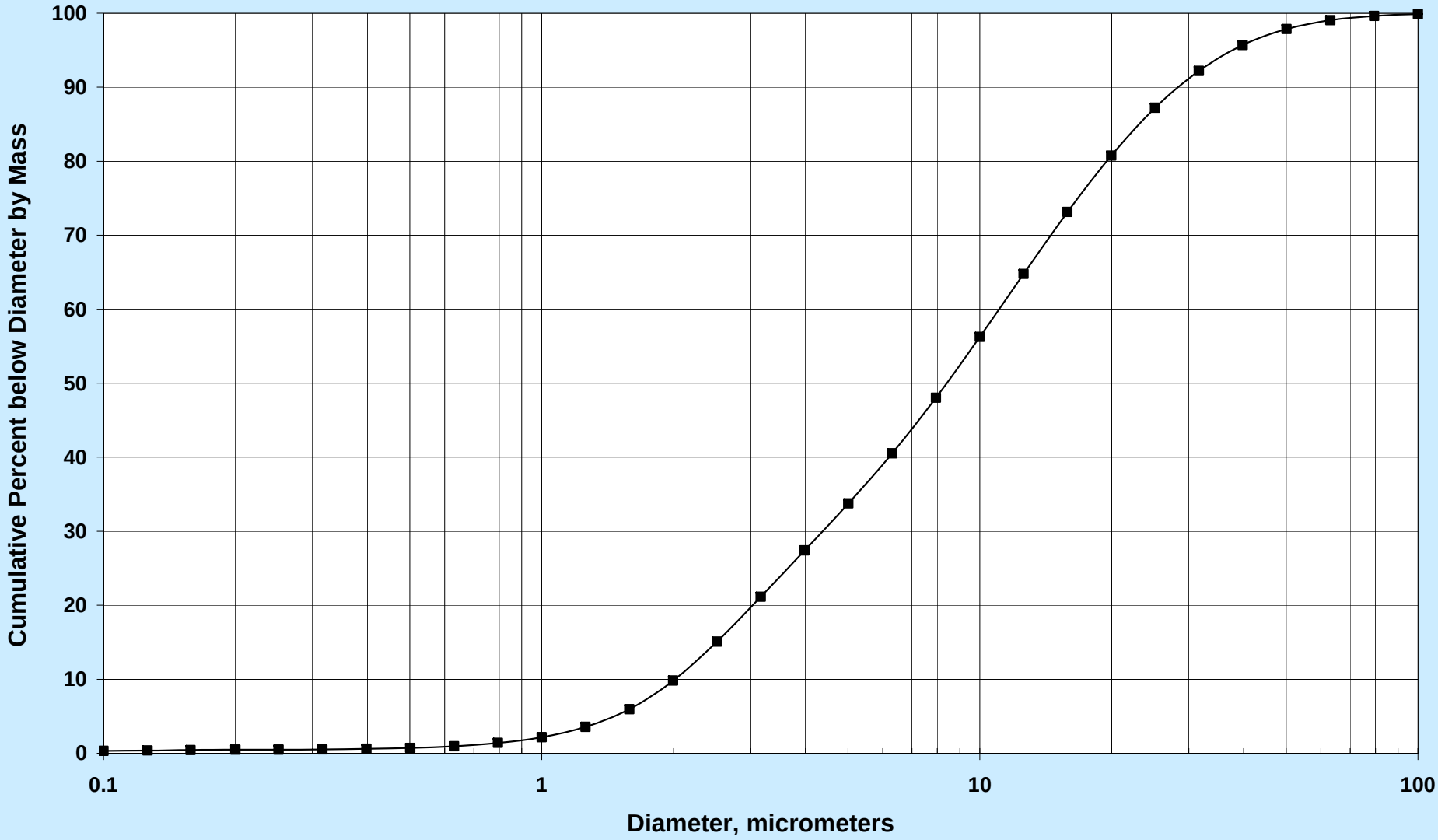
Typical Fly Ash Concentration Exiting Boiler = 5000 mg/dncm

