The Avogadro Group, LLC

Source Emissions Testing and Emissions Specialists

Can your unit pass a Particulate Emission Compliance Test?

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The Test Method Defines Compliance

The Process and its Emission Controls determine actual emissions

But the Test Method defines the results used to determine compliance

There is a difference – and it can be important!

Methods have been developed in attempts to measure actual emissions of:
Filterable PM and Condensable PM

The objective is accurate results for:
- **Primary**, Directly emitted PM, PM10, PM2.5
- Gaseous Precursors to formation of **Secondary** PM2.5 (SO_2, NO_X, VOC, NH_3)

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, PM_{10} & $PM_{2.5}$
- **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

Filterable PM Measurement

- Total FPM - EPA Method 5 and Method 17
  (1970's)
  - Measure Filterable PM only, all sizes of particles together

- PM10, PM2.5 – EPA Method 201A
  (1990, updated 2010)
  - Aerodynamic separation of larger particles, measure particles less than 10 µm or less than 2.5 µm, or both

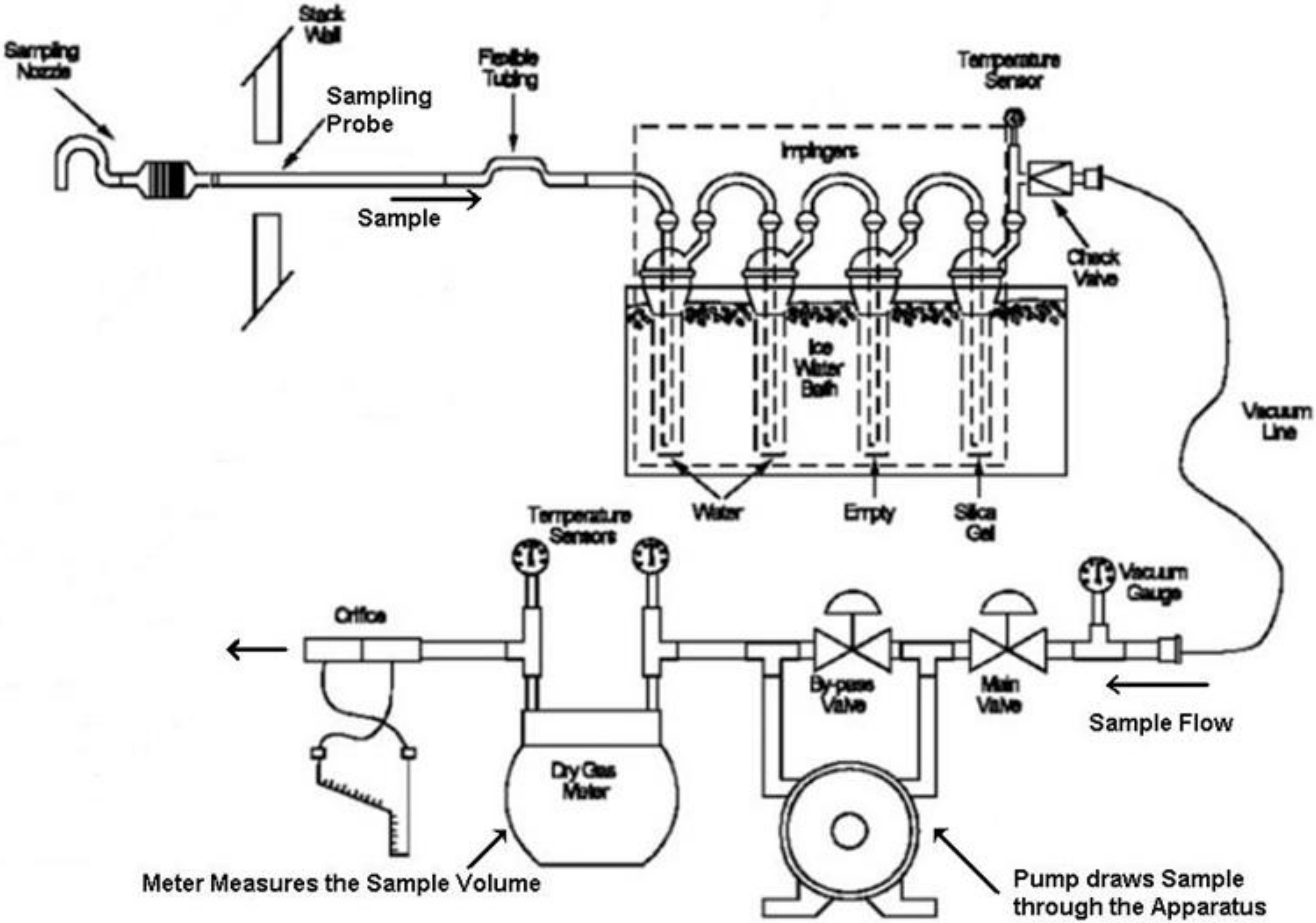
- Measure concentration in units of:

  Mass of PM collected per Volume of stack gas sampled

  Typical units: grains / dscf (7000 grains in a pound)

  or mg / dscm

EPA Method 17 – In-stack Filter



Sampling Probe

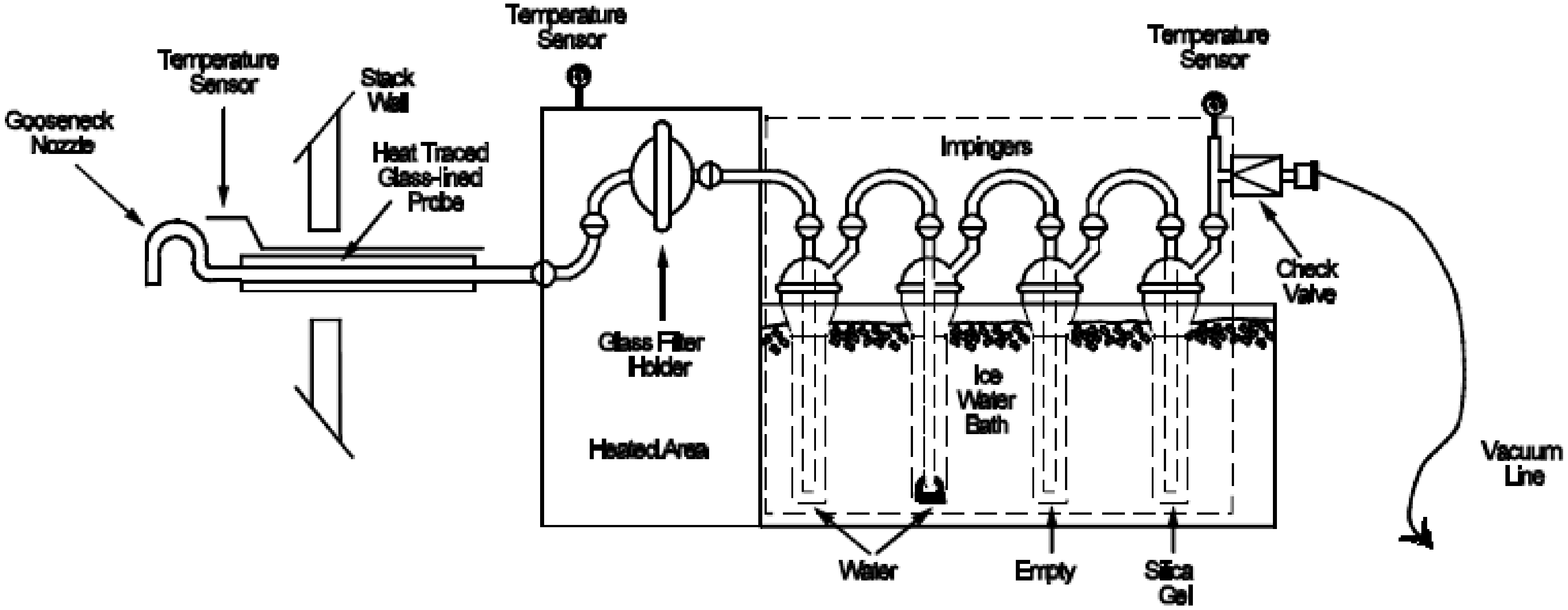
Sample

Sample Flow

Meter Measures the Sample Volume

Pump draws Sample through the Apparatus

EPA Method 5 – Heated Filter



Filterable PM Measurement

- Solid particles – capture not temperature dependent
  - fly ash, elemental carbon (soot), etc.

