

The Avogadro Group, LLC

Source Emissions Testing and Emissions Specialists

Comparing the Performance of EPA Method 202 and CTM-039 for CPM Measurements

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NCASI Workshop 2013

PM2.5 Measurement Challenges

- Test methods may not measure low enough to quantify low-concentration emissions

- Lowering emission limits:

NSPS Limits in 1970's – Filterable PM
125 mg/m³ (125 mg in ~1-hour test run)

NSR Limits Today – including CPM
2 to 15 mg/m³ (as low as 8 mg in 4-hour run)

PSD SER ton/yr Thresholds
0.8 to 6 mg/m³ (as low as 2 mg in 4-hour run)

PM2.5 Measurement Challenges

- Lowering emission limits:

NSR Limits Today – including CPM

2 to 15 mg/m³ (as low as 8 mg in 4-hour run)

PSD Significant Emission Rate ton/yr Thresholds

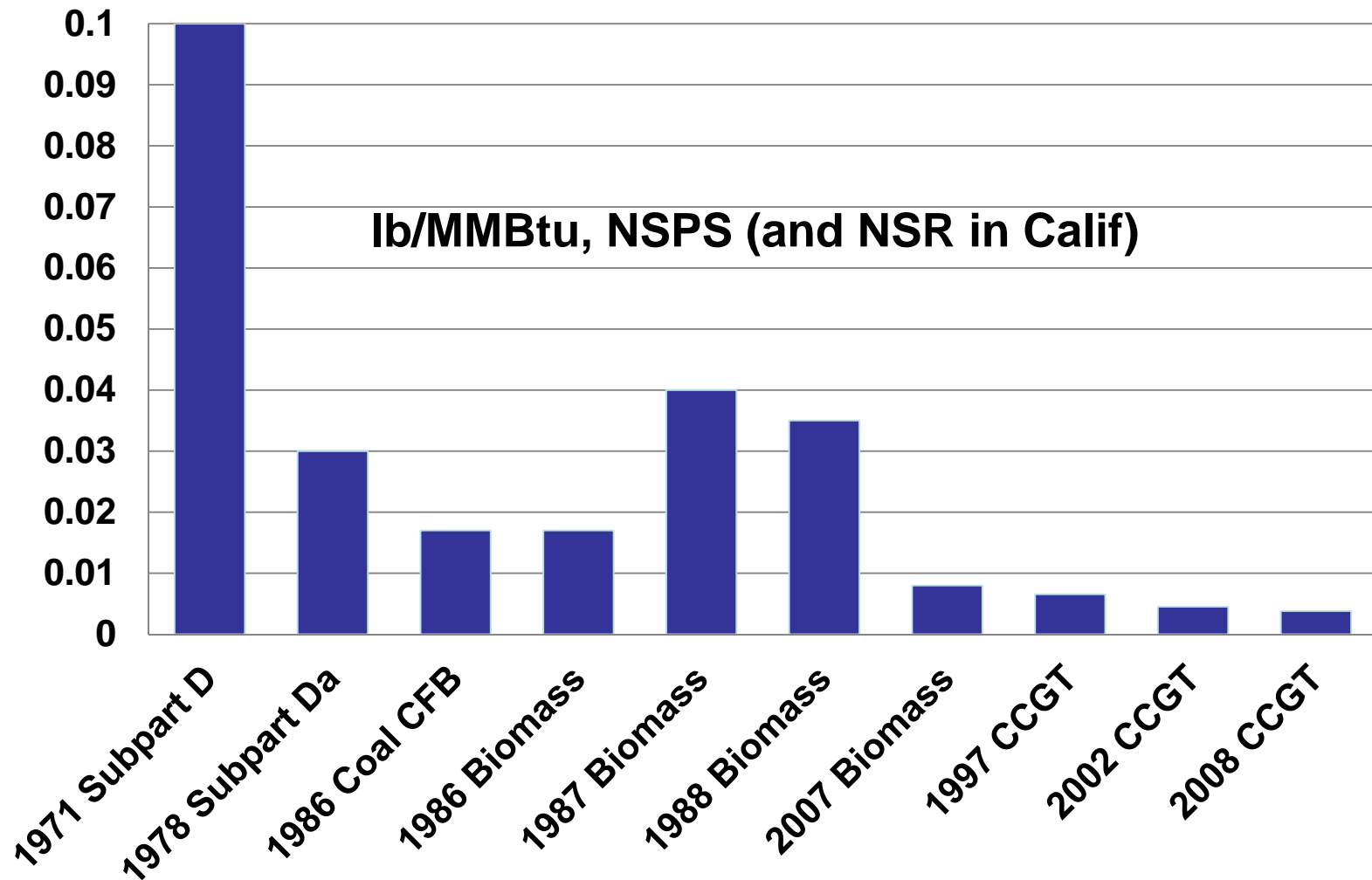
0.8 to 6 mg/m³ (as low as **2 mg in 4-hour run**)

or in other units:

0.0015 to 0.005 lb/MMBtu

– even lower than what's shown in the next chart:

Emission Limits



PM2.5 Measurement Challenges

- Include Condensable Particulate Matter
- Background residue (blanks)
- Contamination (from field/lab environment)
- Laboratory Detection Limits
(how low can we really measure)
- Bias / artifact in the measurement of CPM
*- when you must model for PSD or NSR,
what are the real emissions of
Primary and Secondary PM2.5?*
- Limitations in application of the reference
methods (and possible or future solutions)

What is Particulate Matter?