Typical Soluble Sulfate Concentration in Ash is 1% to 5%

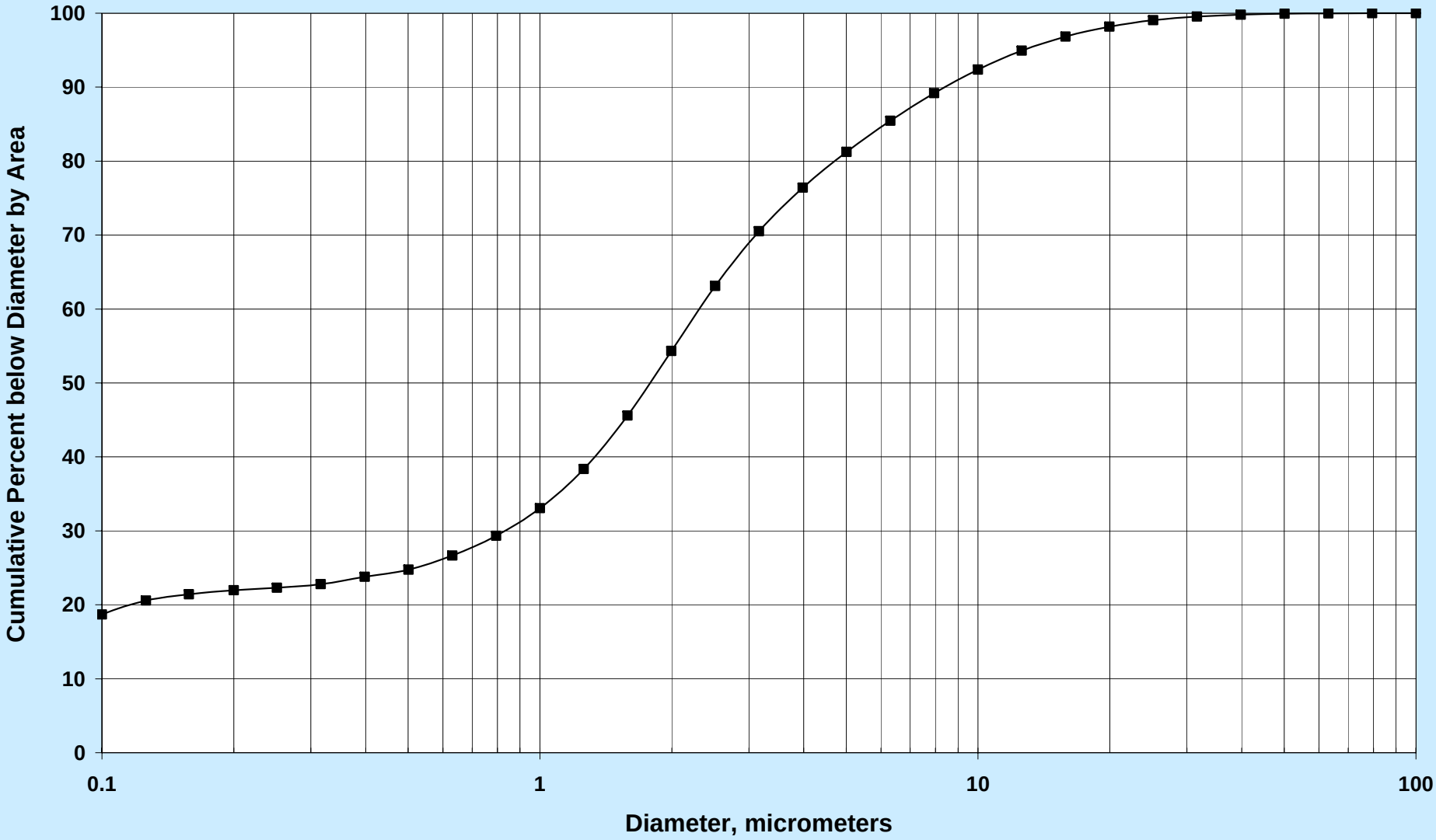
% Sulfate	Sulfate Mg/dncm	Equivalent ppm Sulfate	Sulfate ppm Downstream of 99.5 % Collector
1	50	12.5	0.25
2	100	25	0.5
5	250	62.5	1.25

Conclusion: Method 8 won't work at boiler exit conditions!

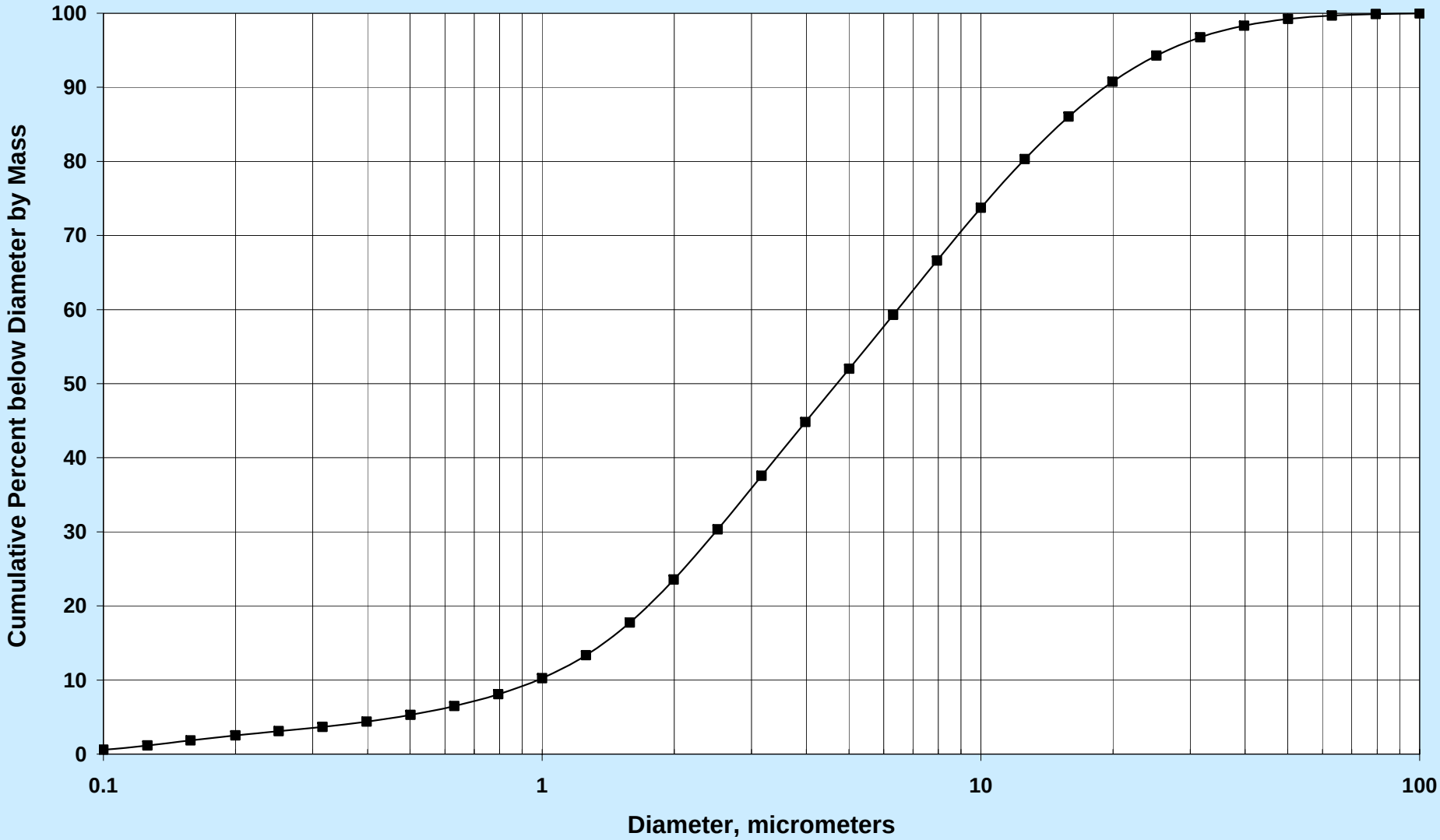
And may not be acceptable downstream of particulate collector.