- Liquid particles – capture is temperature dependent

  Different compounds condense at different temp's
  - sulfuric acid droplets (condensed SO_3+H_2O)
  - semi-volatile organics (organic carbon – smoke)

  Filter temperature affects capture, **defines results**
  EPA Method 5 – 250°F – some sulfuric acid captured
  EPA Method 5B – 320°F – no sulfuric acid
  EPA Method 17 – In-stack filter at stack temperature
  - what's captured will depend on stack temp
  - cannot be used in "wet" stacks such as scrubbers

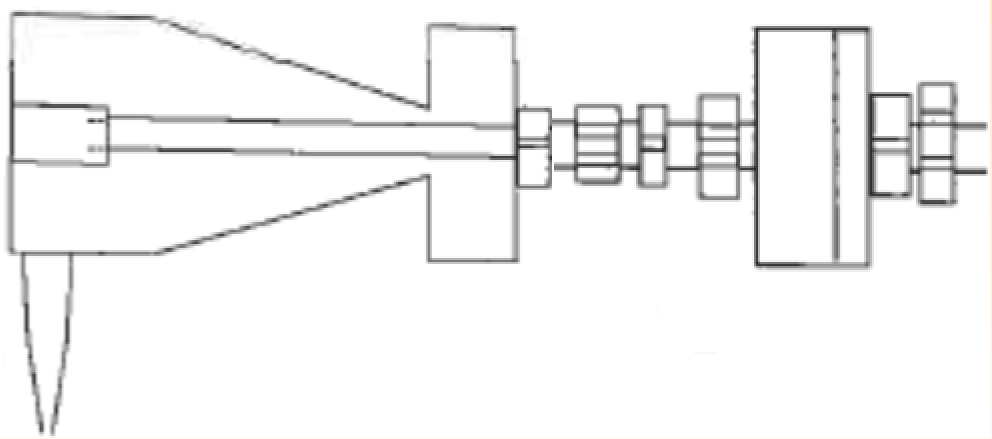
  Compounds in vapor phase at filter temp pass through

Filterable PM_{10} Measurement

- EPA Method 201A – 1990 Version

  Aerodynamic separation - collection of particles < 10µm
  (similar to separation in ambient monitor)

  In-stack Filtration
  - Can’t be used in “wet” stacks (FGD, etc.) because water droplets may form within cyclone and filter will get wet
  - Usually limited to temperature < 500°F

