Worldwide Pollution Control Association

IL Regional Technical Seminar

September 13-15,2011

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MEASUREMENT ISSUES WITH CONDENSABLE PARTICULATE

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Clean Air Engineering

Presented at

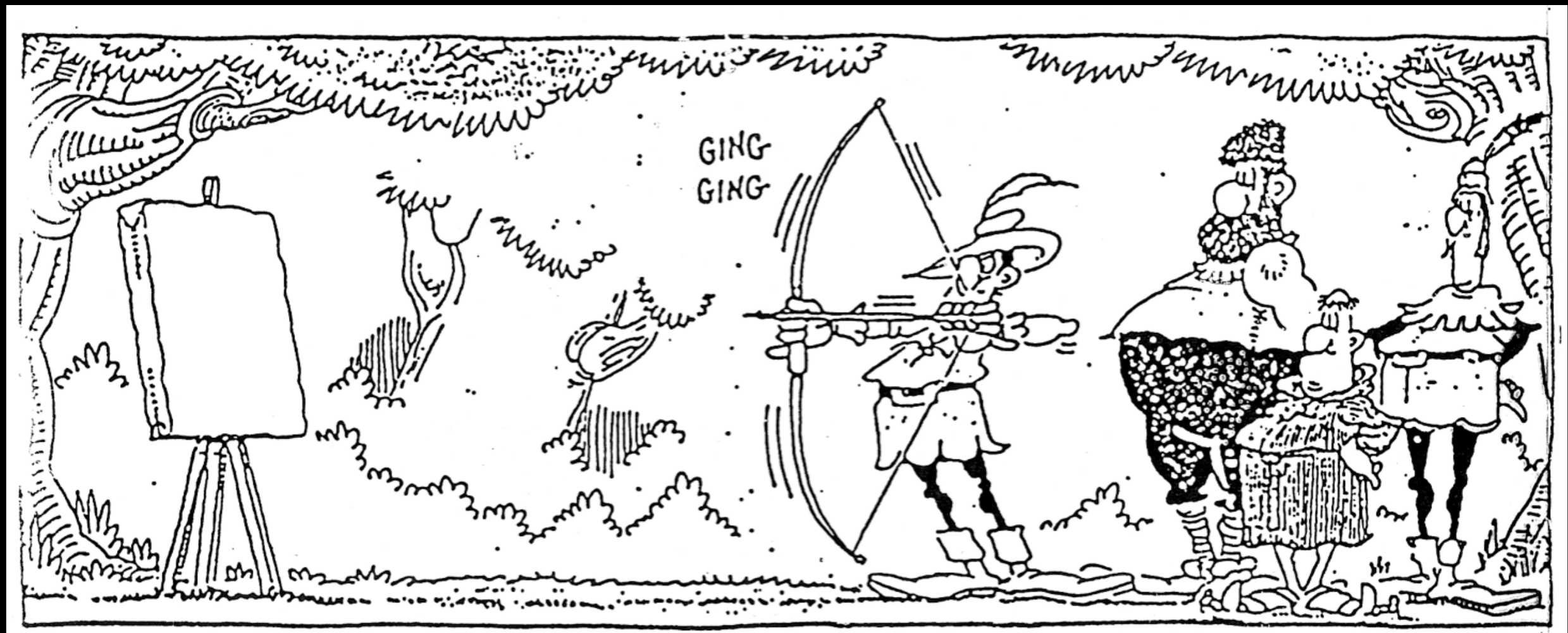
WPCA Illinois Regional Technical Seminar

September 13-15, 2011 • Bloomington, Illinois

The Stack Test

An Allegorical Tale

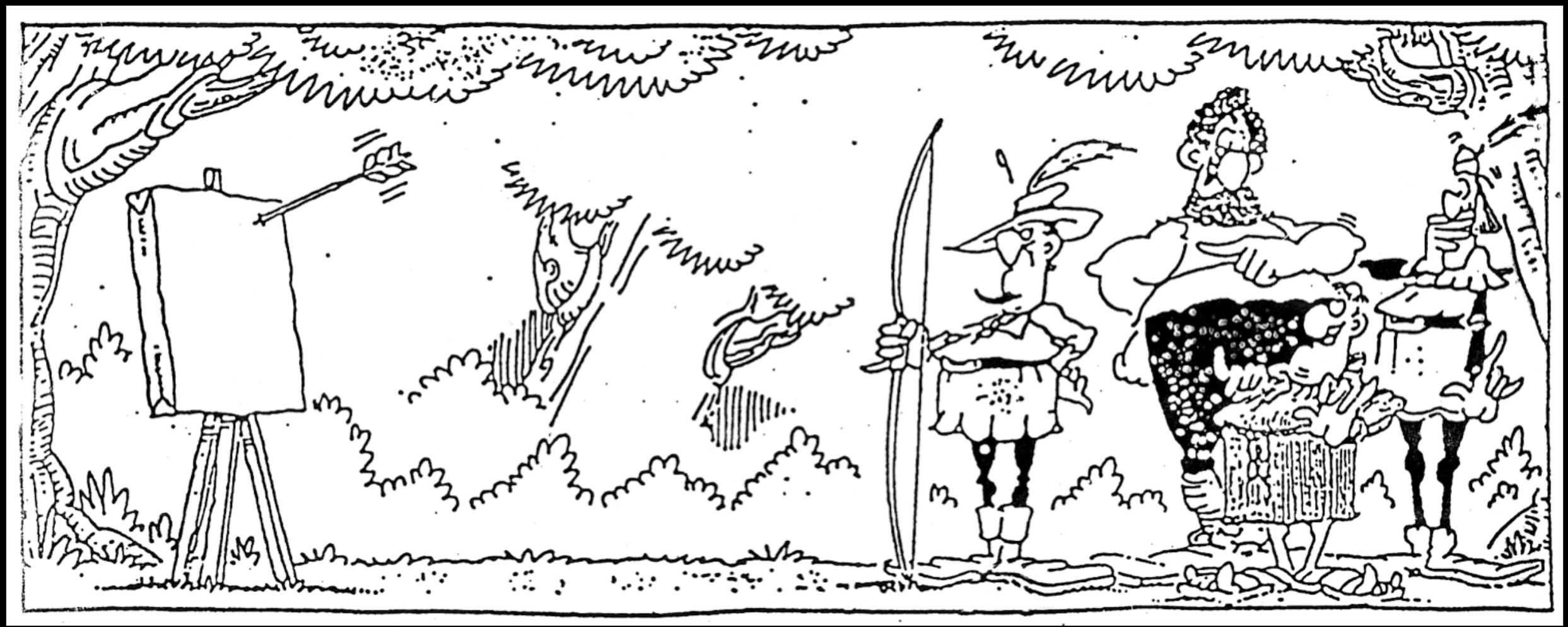
Step 1: Test Preparation



The Stack Test

An Allegorical Tale

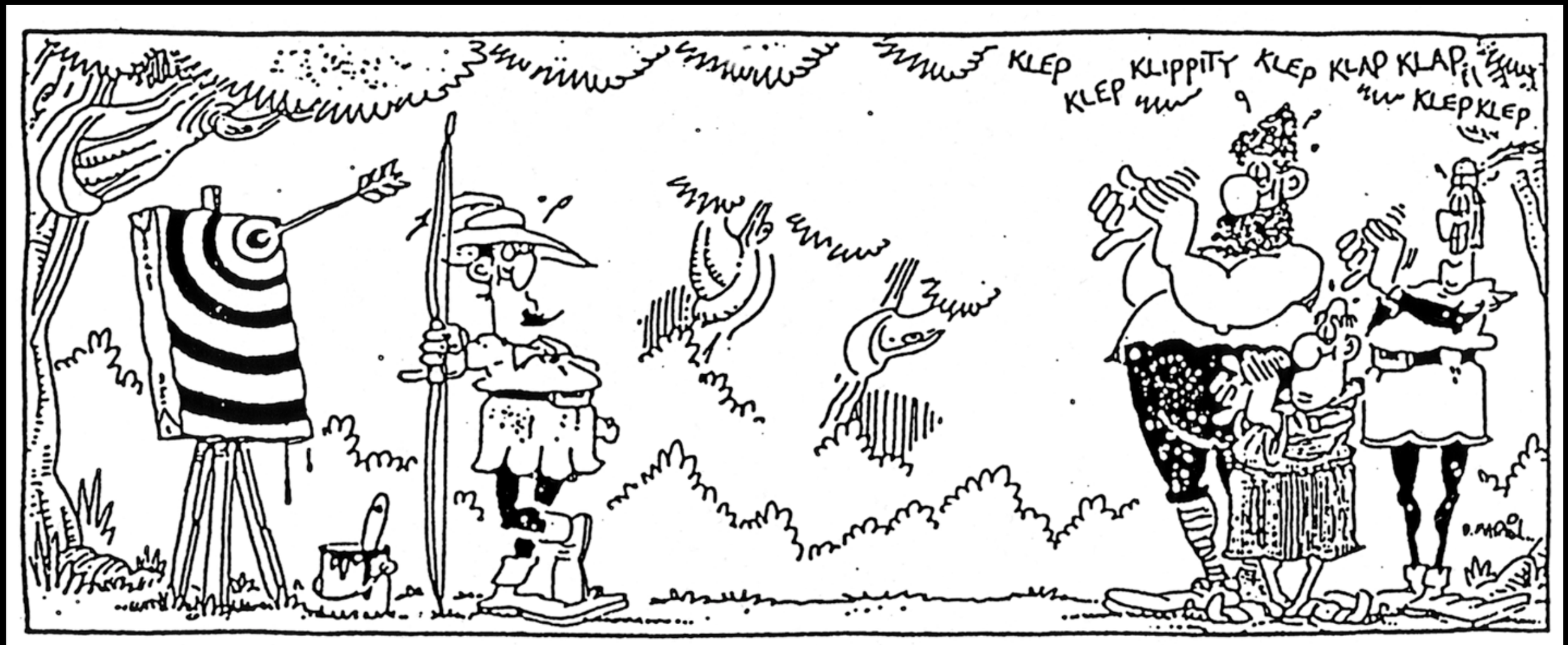
Step 2: The Test



The Stack Test

An Allegorical Tale

Step 3: Data Analysis



What is Particulate?