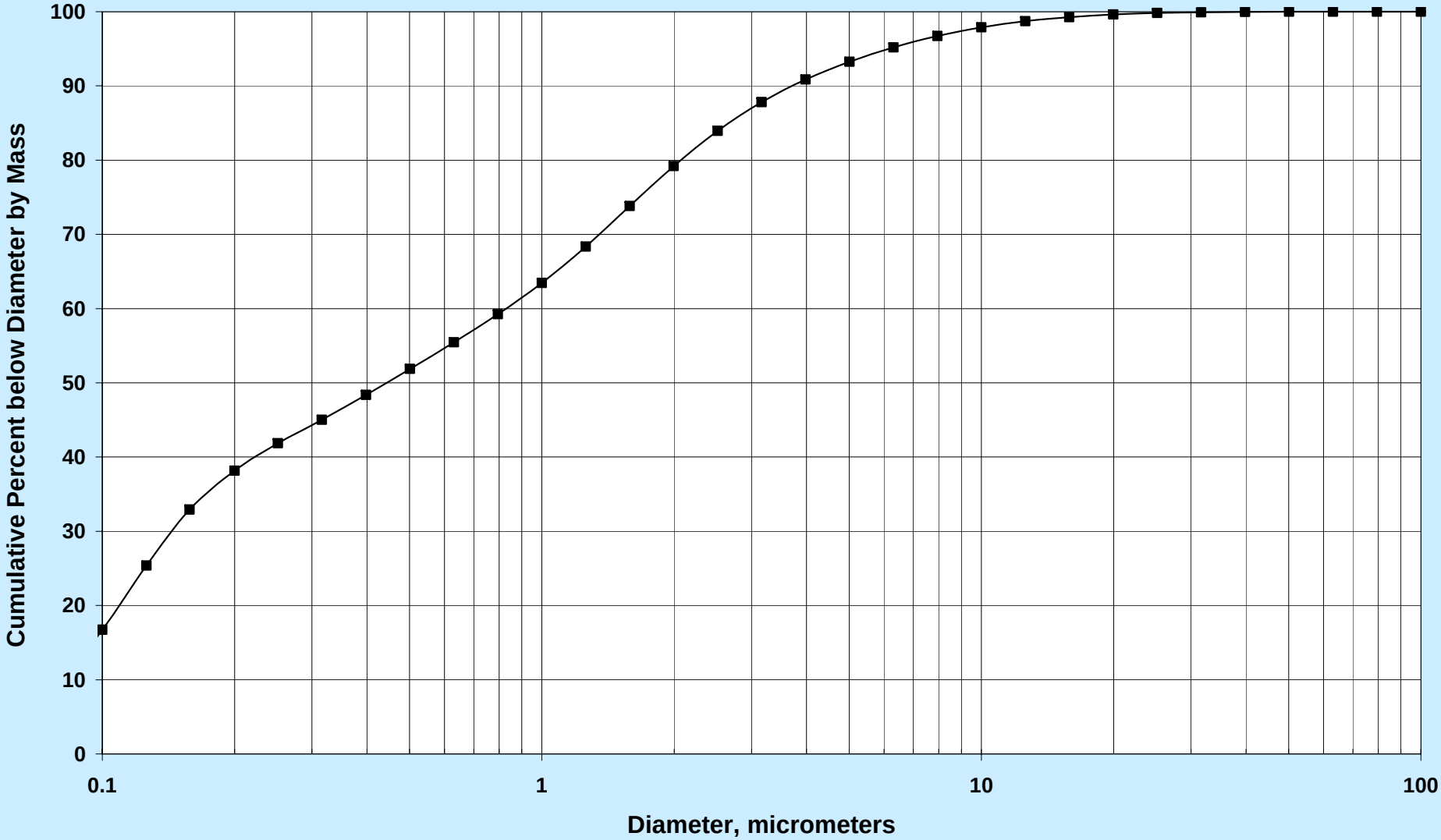
ESP Inlet Size Distribution on a Cumulative % by Mass Basis