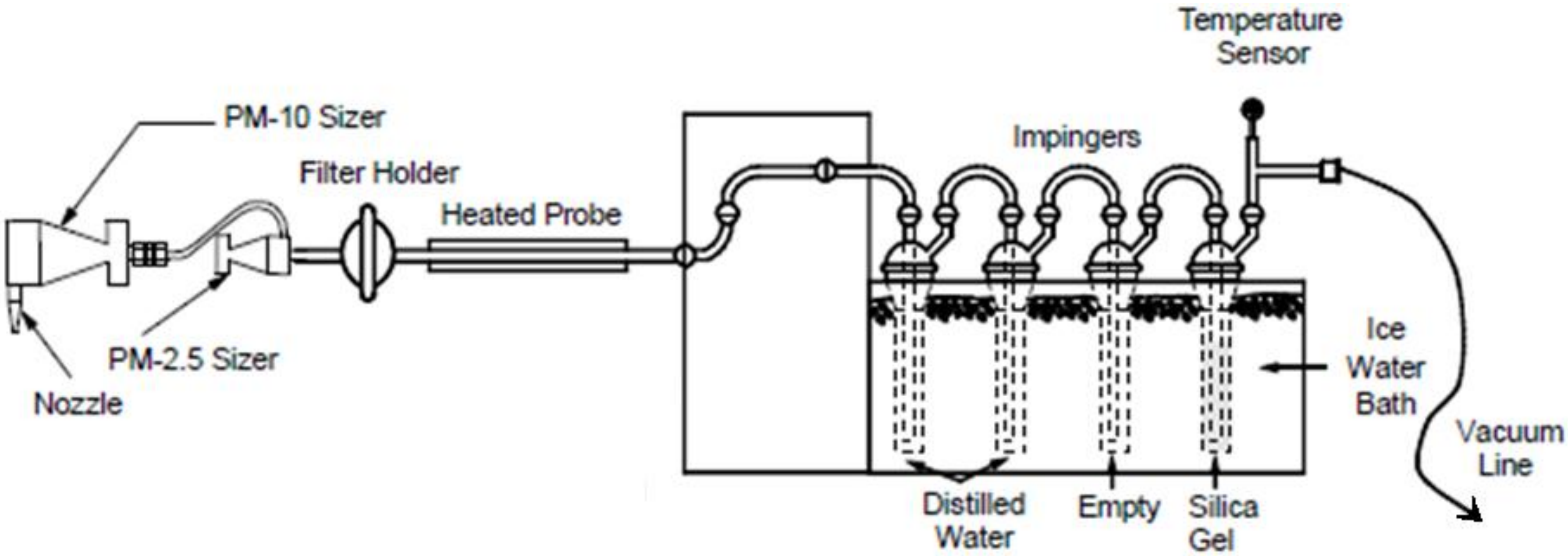


PM10 Cyclone In-stack Filter Holder

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

- EPA Method 201A – 2010 revision
  - PM10 and/or PM2.5 Cyclones for Aerodynamic separation of larger particles (similar to ambient monitor)
  - In-stack Filtration, not for “wet” or “hot” stacks

EPA Method 201A –
In-stack Sizing and Filtration



Filterable PM, PM10, PM2.5 Measurement Issues

Hot Stacks > 500°F
    Probably can’t use 201A, so:
    Measure Total FPM, call it all PM10 or PM2.5

Wet Stacks (scrubber exhaust)
    Can’t use 201A, so:
    Measure Total FPM, call it all PM10 or PM2.5
    - This can over-represent PM10 or PM2.5 emissions!
    Large droplets would make larger particles

NOTE: Wet-stack methods are in development!
- The larger droplets will be cut out of sampling
- Then the larger particles will be cut out, too
- one method includes dilution, the other does not

The method development needs FUNDING!

Filterable PM, PM10, PM2.5 Measurement Issues

Low FPM emitters with low emission limits have other issues:

Method selection – Tester technique

Contamination –
- Dirty apparatus, glassware, recovery area – all methods
- Corrosion of stainless steel cyclones for PM10 or PM2.5

can cause higher results than for Total PM!

Detection limit – Sample volume
- Measurement can be 2 mg or less
- DL between 0.2 and 1 mg
- Uncertainty is about 1 to 5 mg

Method 5 collects more sample more quickly – this can help

Choose the **method** and the **tester** wisely!

Traditional CPM Measurement

- Designed to capture what went through the filter:
  - inorganics (SO_3/Sulfuric Acid Mist, etc.)
  - organics (semi-volatile)
- *SCAQMD, CARB, ODEQ, WDOE methods (1960's, 1970's) – include Filterable and Condensable PM*

  (we have been measuring CPM on the West Coast for decades…)
- EPA 202 (1990 version "Old 202")
- Sample bubbles through water in impingers
- Collects CPM really well – at < 68°F
- ***But*** – Gases dissolve in that water, too…

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)