Particulate

Primary

Secondary

Filterable

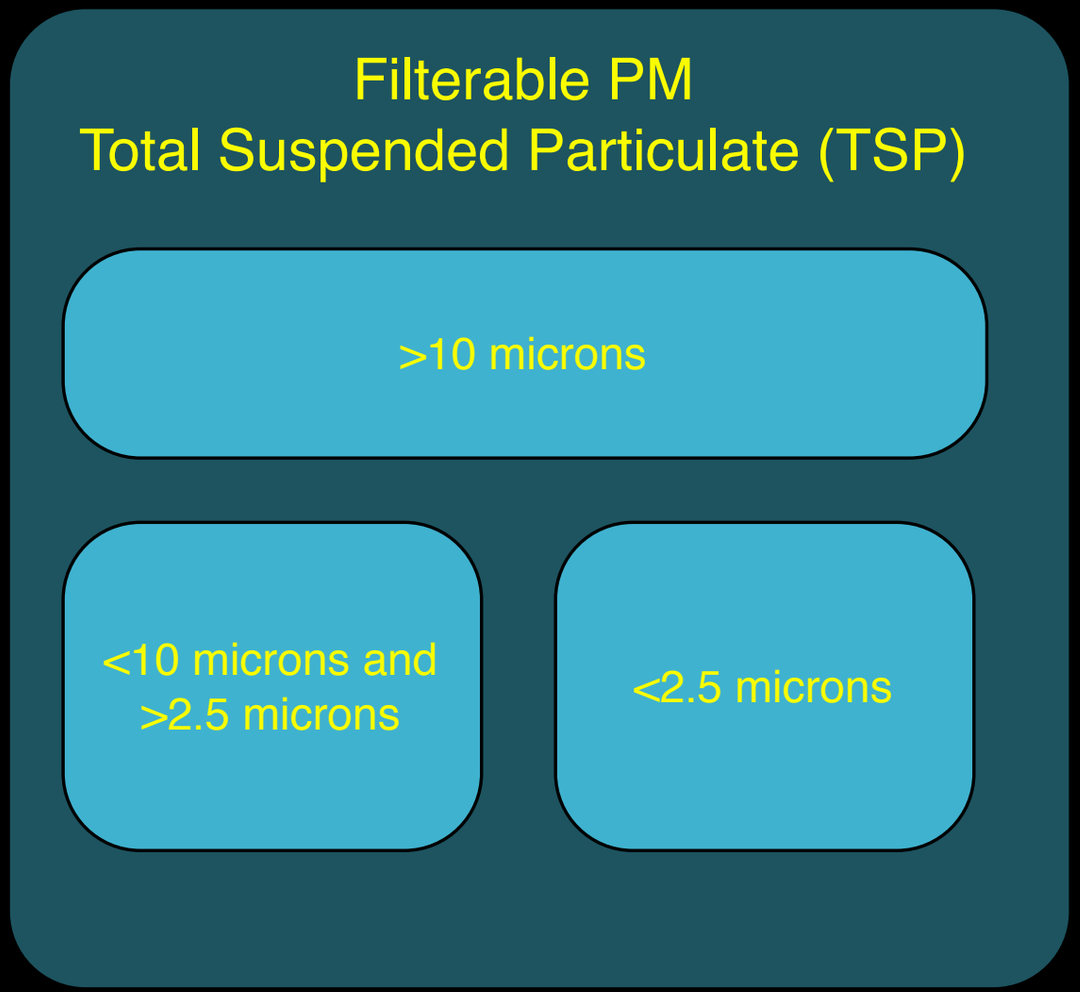
>10 µm

>2.5µm and <10µm

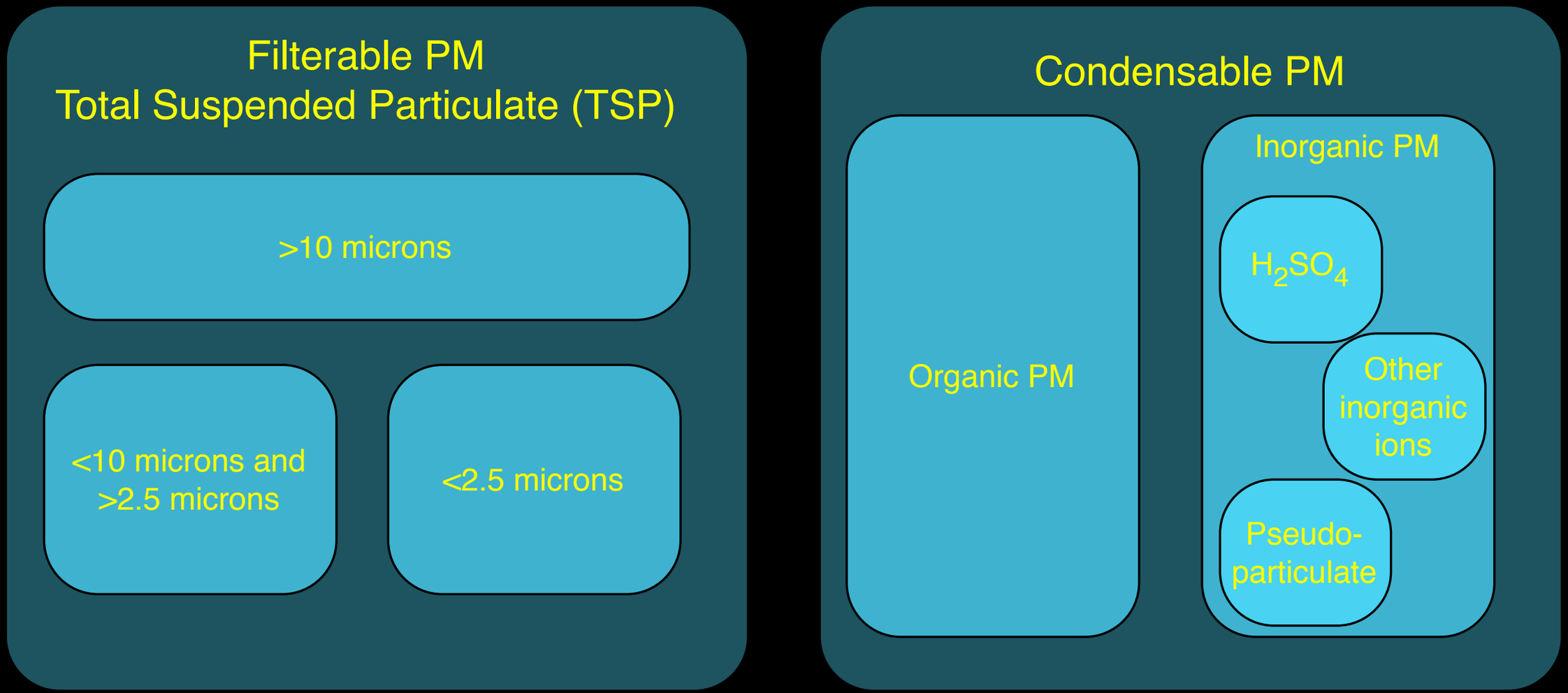
<2.5 µm

Condensable

What is Particulate?



What is Particulate?