ESP Inlet Size Distribution on a Cumulative % by Area Basis



ESP Outlet Size Distribution on a Cumulative % by Mass Basis



ESP Outlet Size Distribution on a Cumulative % by Area Basis

In addition to artifact sulfate from particulate, some SO_2 may be oxidized in SO_3 impinger adding another positive bias.

Alternative: Controlled Condensation Method

1. **Heat sample stream to ensure all H_2SO_4 is in vapor phase**
2. **Filter sample stream to remove particulate**
3. **Condense acid at temperature above moisture dew point**

Problems with Controlled Condensation Method

1. Uptake by reactive particulate results in negative bias from filtration step.

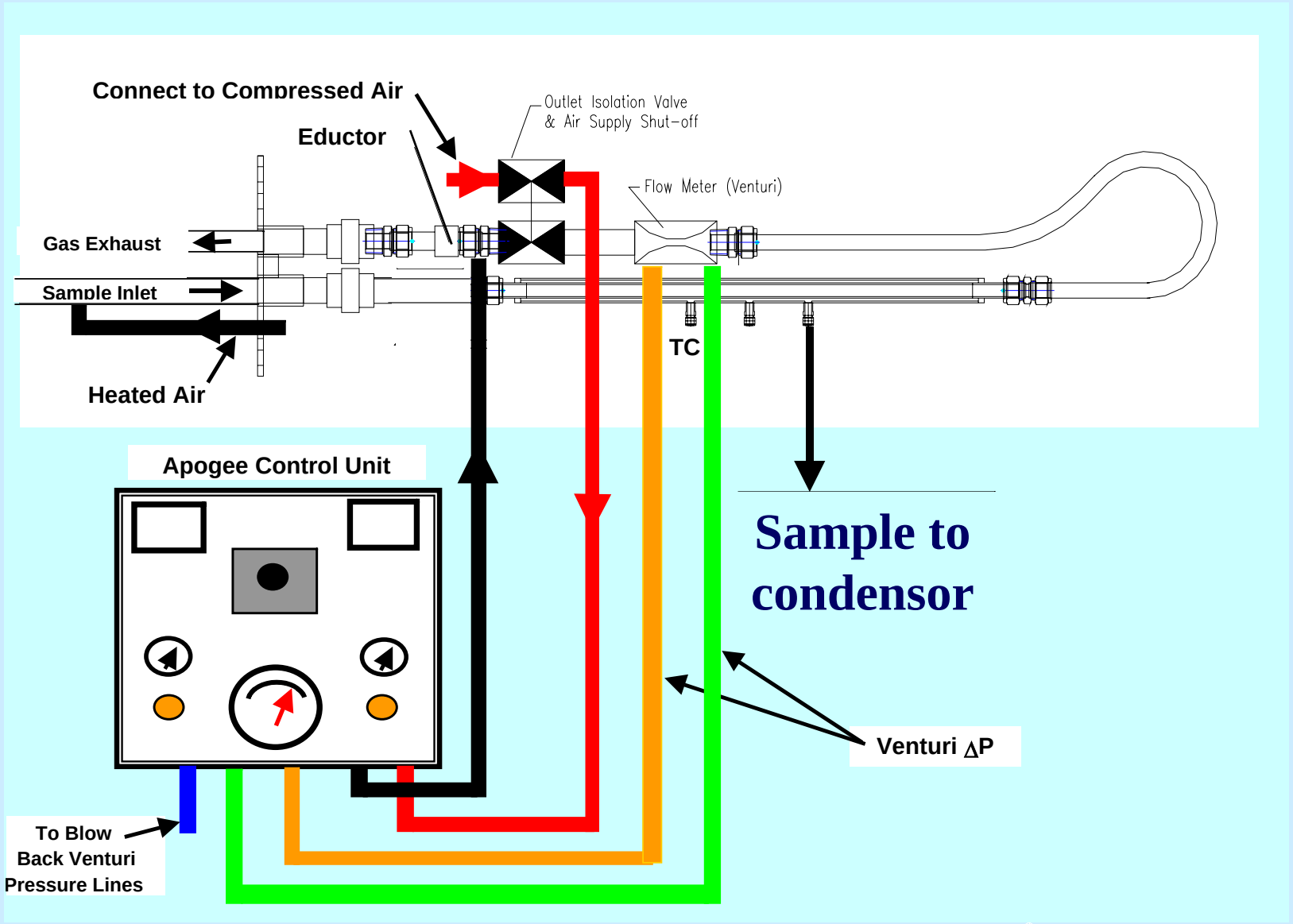
2. Ensuring that all condensed H_2SO_4 is vaporized ahead of filter.

Proposed solution to both problems

Use a modified Apogee QSIS type probe.