Mass/volume measured at Ambient Monitor
Emissions - Mass/volume measured at Stack

Primary Particulate

- **Filterable PM** (*primary “front half”*)
 - **Solid or liquid particles** at stack or filter temperature- PM, PM₁₀ & PM_{2.5}
- **Condensable PM** (*primary “back half”*)
 - **Vapor or gas** at stack conditions - Organic and inorganic
 - Condenses and/or reacts upon cooling and dilution in ambient air, **forms solid or liquid particles immediately** after stack discharge
 - All assumed to be in the PM_{2.5} size fraction

Secondary Particulate

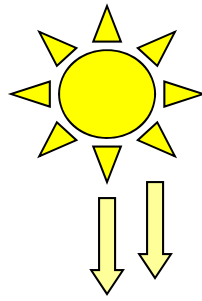
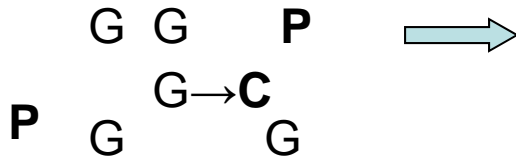
- **Vapor or gas** at stack conditions and after discharge
- Forms PM by chemical reactions in atmosphere downstream of release point

What are we trying to measure?

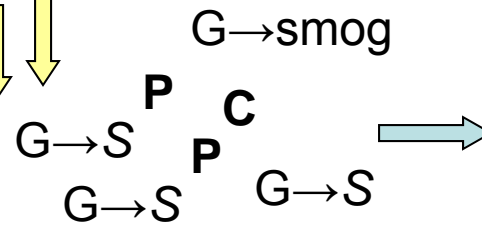
Primary Particulate Matter less than 2.5 μm

Primary PM2.5 Emissions

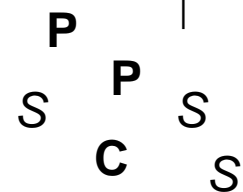
- **P**articles
- **C**ondensable PM from some Gases just after release to atmosphere



Photochemistry – other Gases (precursors) to *Secondary PM2.5* and to smog (ozone, etc.)

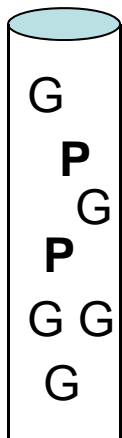
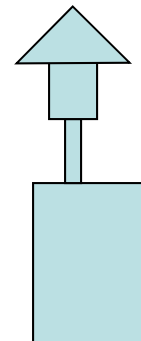


Gaseous smog (O_3)



Ambient Monitor – collects all **P C & S**

Ambient PM2.5 commonly mostly secondary



Standard stack tests – Easily measure Particles and Gases at stack conditions

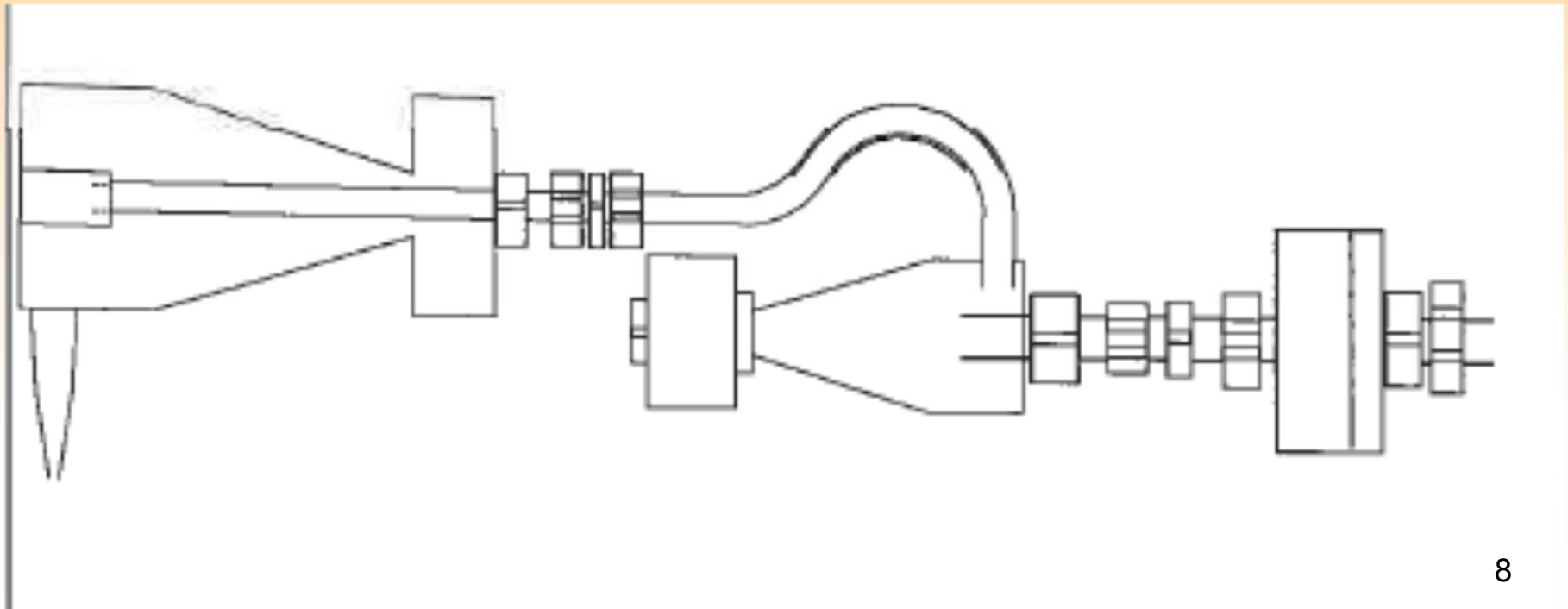
We must measure Primary Emissions

- Particles and Condensables
- Gases

(use models to predict Secondary PM2.5)

Filterable PM_{10} – $PM_{2.5}$ Measurement

- EPA Method 201A – 2010
PM10 and/or PM2.5 Cyclones for Aerodynamic separation of larger particles (similar to ambient monitor)
In-stack Filtration
 - Can't be used in "wet" stacks (FGD, wet scrubbers)
 - Limited to temperature $<500^{\circ}F$ (or even $400^{\circ}F$)