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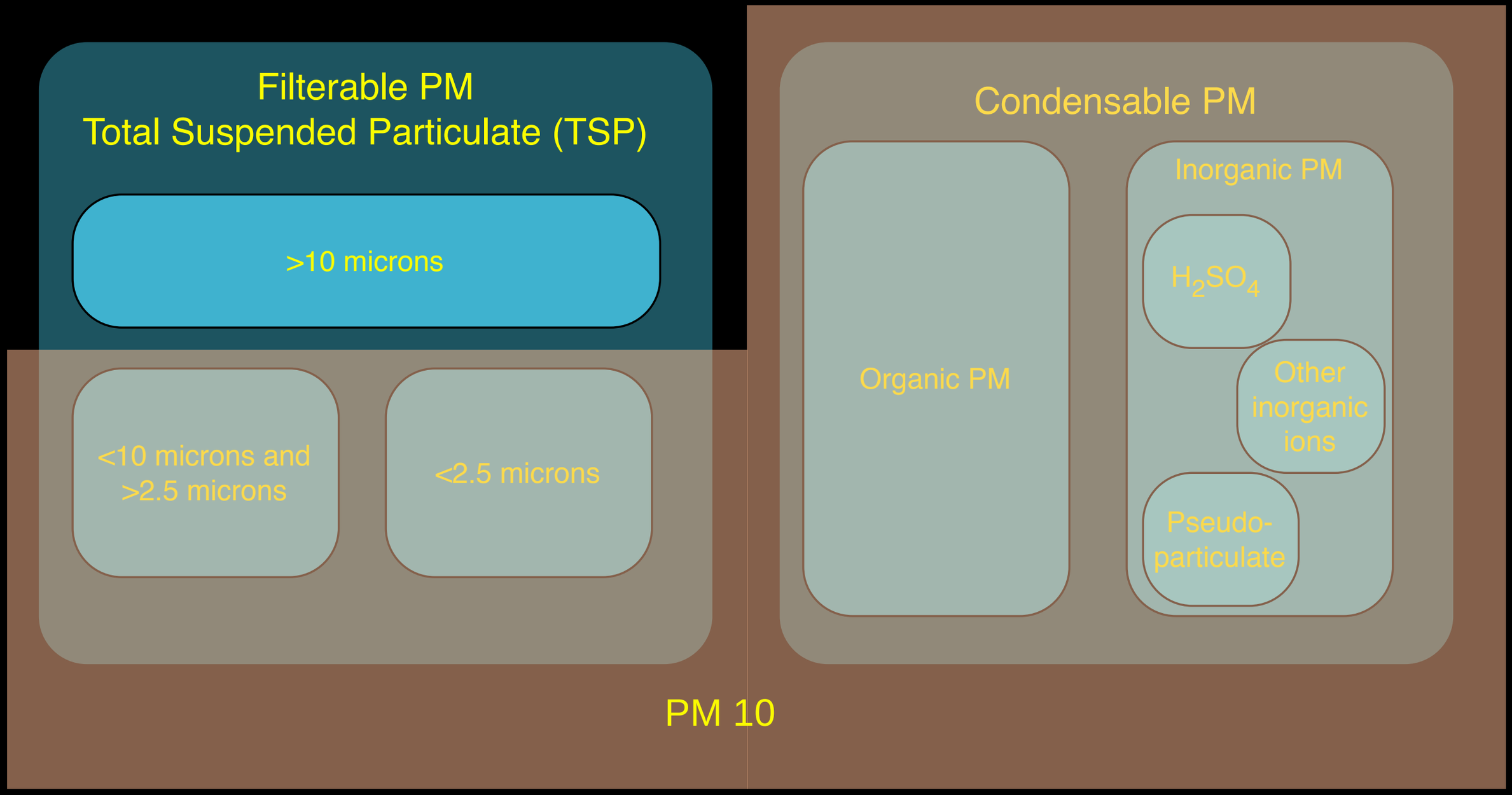
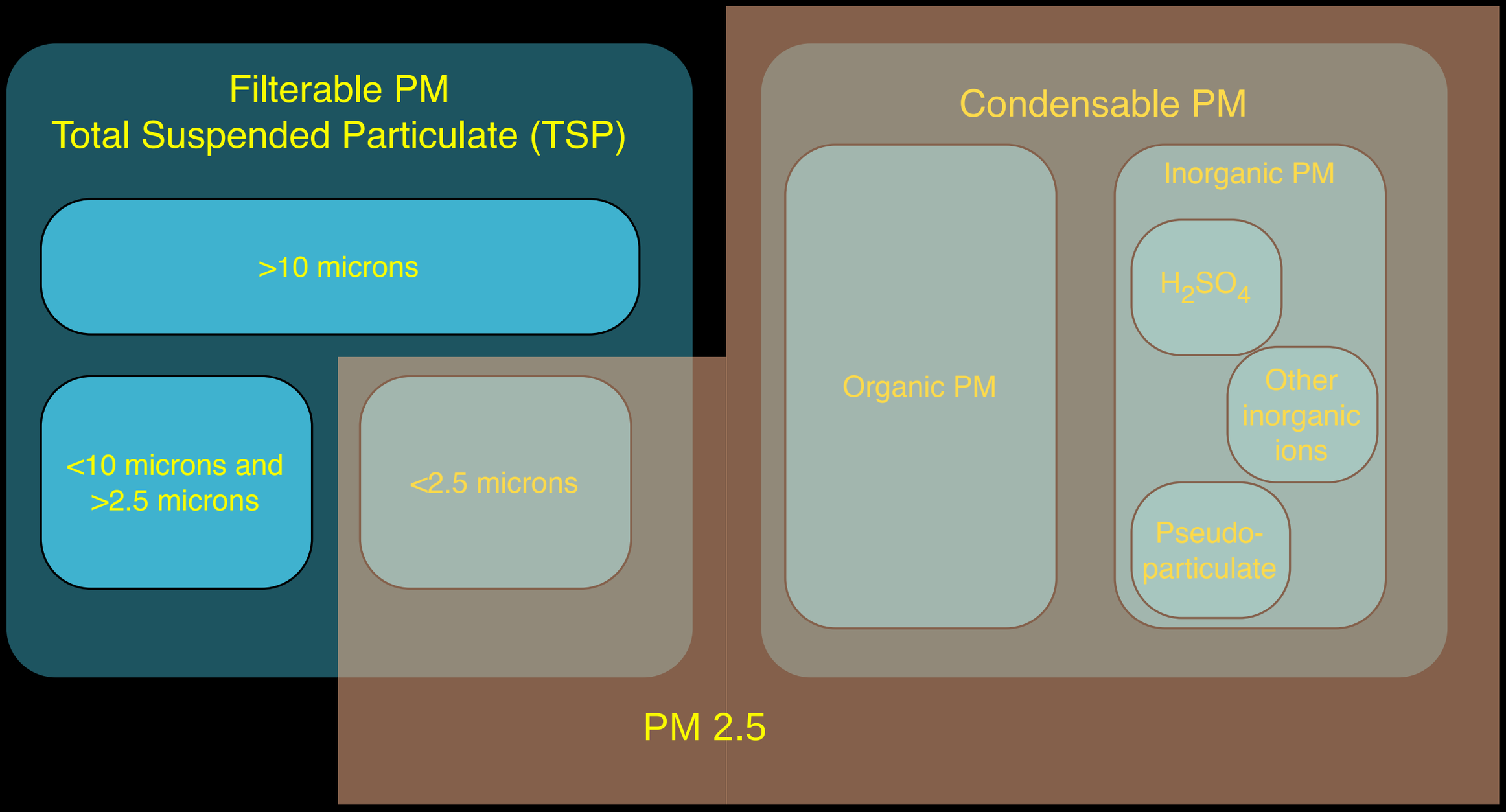


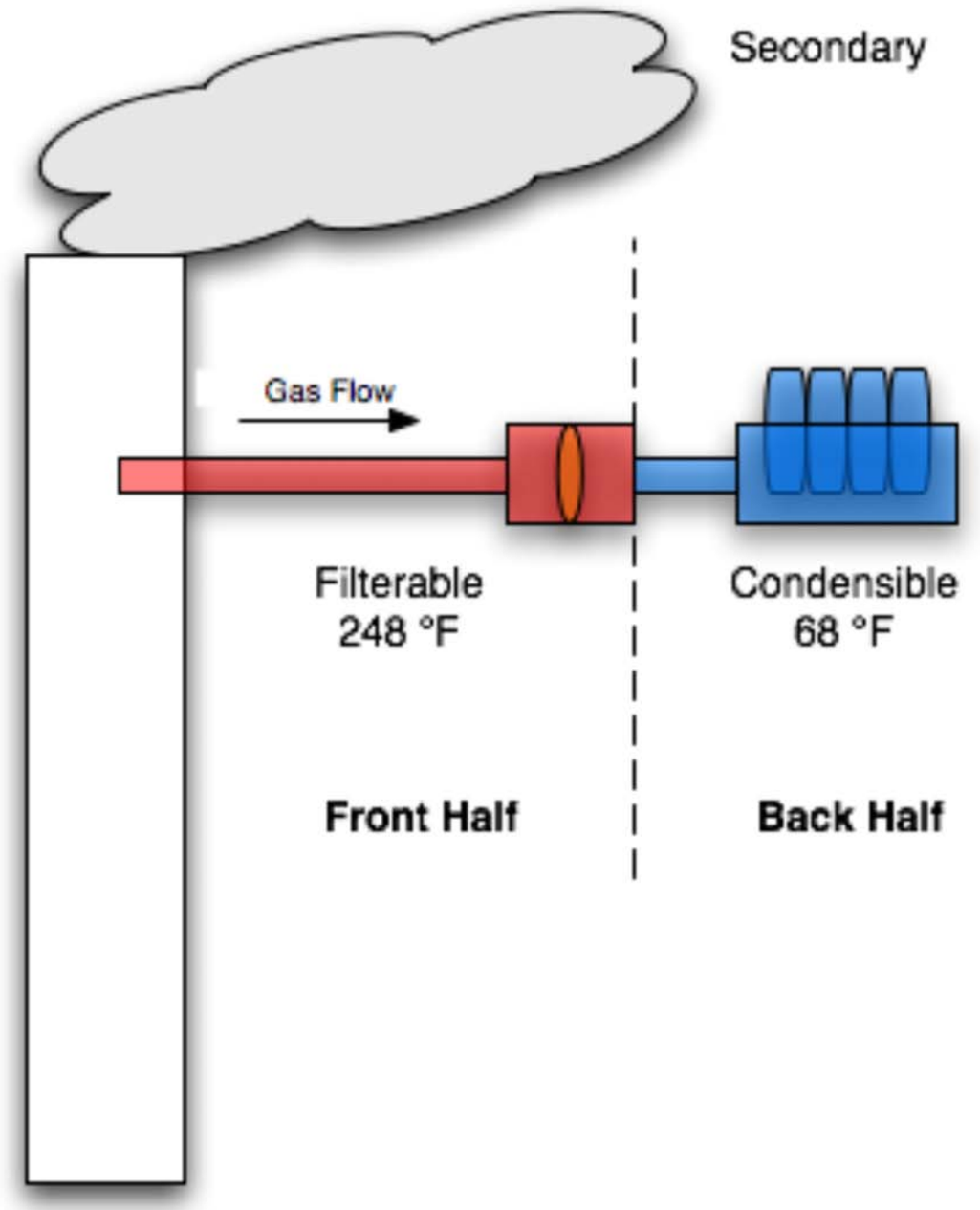
What is Particulate?



Particulate is defined by the method used to measure it...

Higher Probe Temperatures Result In...