Self-cleaning filter ensures that sample does not pass through particulate cake.

Use hot gas mixed with sample stream to ensure all H_2SO_4 is in vapor phase.



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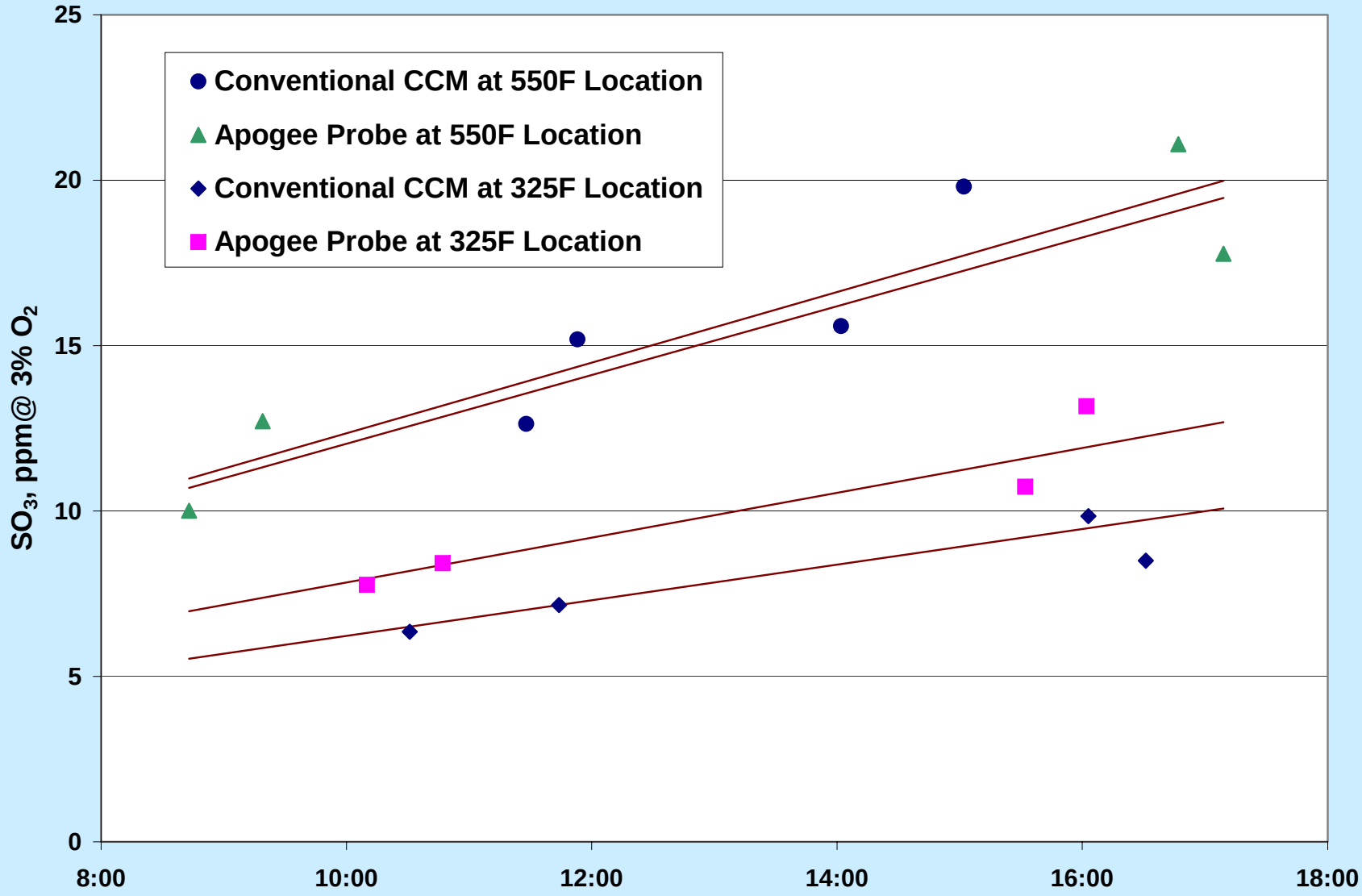