Filterable PM₁₀ – PM_{2.5} Measurement

- EPA Method 201A – 2010
PM10 and/or PM2.5 Cyclones
 - PM10 cyclone usually requires a 6-inch diameter port
 - Both cyclones together always needs a 6-inch
 - PM2.5 by itself can fit through a 4-inch port



Filterable PM_{2.5} Measurement Issues

Method changes have been updates and improvements – Challenges remain:

Contamination –

- Dirty apparatus, glassware, recovery area
- Corrosion of stainless steel cyclones

Detection limit – Low concentrations

- Measurement can be 2 mg or less
- DL between 0.2 and 1 mg
- Blanks between 0.03 and 0.3 mg
- Uncertainty between 1 and 5 mg (5 X DL)

Application limitations – Wet stacks, High Temp 10

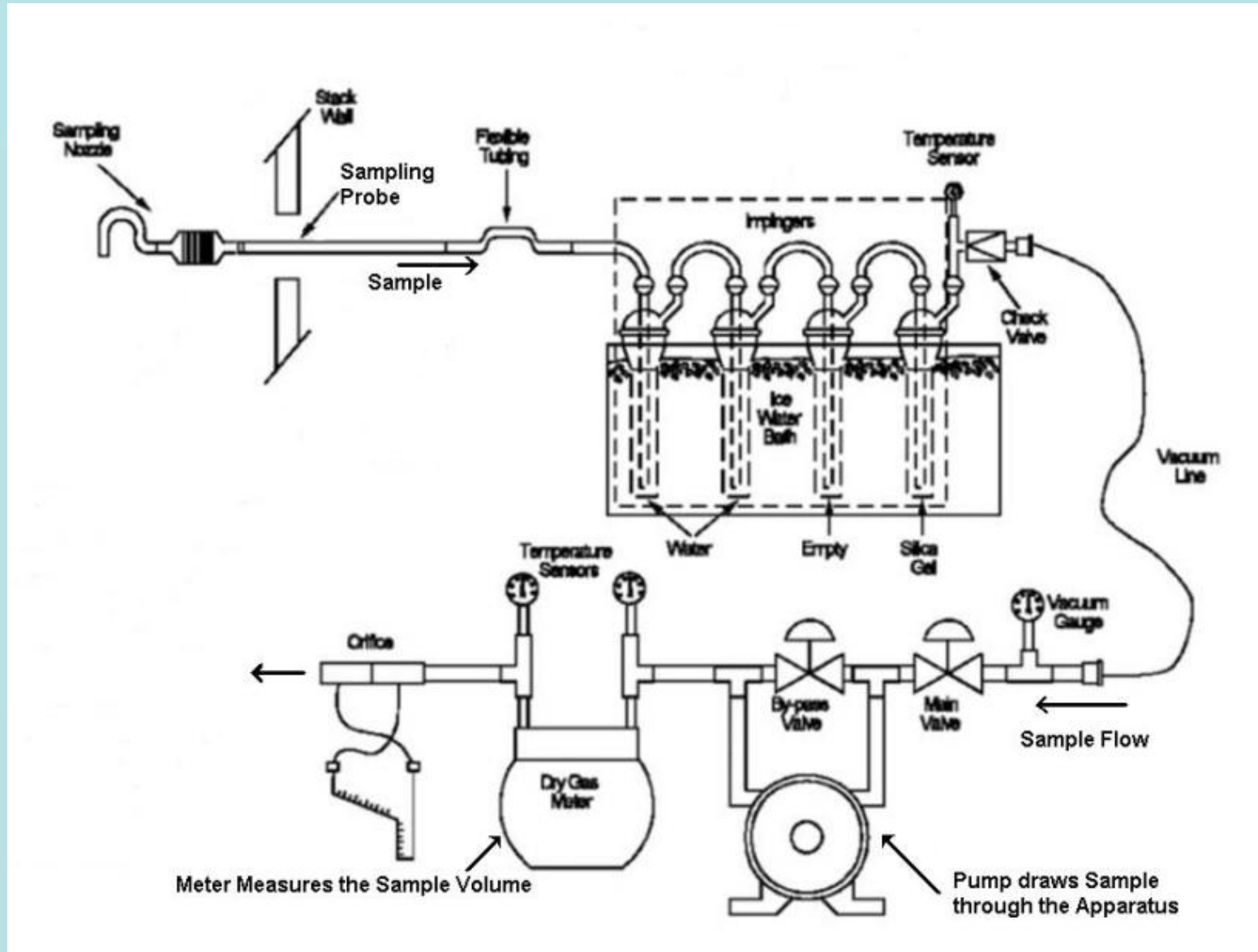
Filterable Methods Comparison

- Method 201A results can be lower than Method 5 results (PM_{2.5} is a subset of PM₁₀, which is a subset of total PM)
- The difference may be small for highly controlled solid-fuel sources, or for gas-fired sources (nearly all the PM is PM_{2.5})
- For low emitters, it's possible to get higher results for PM₁₀ or PM_{2.5} (Method 201A) than for Total PM by Method 5
 - Higher background blank/contamination

Traditional CPM Measurement

- CARB, SCAQMD, ODEQ, WDOE Methods (1960's, 1970's), EPA 202 (1990)
- Sample bubbles through water in impingers
- Collects CPM really well – down to $< 68^{\circ}\text{F}$
- ***But*** – Gases dissolve in that water, too...