Lower Filterable PM
Higher Condensable PM



Test Methods

Particulate Test Methods

Filterable

Method 5: Total Suspended PM

Method 5B: Non-sulfate Total PM

Method 5F: Non-sulfate FCCU Total PM

Method 17: In-stack Particulate

Method 201: Filterable PM 10

Method 201A: Filterable PM 10/2.5

Condensable

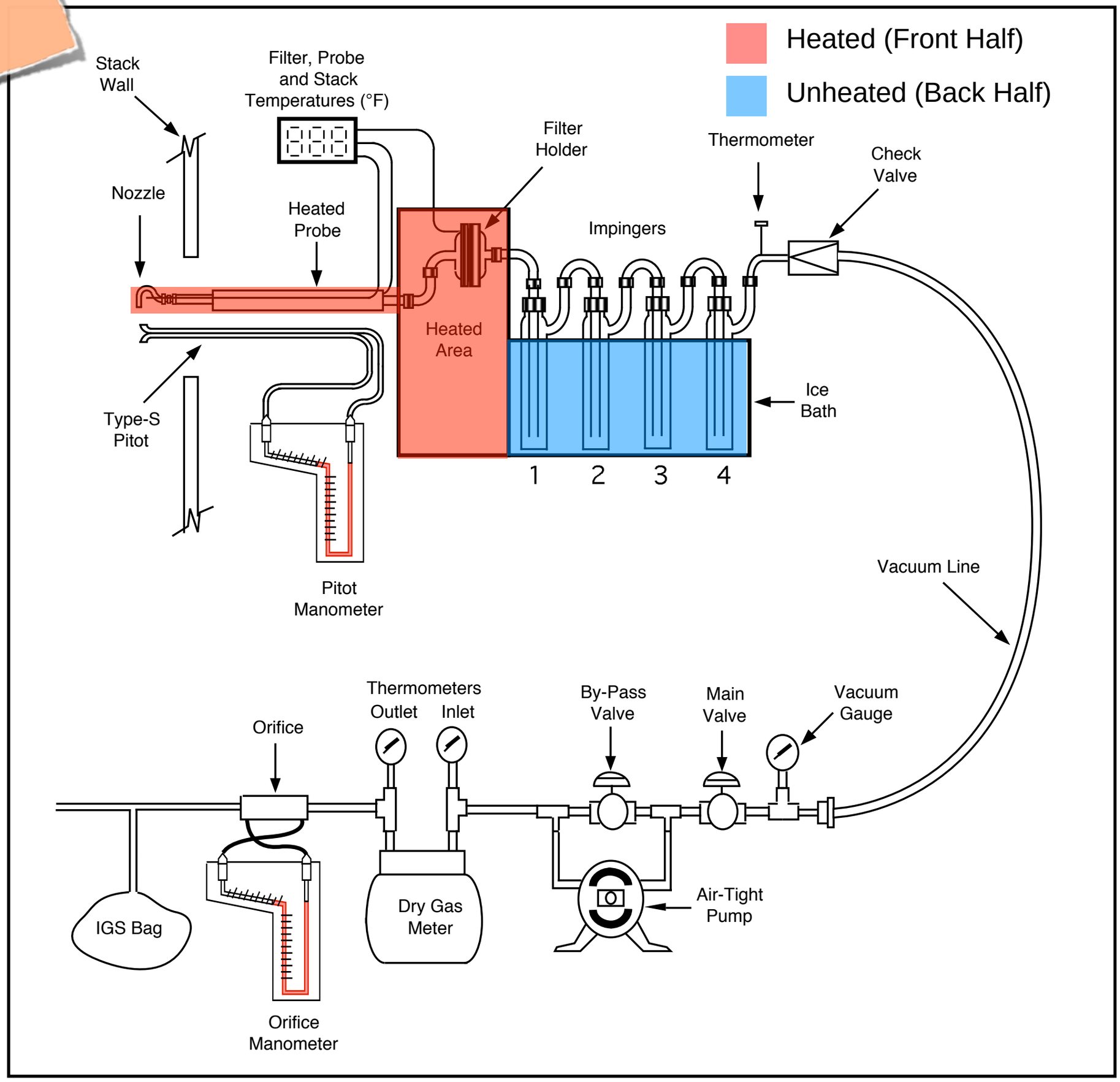
Method 202: Condensable PM

Method 5

Method 5
248 °F
No BH

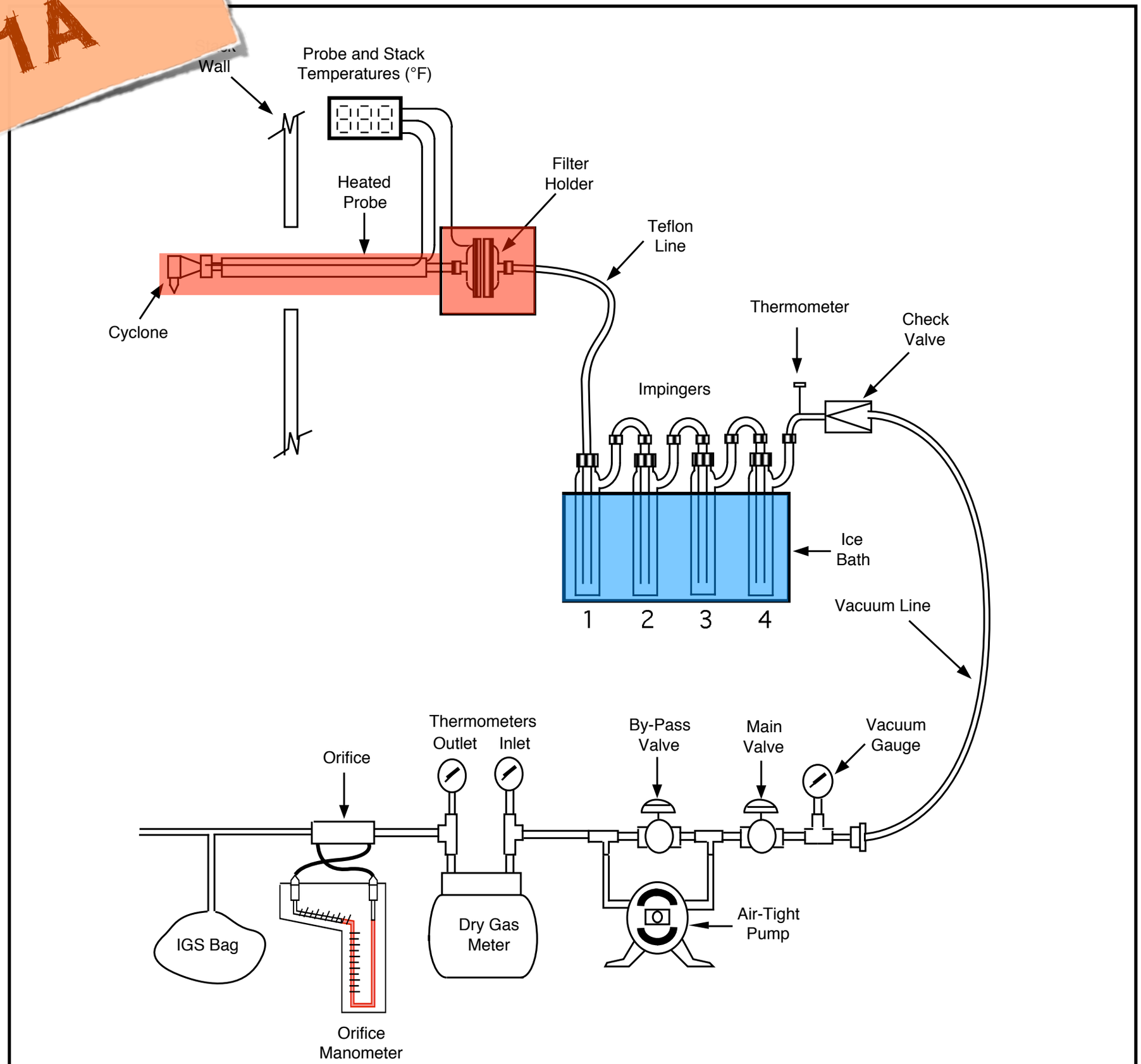
Method 5B
320 °F
No BH

Method 5F
320 °F
No BH
Sulfate Filter



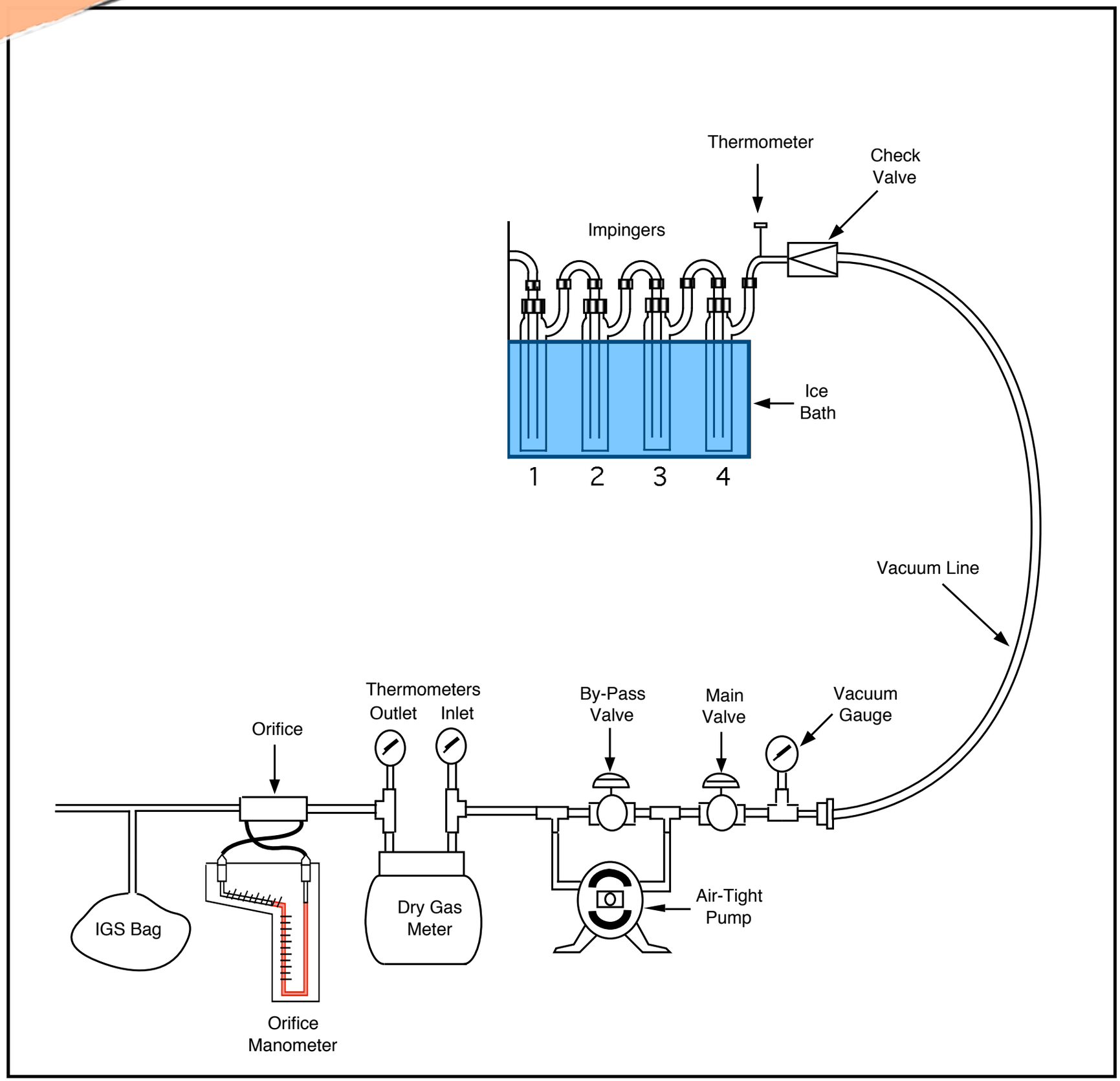
Method 201A