Initial Trial of Concept

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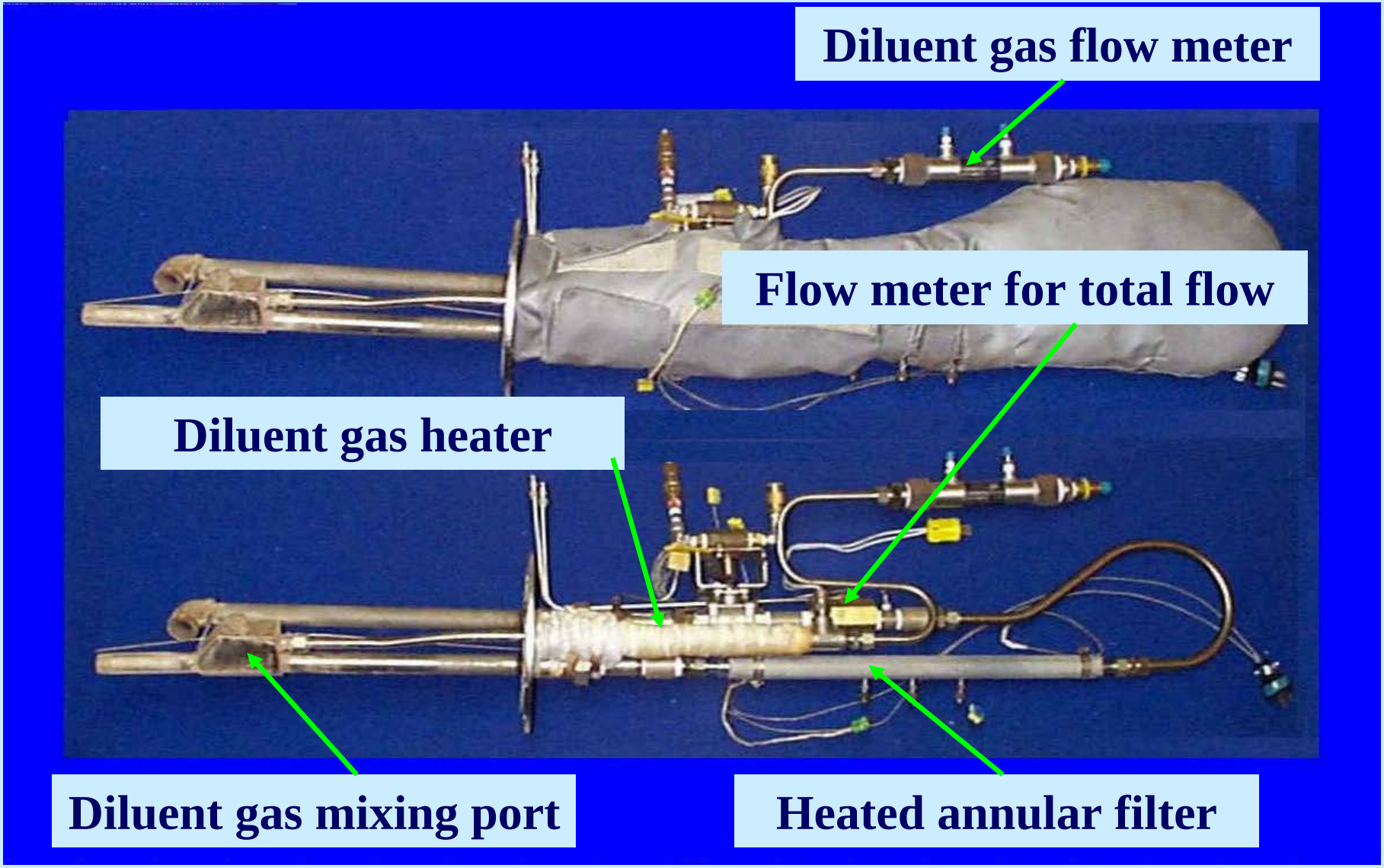

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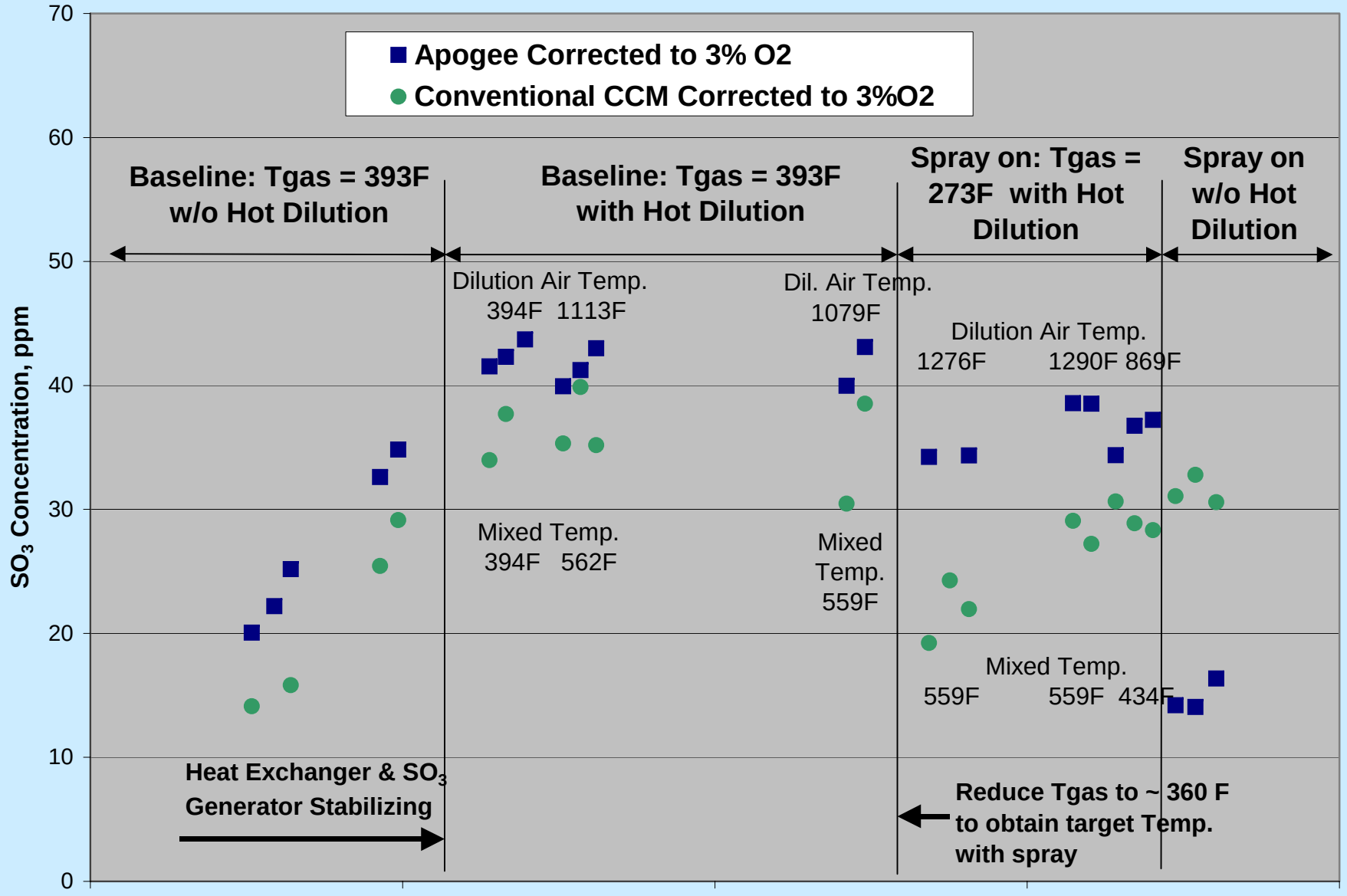