Traditional CPM Measurement



Maximized gas-liquid contact



Traditional CPM Measurement

Gases dissolve and create **artifact** “CPM”

some SO_2 gets oxidized to sulfate

SO_2 , NH_3 , HCl in solution dry down to:

- Ammonium Sulfate, Ammonium Bisulfate
(forms from SO_2 oxidation to sulfate in solution)
- Ammonium Chloride (forms readily)

The artifact salts confuse the division between

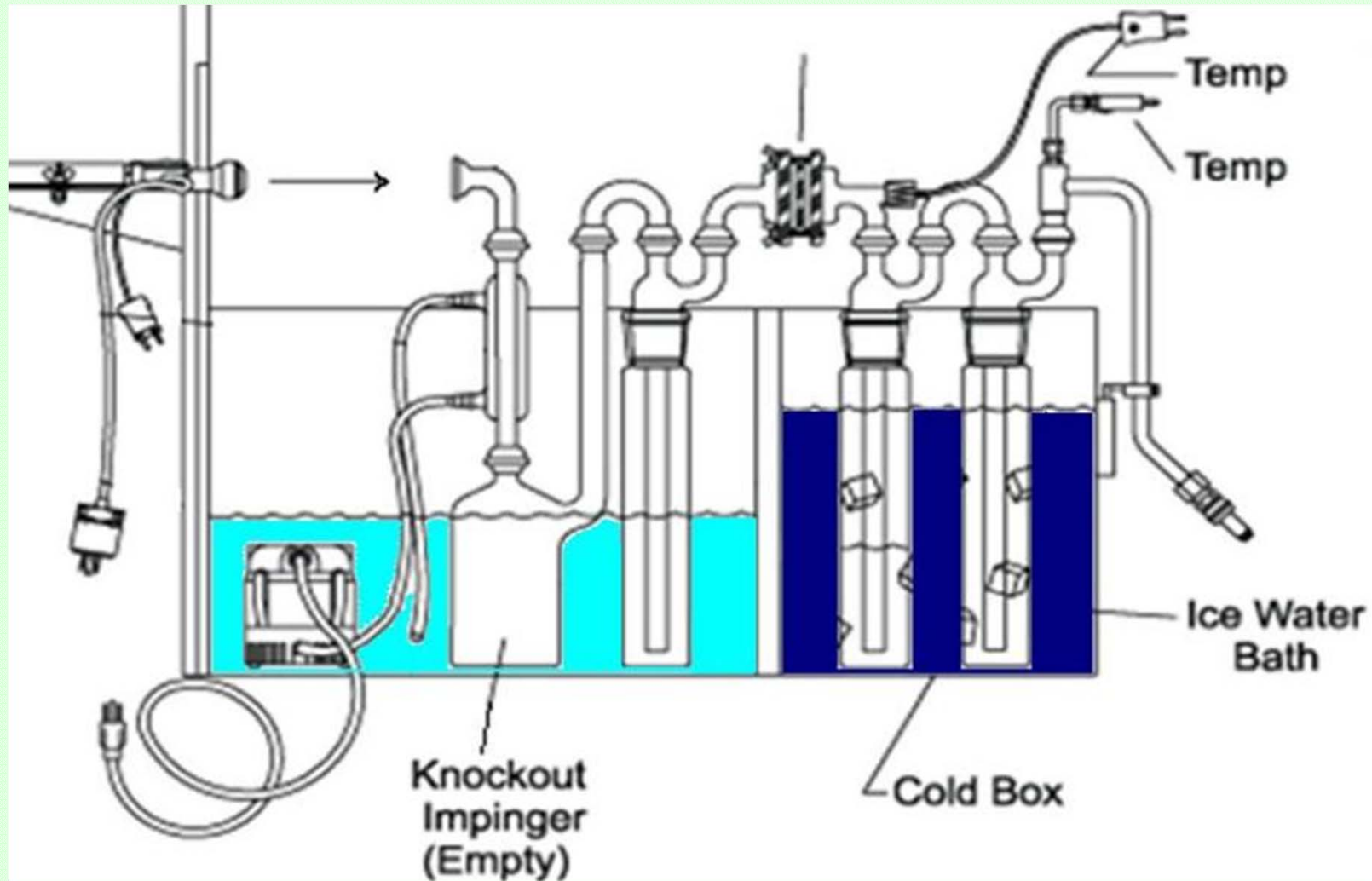
Primary $\text{PM}_{2.5}$ and

Secondary $\text{PM}_{2.5}$ formed from precursor gases

**SO_2 , NH_3 , HCl get counted as gaseous
AND as PM emissions!**

Revised CPM Measurement

- EPA 202 (2010) - No bubbling of sample through water



Revised CPM Measurement



Revised CPM Measurement

Minimizes gas-liquid contact

Collects condensate (including water) at $<85^{\circ}\text{F}$

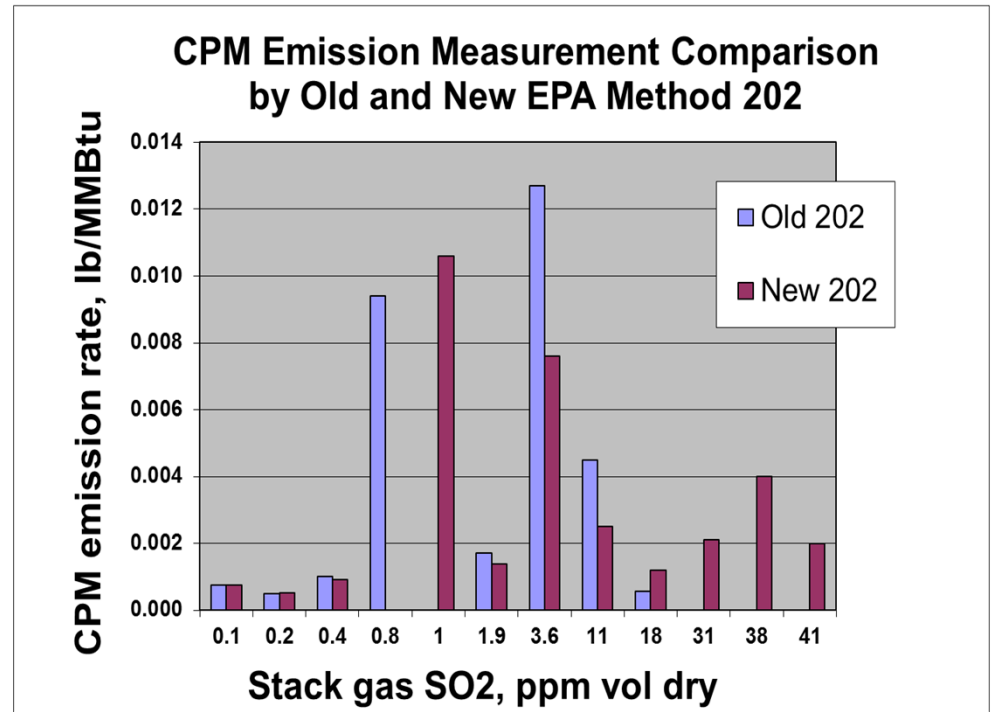
Gases should dissolve less; SO_2 stripped out by post-test purge with pure Nitrogen