A PM 2.5 or PM 10 cyclone (or both) may be attached to the probe

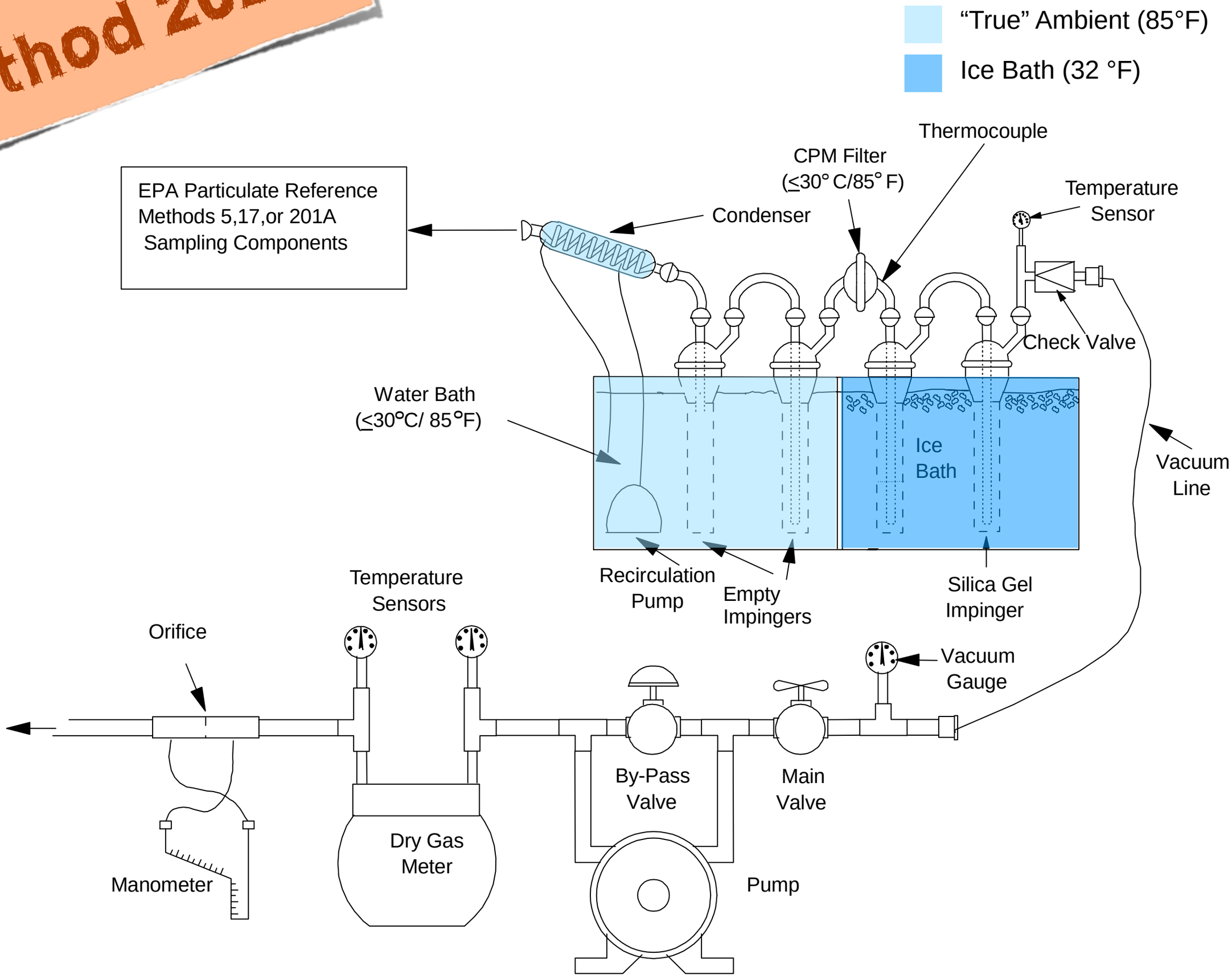


M201A, Cat w/BH, OSF

Method 202 (old)



Method 202


"True" Ambient (85°F)
Ice Bath (32 °F)
EPA Particulate Reference Methods 5,17,or 201A Sampling Components
Thermocouple
CPM Filter (≤30° C/85° F)
Temperature Sensor
Condenser
Check Valve
Water Bath (≤30°C/ 85°F)
Ice Bath
Vacuum Line
Recirculation Pump
Empty Impingers
Silica Gel Impinger
Temperature Sensors
Orifice
Vacuum Gauge
By-Pass Valve
Main Valve
Dry Gas Meter
Manometer
Pump

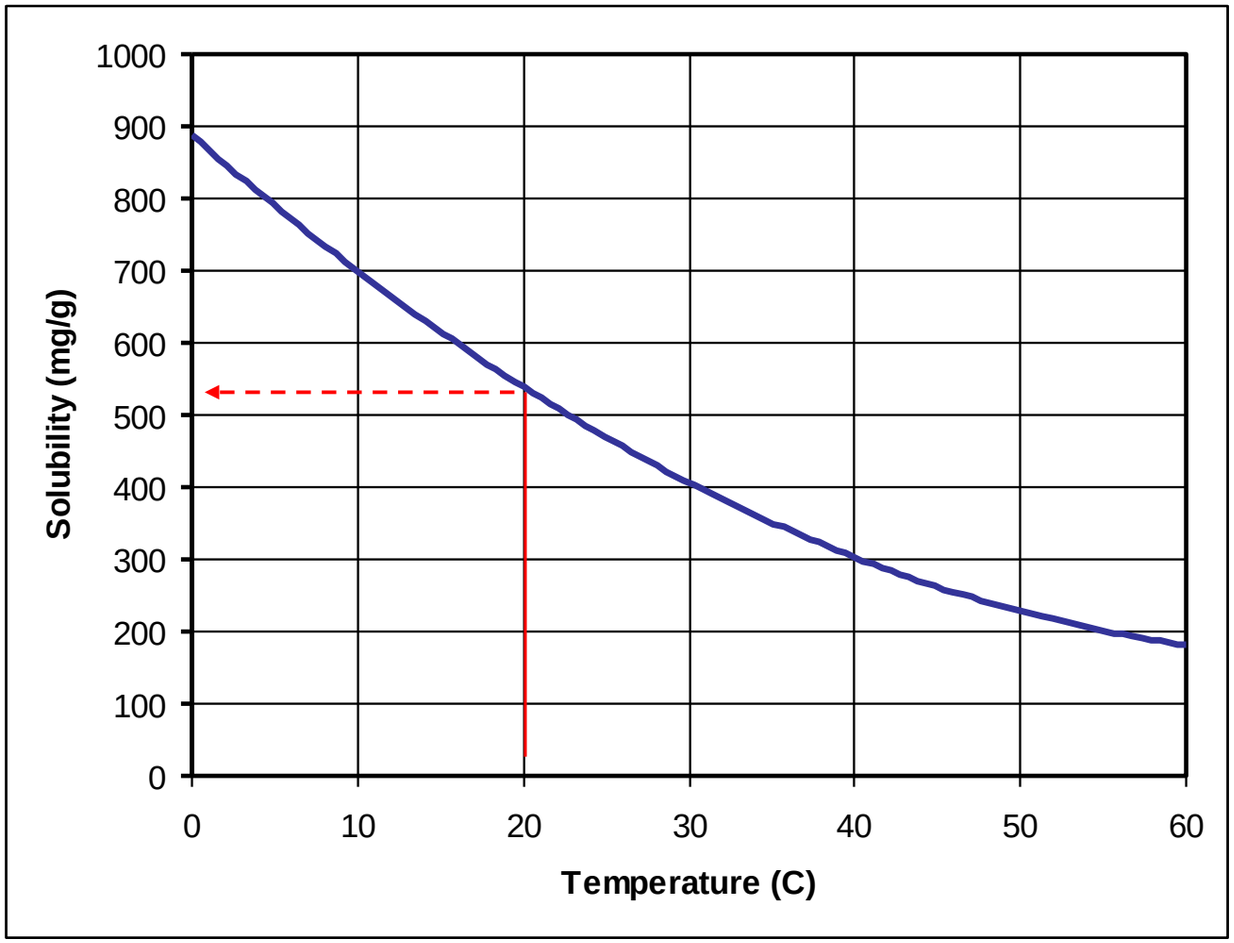
Why did they change Method 202?