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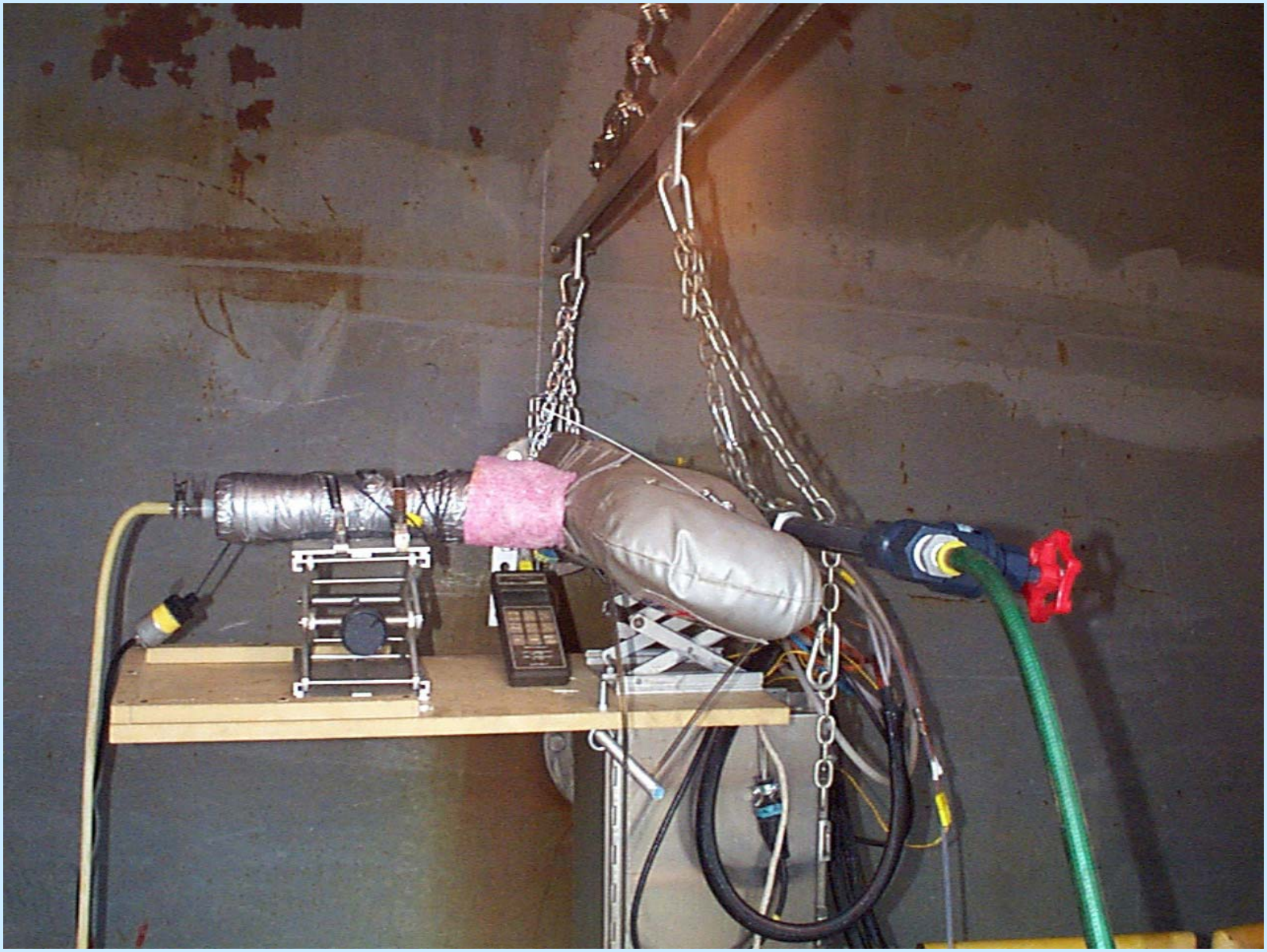