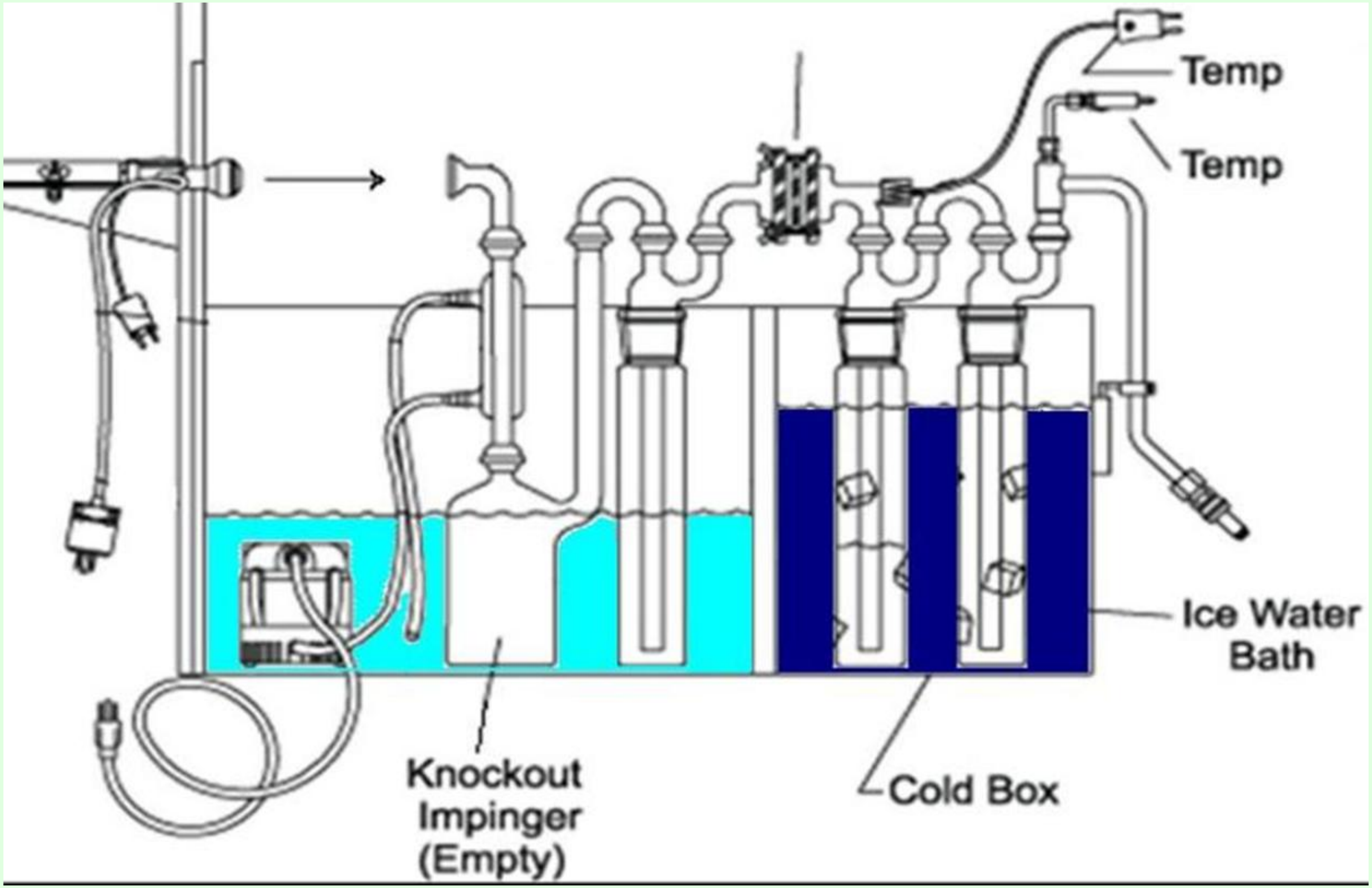
– Ammonium Chloride (forms readily – some of this may be actual CPM rather than artifact)

The artifact salts confuse the division between
Primary PM2.5 and
Secondary PM2.5 formed from precursor gases

SO_2, NH_3, HCl get counted as gaseous emissions 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^{o}F
- Gases should dissolve less; SO_2 stripped out by post-test purge with pure Nitrogen