Too many options - inconsistent results
Creation of sulfate artifacts (high bias)

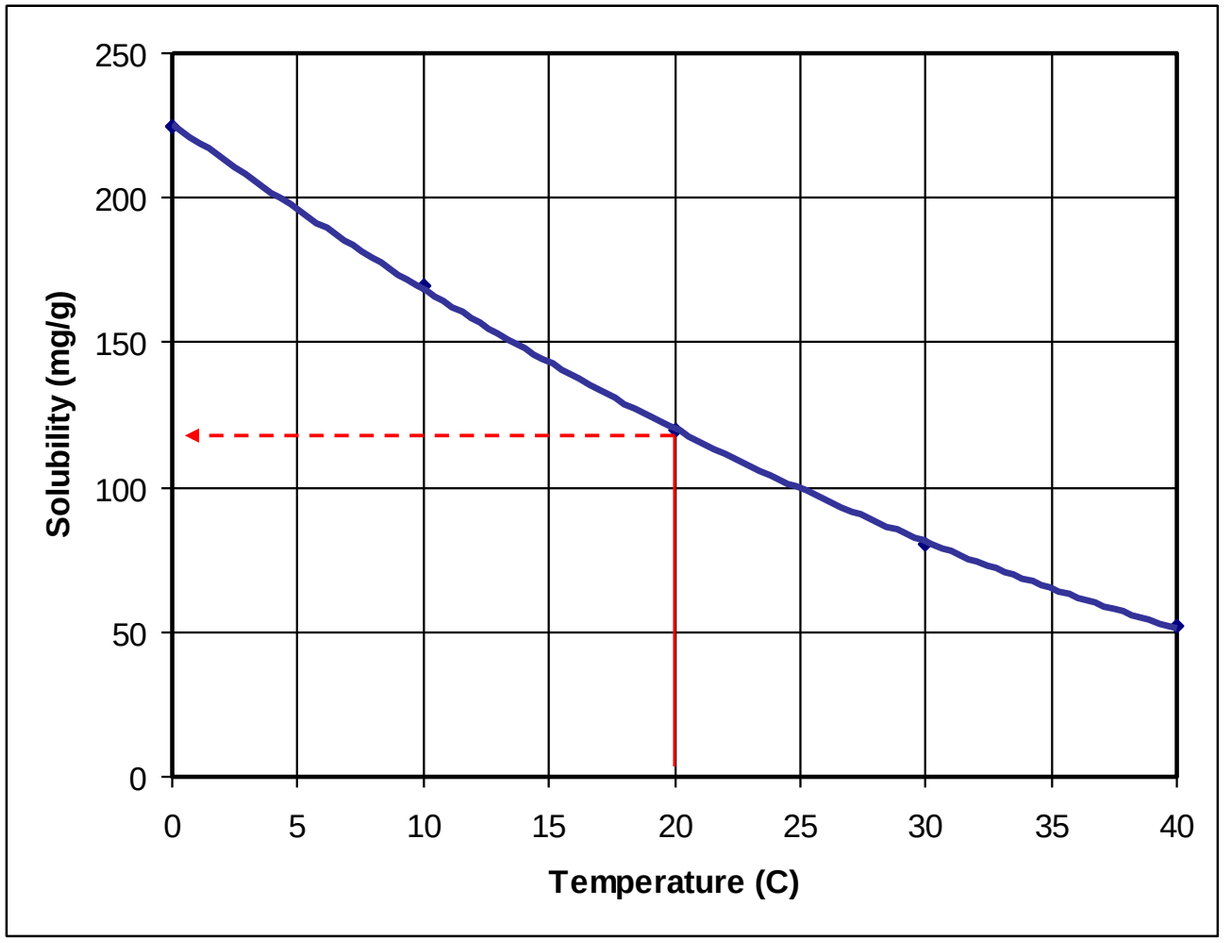
However...

There are issues with the new method

Solubility of NH_3 in Water



Solubility of SO_2 in Water



The presence of free NH_3 in the flue gas is the catalyst for the dissolution of SO_2.

NH_3 has a great affinity for water. One volume of water at 0°C will absorb more than 1000 volumes of NH_3.

NH_3 raises pH in impinger

which greatly enhances...

SO_2 collection effciency

resulting in...

Formation of ammonium salts in impinger

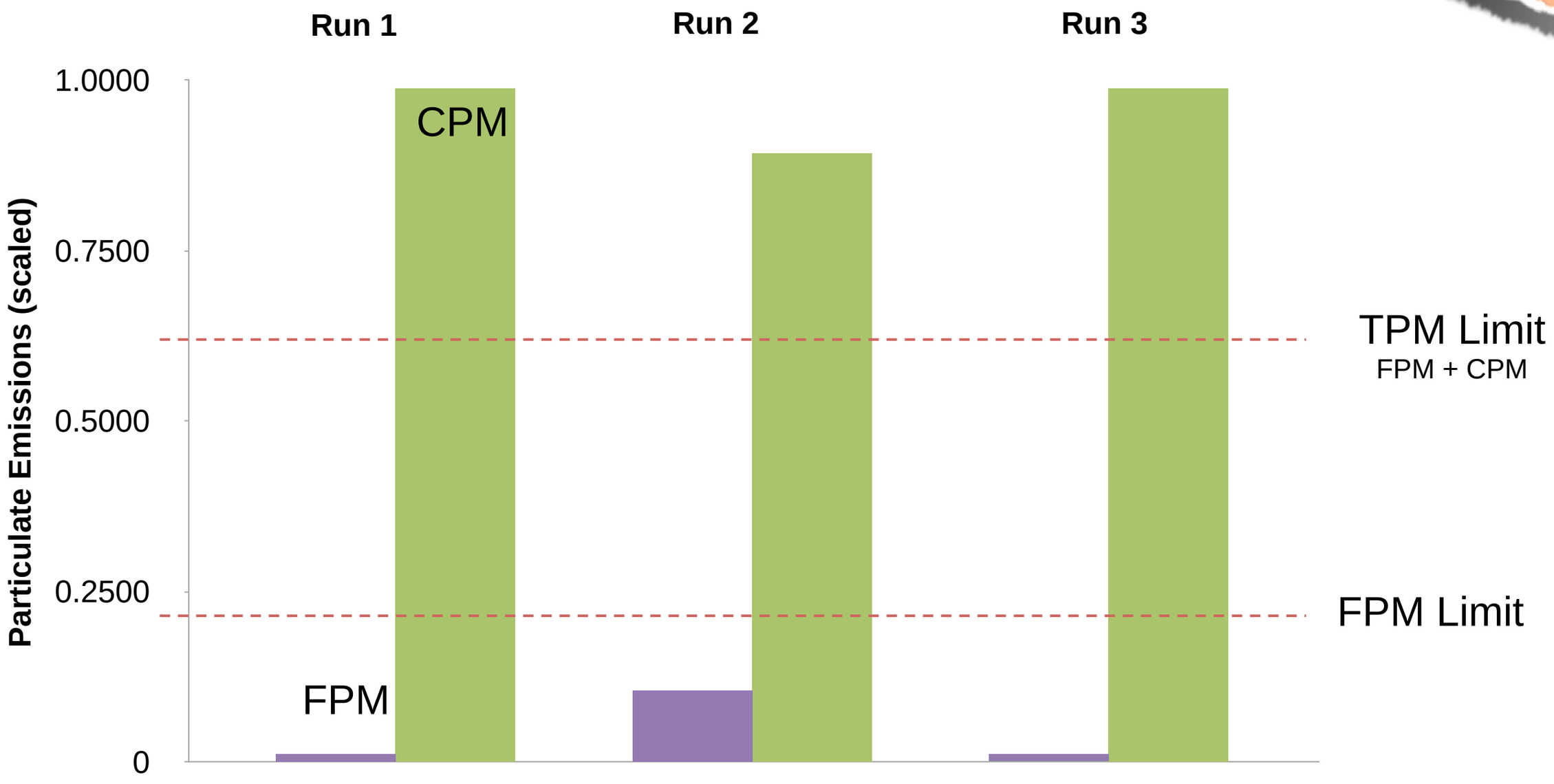
NH_3 (gas) + SO_2 (gas) + H_2O (liq) → NH_4 (liq) + HSO_3 (liq) + time, O_2 <-> $(NH_4)HSO_4$

$2NH_3$ (gas) + SO_2 (gas) + H_2O (liq) → NH_4 NH_4 (liq) + SO_3 (liq) + time, O_2 <-> $(NH_4)_2SO_4$