This can work quite well on stacks with little or no ammonia

But – when ammonia is present, we still measure artifact ammonium salts (often about as much as with the old methods)

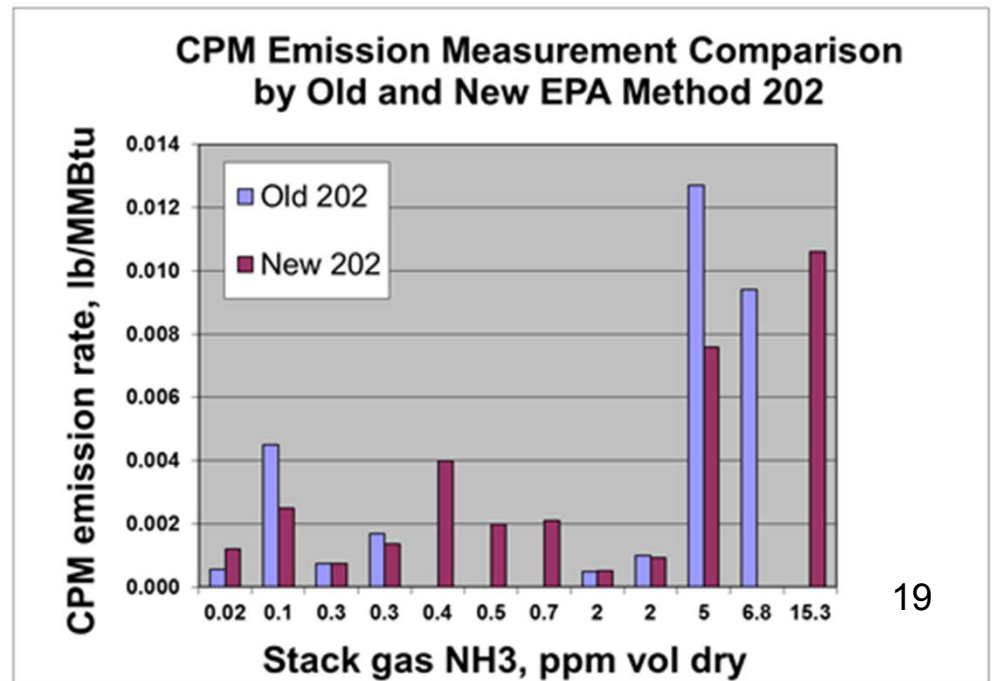
CPM vs. SO₂

Various types of sources,
x-axis is not linear,
Highest results are **not** the
highest SO₂



CPM vs. NH₃

Same data as above,
correlates more closely with
NH₃ than with SO₂



CPM Measurement Issues

Field Blanks

- Average for organic fraction 0.3 to 0.5 mg
- Average for aqueous fraction 0.6 to 1 mg
- Total field blank typically 0.9 to 1.5 mg
- We do get occasional results greater than 2 mg, almost always less than 3 mg

Method is more complex to set-up and operate

- At some locations, must have 2 persons rather than one – cost is greater

Method requires Nitrogen purge – we get 3 purges per N₂ cylinder – so cost is greater

Laboratory analysis takes longer

- Evaporation at lower temperature than the old methods
- Weigh to constant of 0.1 mg – one weight per day

CPM Measurement Issues

Artifact

- Ammonium Sulfate $(\text{NH}_4)_2\text{SO}_4$
- Ammonium Chloride NH_4Cl

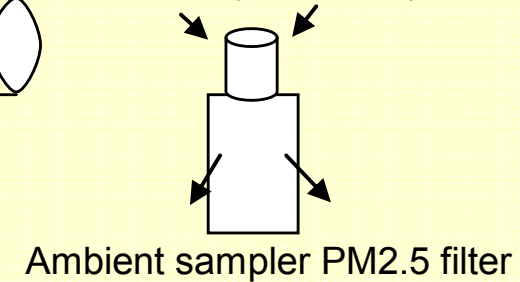
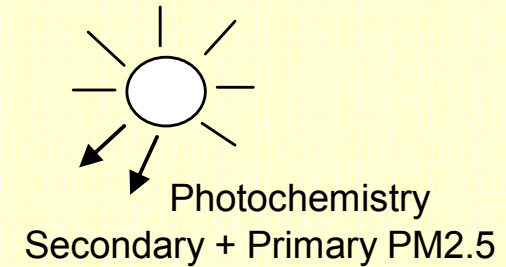
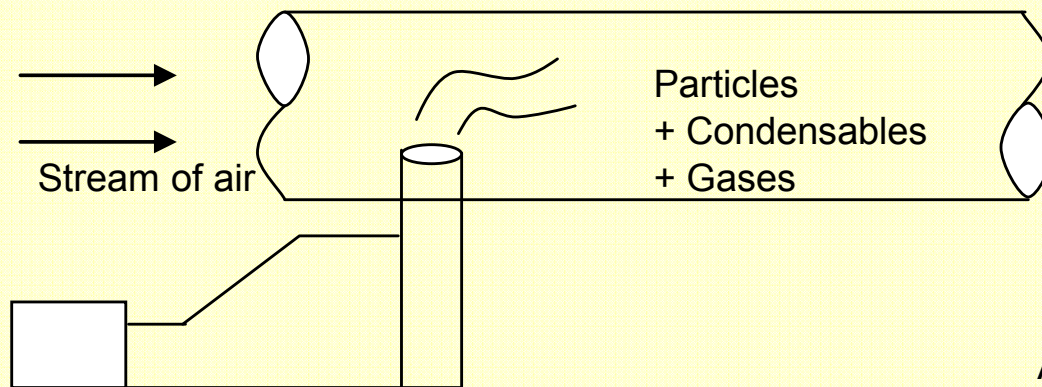
How do we know there is artifact? Might some of this actually form in nature and be actual CPM?