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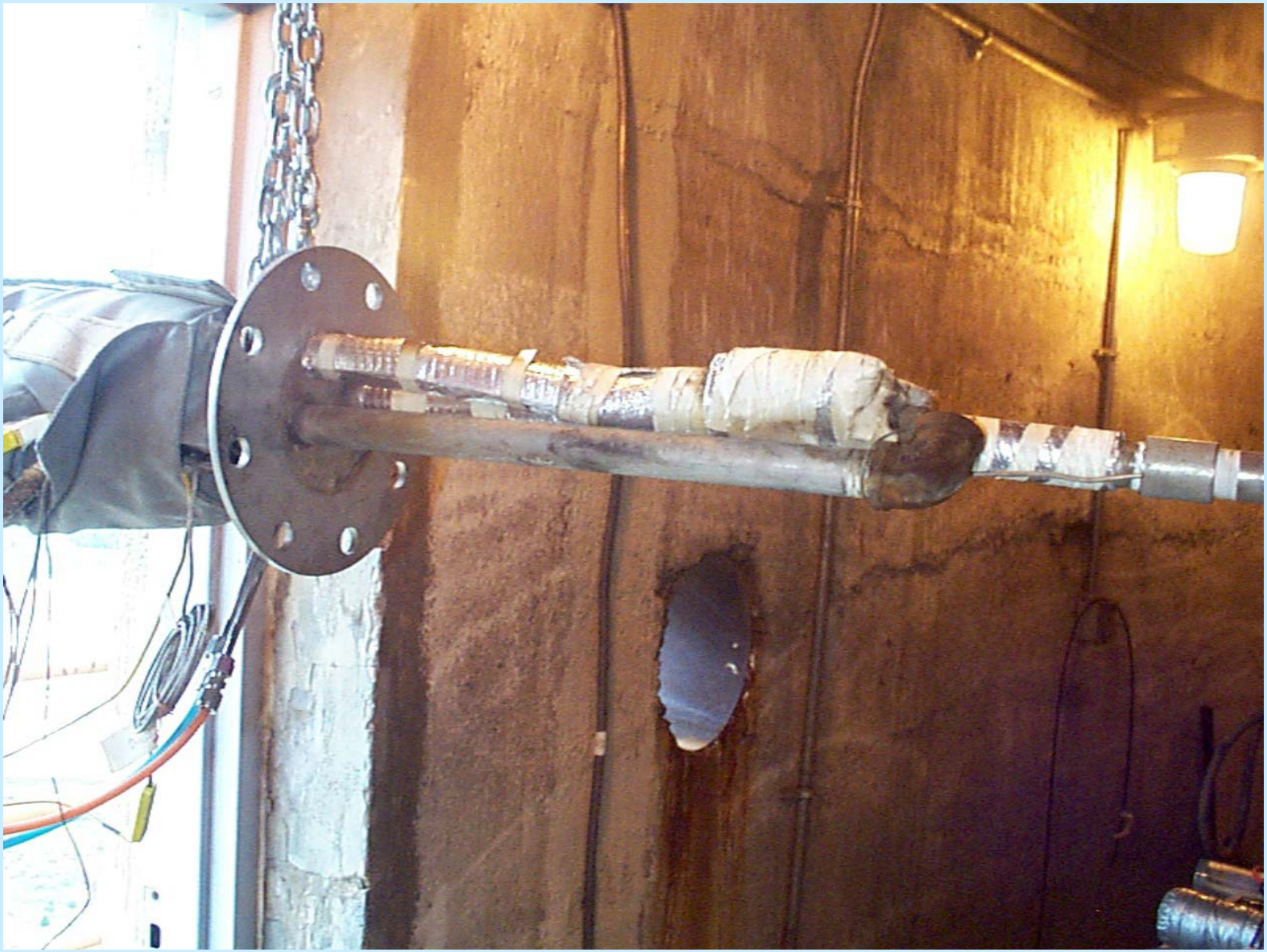
Measurements on Stack Downstream of Scrubber

Standard Controlled Condensation Probe				Hot-gas Dilution Probe		
	SO_3, ppm @ 3% O_2				SO_3, ppm @ 3% O_2	
Test Run	Average	Range		Mixed Gas Temperature,°F	Average	Range
1	19.3	18.7 – 20.7		419	14.1	12.7 – 15.5
				445	18.4	18.4 - 18.4
2	18.0	17.6 – 18.6		480 – 490	17.0	16.2 – 17.9



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Conclusions

A probe has been developed that appears to minimize or eliminate bias in the measurement of SO_3/H_2SO_4 due to uptake of by ash.

The probe can be used in sampling both "hot/dry" and "cold/wet" flue gas environments.

The work described here was conducted as a part of Work Assignment Numbers 0-3 & 1-4 of EPA Contract No. EP-C-04-056, "Evaluation and Mitigation Of Visible Acidic Aerosol Plumes From Coal-Fired Power Boilers," for the Office of Research and Development of the Air Pollution and Prevention Control Division of the U.S. EPA National Risk Management Research Laboratory.

Dr. C. Andrew Miller was the EPA technical project manager for the work.

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