A Case Study

The Problem

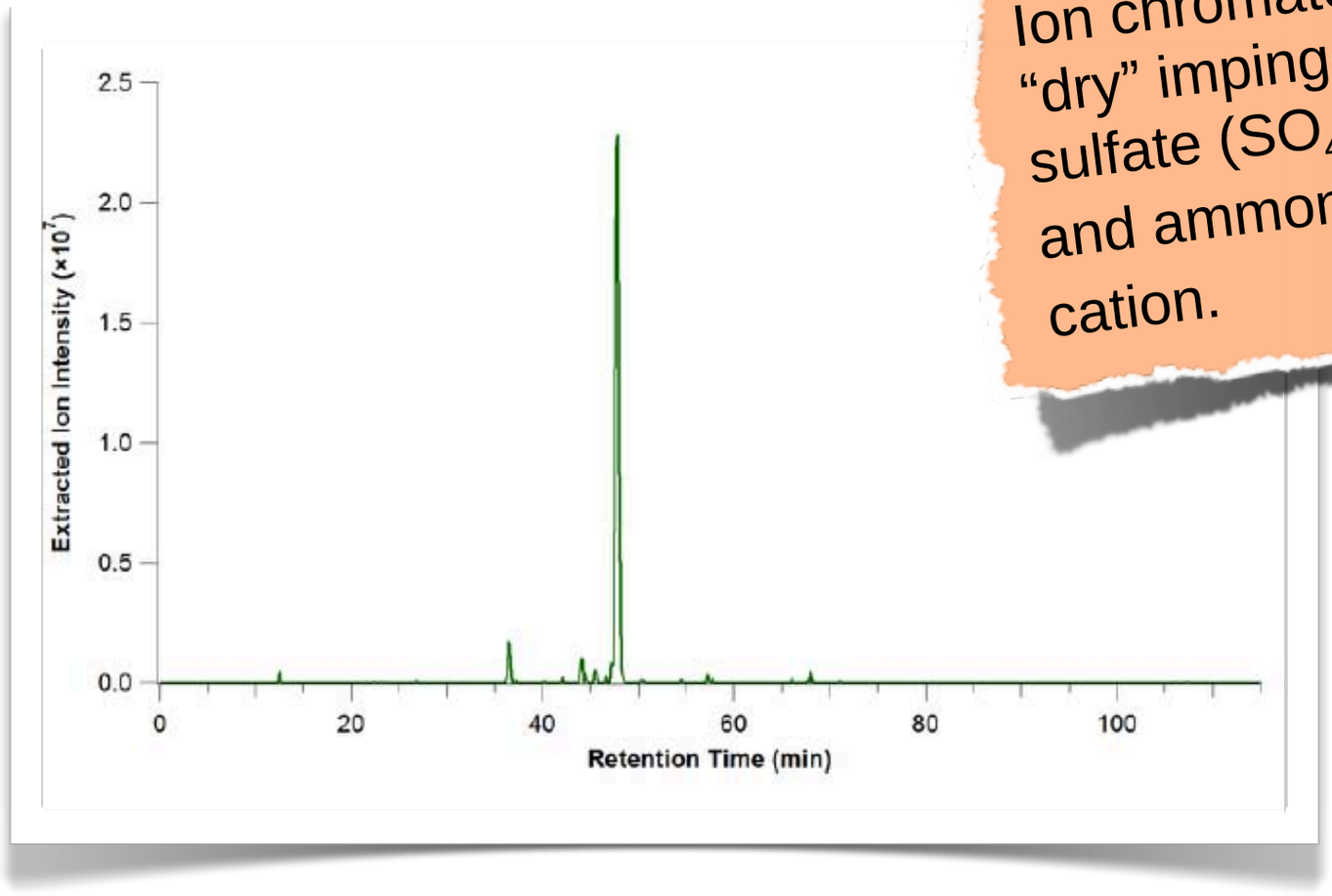
Recent test results
400 mmBtu PRB-fired boiler w/ SNCR using the new Method 202



Flue Gas

H_2SO_4 < 1 ppm by simultaneous CCM
NH_3 >> 10 ppm by simultaneous FTIR
SO_2 ~ 35 ppm by simultaneous FTIR

Investigation



Ion chromatographic analysis of the "dry" impinger catches showed that sulfate ($SO_4^{=}$) was the only anion found and ammonium (NH_4^{+}) was the only cation.

The sulfate found was far in excess of the sulfate available from the H_2SO_4 in the flue gas

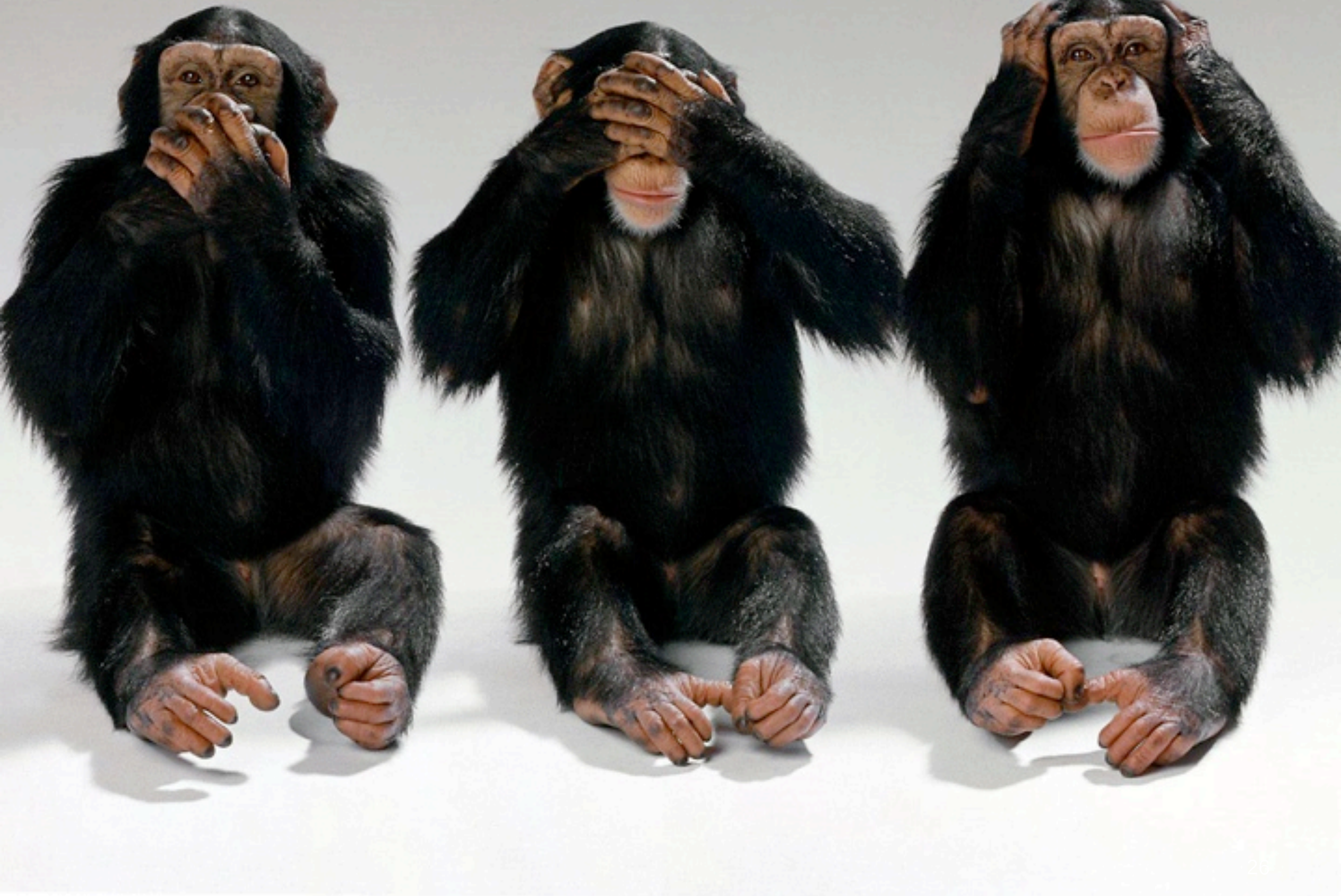
Conclusion: NH_3 is absorbed in the impinger, increasing the pH and greatly enhancing the scrubbing and oxidation of SO_2.

Bottom Line...

About 80 – 90% of the condensable particulate measured did not exist in the stack but was created in the “dry” impingers of the Method 202 sampling train.

It is “false-particulate”

EPA's Take on This Issue



New Definition of CPM From The New Method 202

“CPM means material that is vapor phase at stack conditions, but condenses **and/or reacts** upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack."

EPA believes that gaseous SO_2 and gaseous NH_3 stack will quickly react in the ambient air to form ammonium sulfate (or bisulfate) at or very near the stack exit.

Therefore, even though the components are gaseous when they leave the stack, they must be counted as particulate emissions.

To Bolster Their Argument

They cite studies…

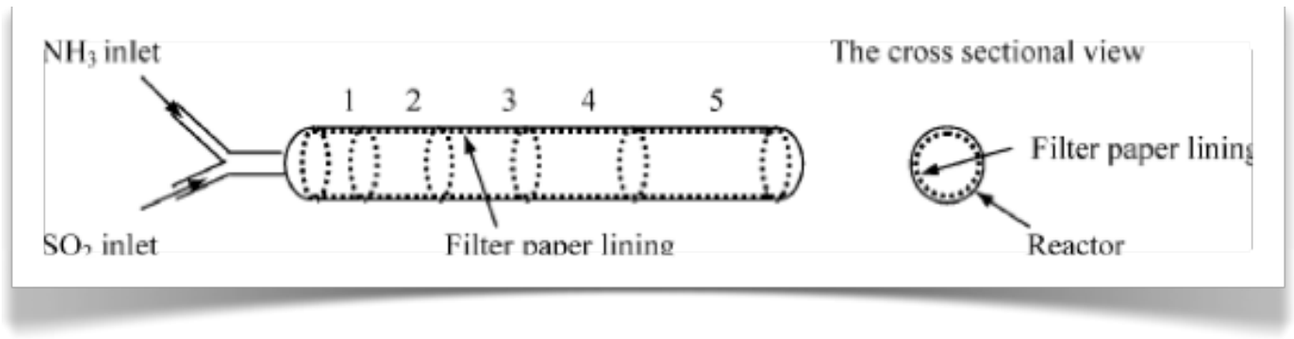
1. Landreth, R. et al., "Thermodynamics of the Reaction of Ammonia and Sulfur Dioxide in the Presence of Water Vapor", The Journal of Physical Chemistry, Vol. 79, No. 17, 1975, pp. 1786-1788.
2. Hartley, E.H., and Matteson, M.J., "Sulfur Dioxide Reactions with Ammonia in Humid Air", Industrial Engineering Chemical Fundamentals, Vol. 14, No. 1, 1975, pp. 67-72.
3. Hirota, K., et al., "Reactions of Sulfur Dioxide with Ammonia: Dependence of Oxygen and Nitric Oxide", Ind. Eng. Chem. Res., Vol. 35, 1996, pp. 3362-3368.
4. Yanxia, G., et al., "Reaction Behavior of Sulfur Dioxide with Ammonia", Ind. Eng. Chem. Res., Vol. 44, 2005, pp. 9989-9995.

These studies show that, indeed, gaseous SO_2 and gaseous NH_3 can combine to form ammonium salts.