Test using a different method...
(The METHOD defines the results)

Dilution Sampler Concept

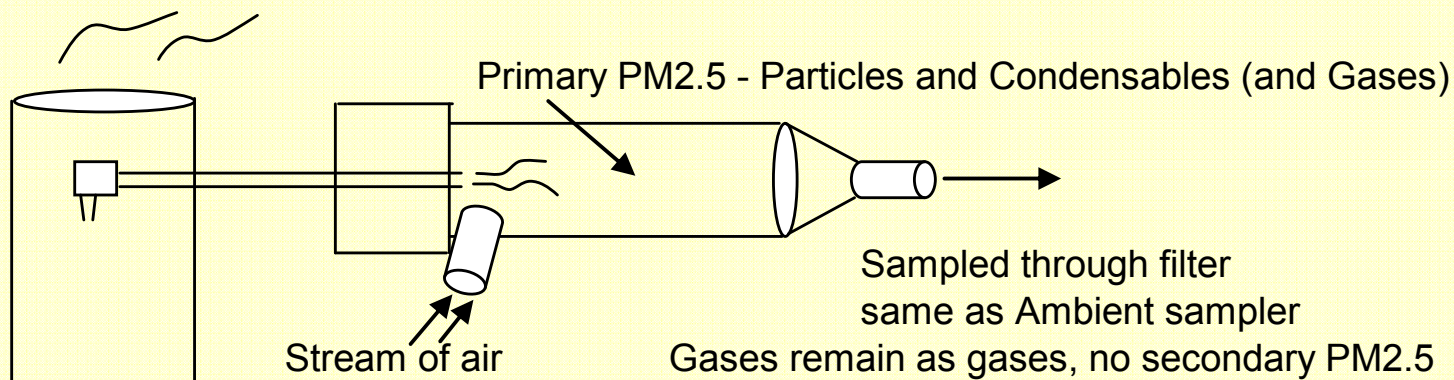
Stack emissions of Primary PM2.5

Emissions into a "virtual" stream of air



Stack sampling of Primary PM2.5 by CTM-039

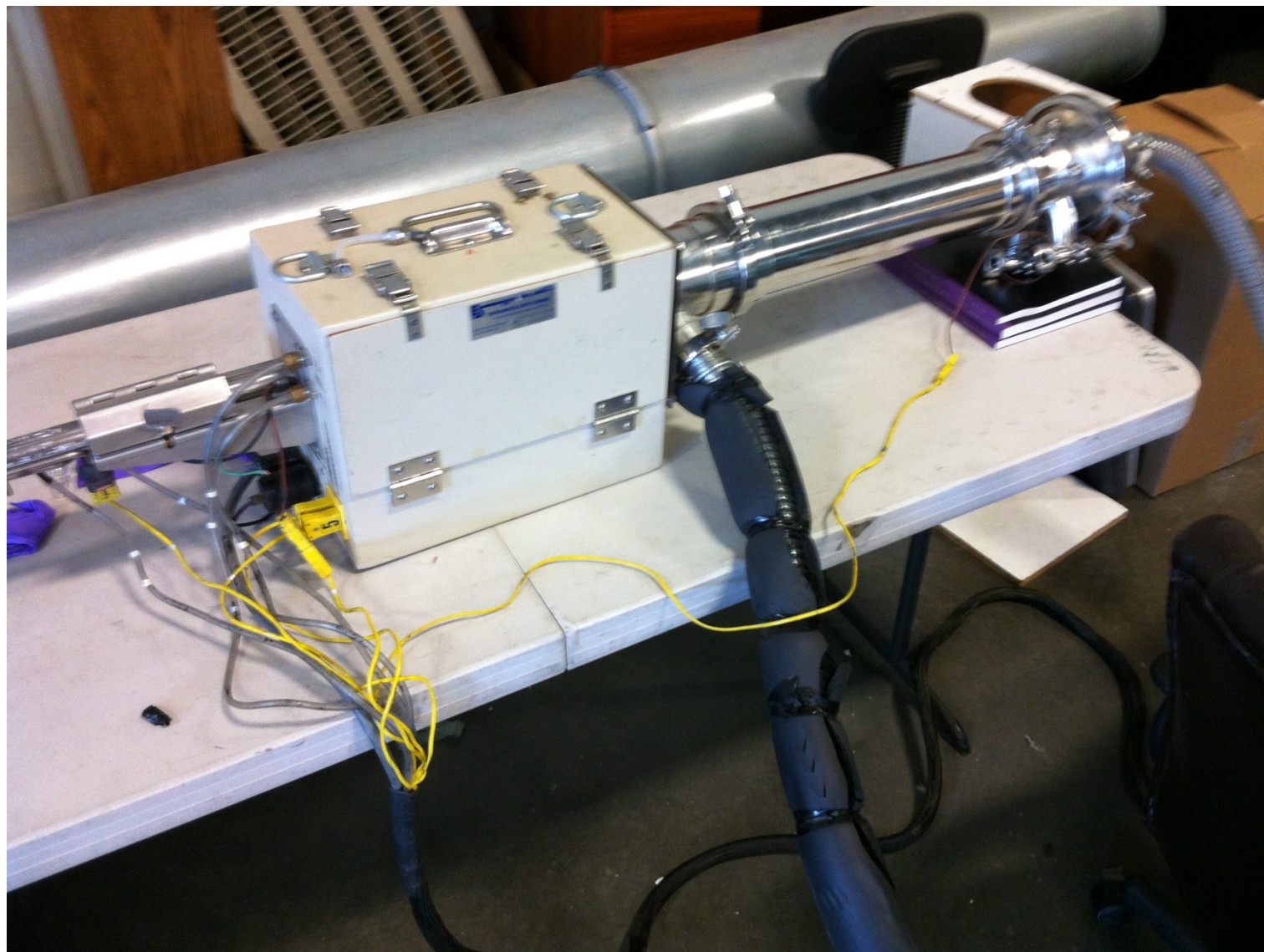
Sample "emitted" into a stream of air



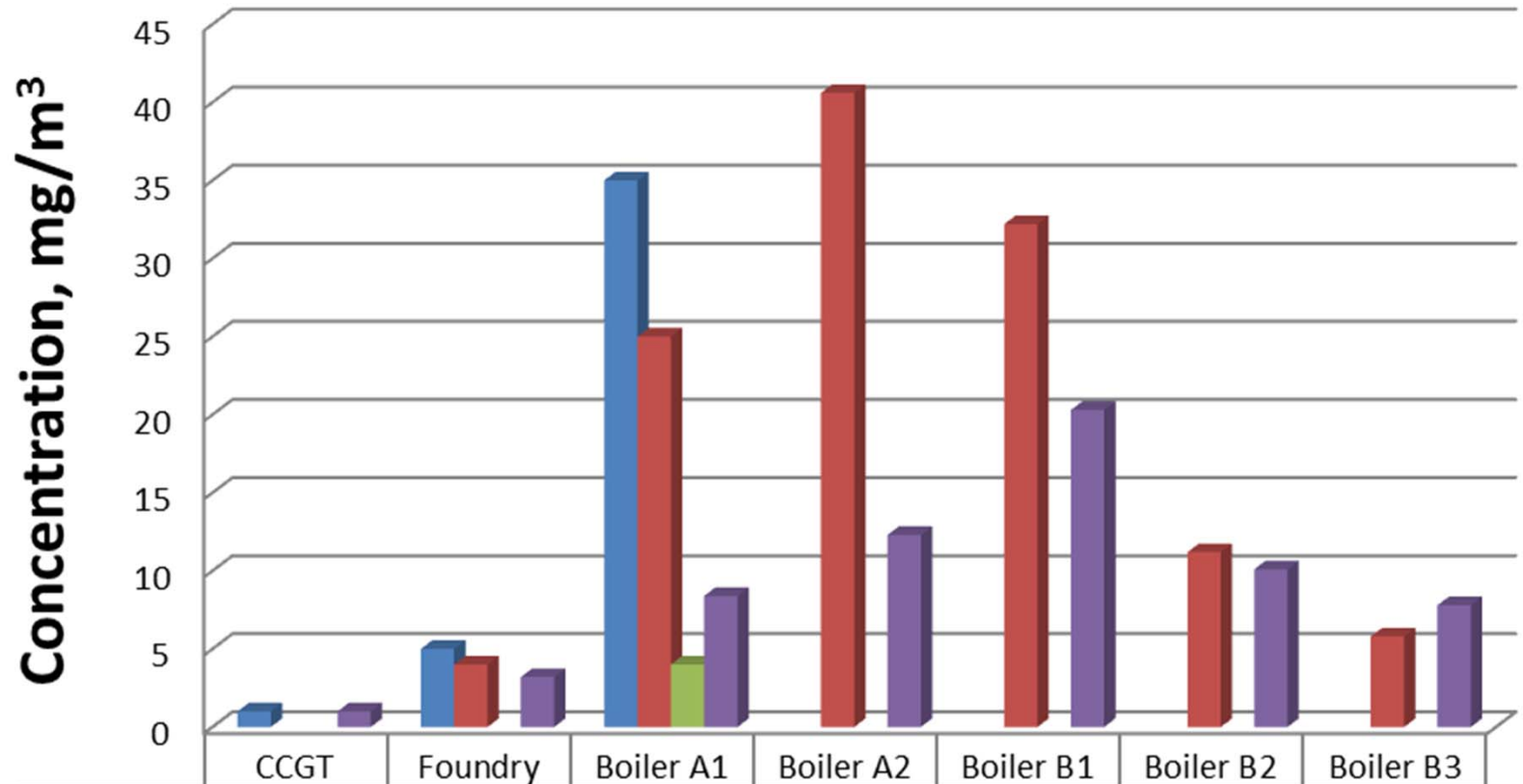
Dilution Method CTM-039 (2004)

- Designed to emulate dilution of stack emissions in ambient air
- Can sample PM10 and/or PM2.5 (or PM) (using the same in-stack cyclones as 201A)
We have also used on wet stacks without cyclones
- Condensables form in the same way as in actual emissions – EPA's *Gold Standard*
- Primary PM2.5 – particles and CPM - all sampled together (like ambient sampling)
- Disadvantage: Expensive new equipment, Not widely embraced

Dilution Method CTM-039 (2004)



CTM-039 PM Test Results Comparison

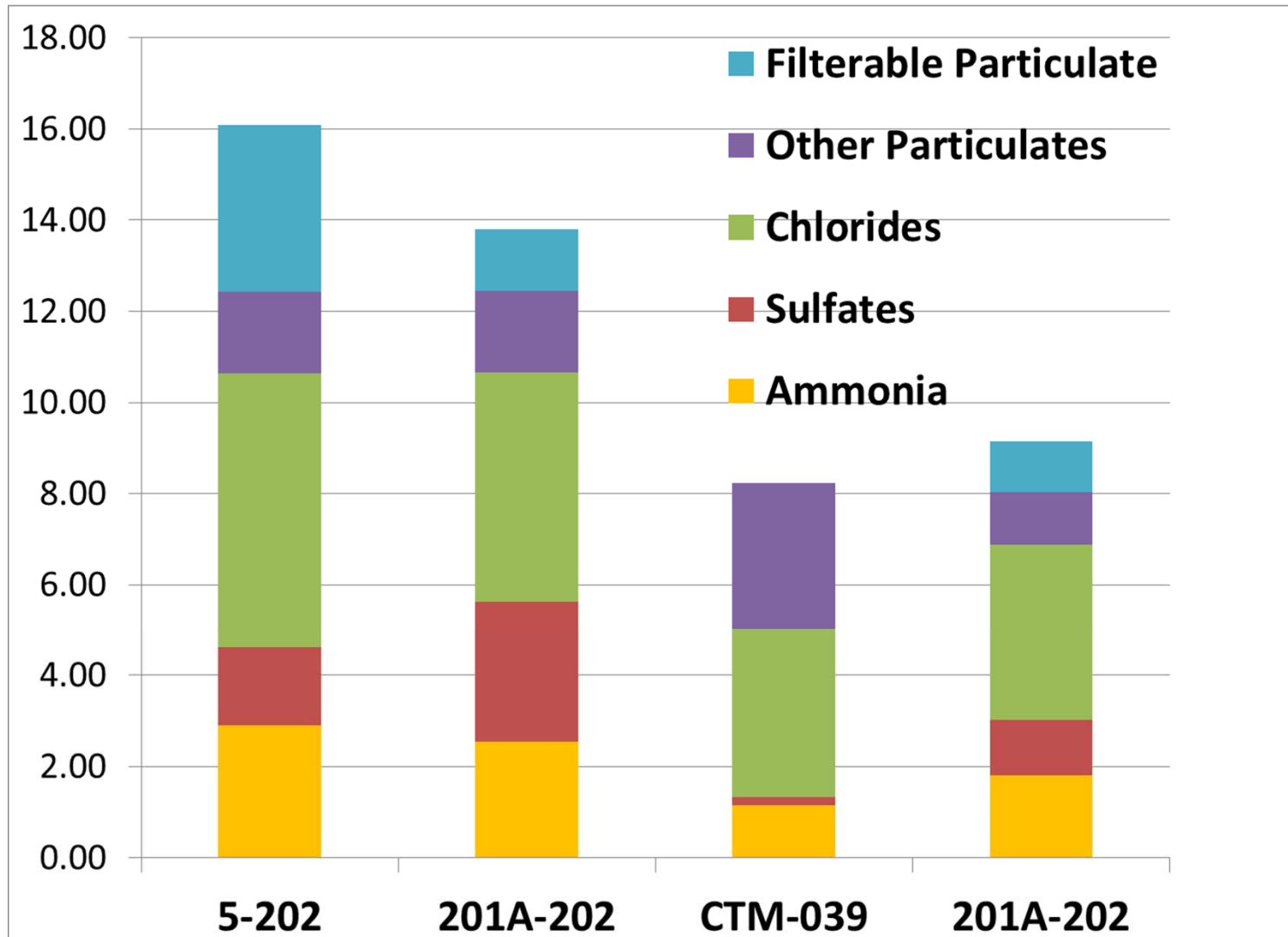


	CCGT	Foundry	Boiler A1	Boiler A2	Boiler B1	Boiler B2	Boiler B3
Old 202	1	5	35				
New 202		4	25	40.6	32.2	11.2	5.8
NH3 Off			4				
CTM-039	1	3.2	8.4	12.3	20.3	10.1	7.8

CPM Methods Comparison

- New 202 can (in some cases) measure less sulfate artifact than the old Method
- Amount of artifact in either method depends on concentration of NH_3 more than SO_2 (excess SO_2 gets purged out)
- Significant artifact remains in new 202 results when Ammonia is present
- CTM-039 appears to greatly reduce artifact from NH_3 and SO_2

Methods Comparison Case Study Solid Fuel w/SNCR, 2 Series of Tests



Case Study Comparison

- Higher fuel Cl content led to higher test results for CTM-039 as well as for Method 202
- Method results will depend on the concentrations of NH_3 , SO_2 and HCl
- CTM-039 was found to greatly reduce ammonium sulfate artifact,
But ammonium chloride remained
- Note: The stack had no visible plume, so ammonium chloride might also be artifact
 - Does it form on the filter fibers during sampling? On the internal walls of the sampler?More study may be needed

CTM-039 Results

- Can be used on wet stacks (with Method 5 nozzle in place of cyclone)
 - But ability to handle moisture is limited (dilution with dry air to low enough dew point)
- Can demonstrate low emissions (with little or no artifact) when Method 202 over-measures due to artifact
- Does not solve all potential “problems”
- Points to the importance of better understanding of the chemistry involved

Wet-Stack PM2.5 Methods

- API-sponsored method
 - Simple nozzle (development needed)
 - Method 202 for CPM
- EPA – EPRI-sponsored method
 - Special nozzle cuts out large droplets that would dry to particles >> PM2.5
 - Dilution, then ambient-type cyclone and sampler for the formed PM2.5
 - More closely emulates natural processes
 - Needs funding to complete evaluation

Conclusions

- Best practices can provide lower field blanks and detection limits for Methods 201A & 202
- Artifact ammonium sulfate still causes results higher than actual primary CPM emissions
- CTM-039 can provide results that better represent actual primary PM_{2.5} emissions - but does not solve all perceived problems
- High-quality, accredited testing companies may provide better results with existing methods or with present or future alternative methods

Questions ???

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