Our Take on This Issue

First of all…

All the tests EPA cites were conducted in small closed glass vessels



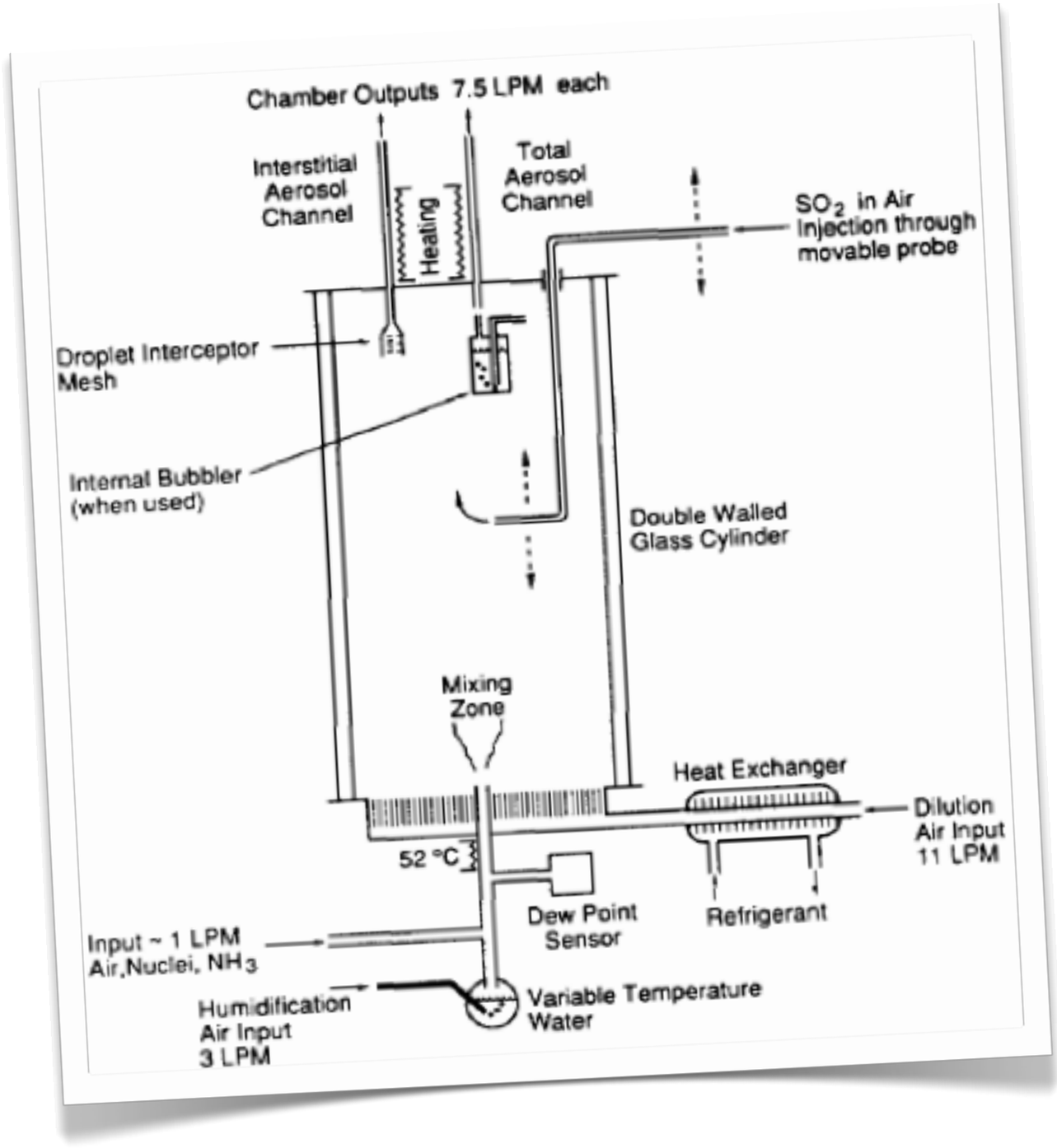
The studies themselves indicate that most of the observed SO_2/NH_3 reactions take place on the glass surfaces of the vessels not in the interior volume of the vessels.

Studies in small enclosed glass vessels are not necessarily representative of actual reactions that will occur in ambient air

And Then…

A study by Hanson* in a cloud chamber found **no appreciable sulfate formation** observed in the presence of NH_3 with water in the vapor phase.

Hansen's study also indicates that **these reactions would not occur immediately at the exit of the stack** but at some distance downwind.



*Hansen, A.D.A., Benner, W.H., and Novakov, T., "Sulfur Dioxide Oxidation in Laboratory Clouds", Atmospheric Environment, Volume 25A, No. 11, 1991, pages 2521-2530.

And Finally...

At the boiler in question there were

No Visible Emissions

even though the amount of TPM measured would have been sufficient to produce a visible plume.

Conclusions

The Takeaways…

The new Method 202 potentially produces an extremely **high bias** (false particulate) when SO_2 and NH_3 are present in the gas stream

The cloud chamber work by Hansen shows that **SO_2 and NH_3 will not react** in the absence of water droplets and will not occur immediately upon exiting the stack

Ammonium sulfate or bisulfate formed in the Method 202 dry impingers **should be considered an artifact**.

EPA should allow for correction of this artifact by substituting inorganic CPM values obtained through controlled condensation (CCM) testing in place of the Method 202 inorganic CPM values.

Particulate Correction

TPM = FPM (M5) + Organic CPM (M202) + Inorganic CPM (CCM)

Other Condensable Issues

Allowable recovery blank value in Method 202: **2.0 mg**

Any blank value above this is added to your PM

Glassware Issues

Glassware Issues

Glassware Issues

Glassware Issues

The new Method 202 requires **EITHER**:

1. Baking glassware to 300 °F, **OR**
2. Sampling train proof blank

Static Issues

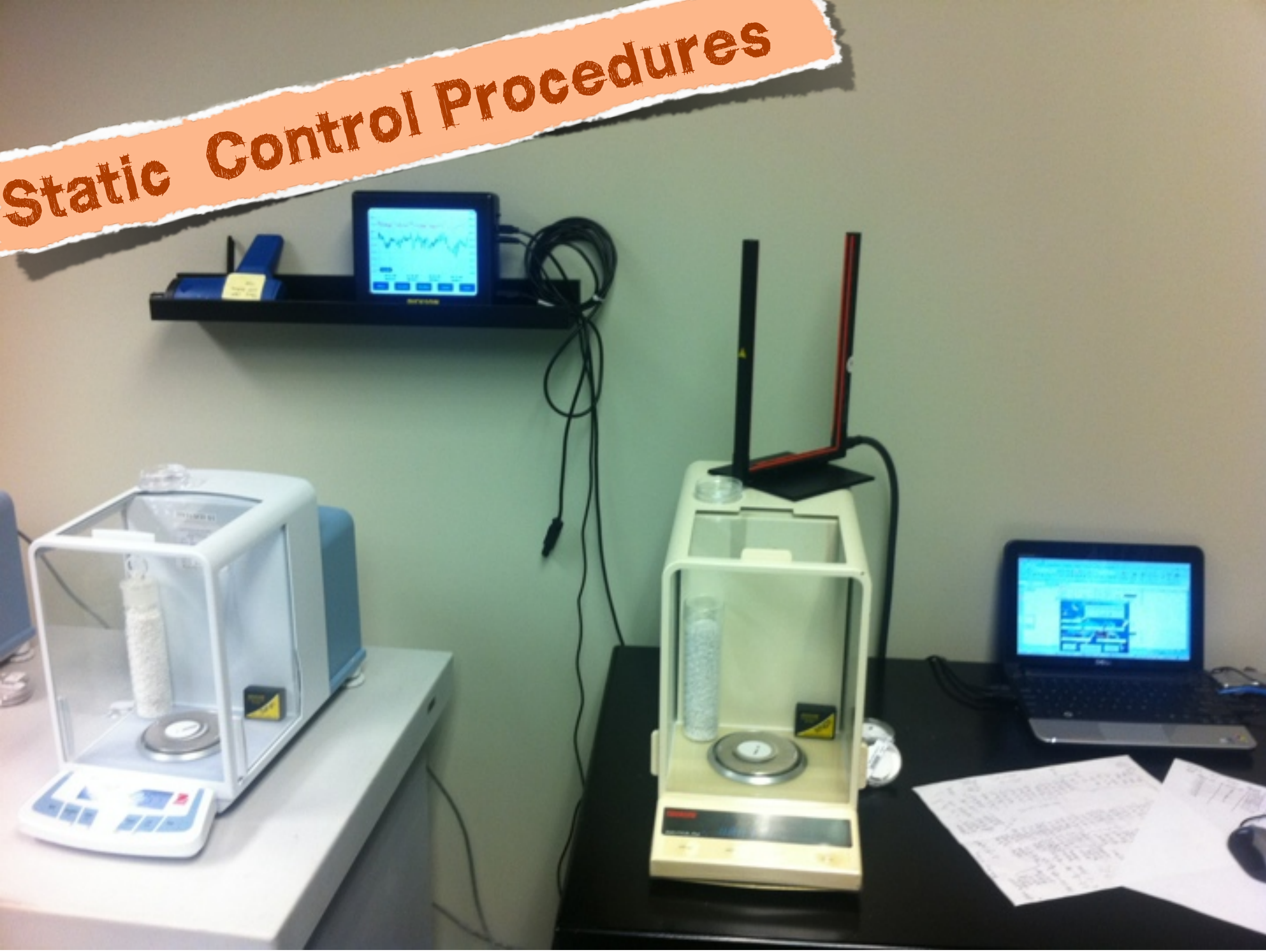
A static charge on a filter or beaker may induce a positive bias in the gravimetric measurement.

During a filter weighing, static charge on the filter induces image charges in the conducting areas of the balance and the filter is electrostatically attracted to the image charges. The balance interprets this attraction as mass, which adds to the overall mass of the filter.

Swanson, J. “A Method to Measure Static Charge on a Filter Used for Gravimetric Analysis”, Aerosol Science and Technology, 2008

Static Control Procedures

Static Control Procedures



Static Control Procedures

Implementation of stringent glassware cleaning and static control procedures reduced blank values to one third of the previous values

To minimize your risk, insist on...

lab and field reagent blanks
baked glassware
field train proof blank
field train recovery blank
best practice for static control

Fini

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