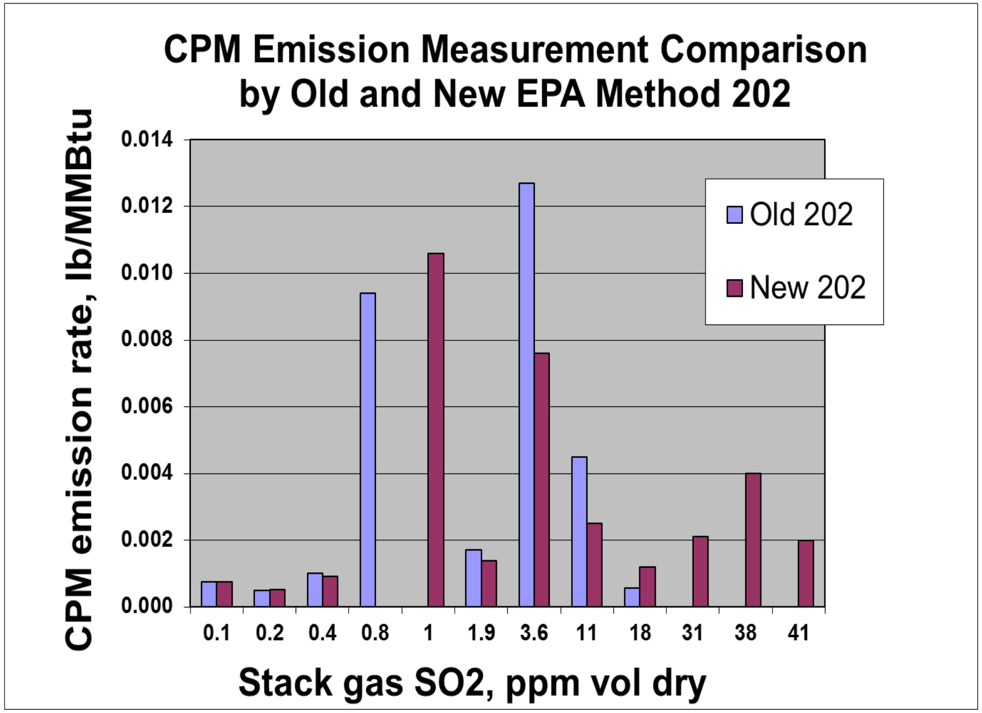
Hypothesis: *Much less artifact*

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)

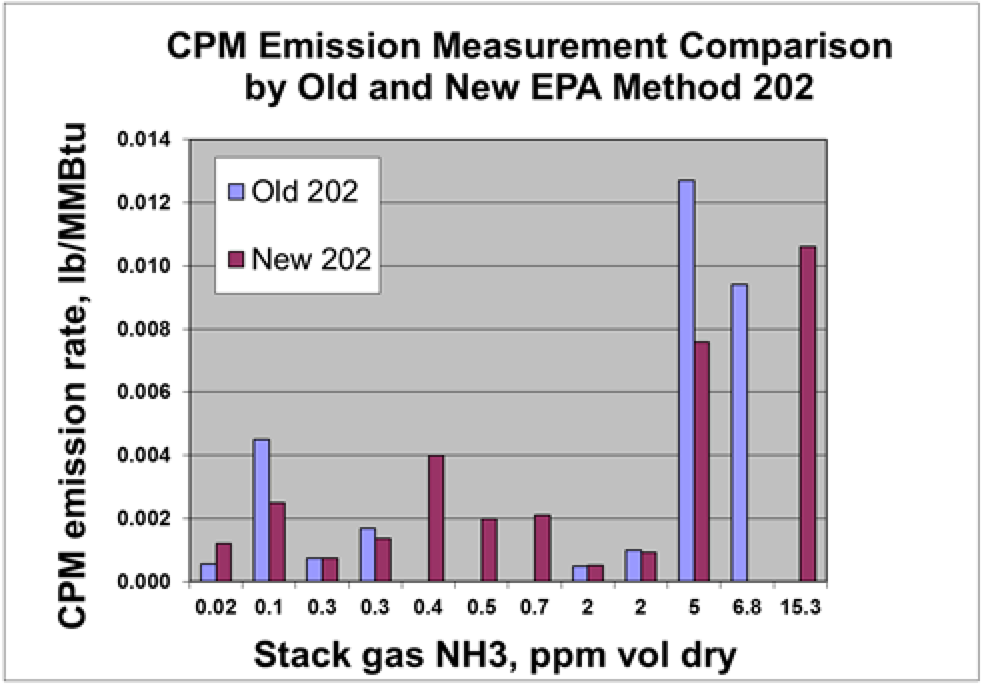
CPM vs. SO2

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



CPM vs. NH3

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

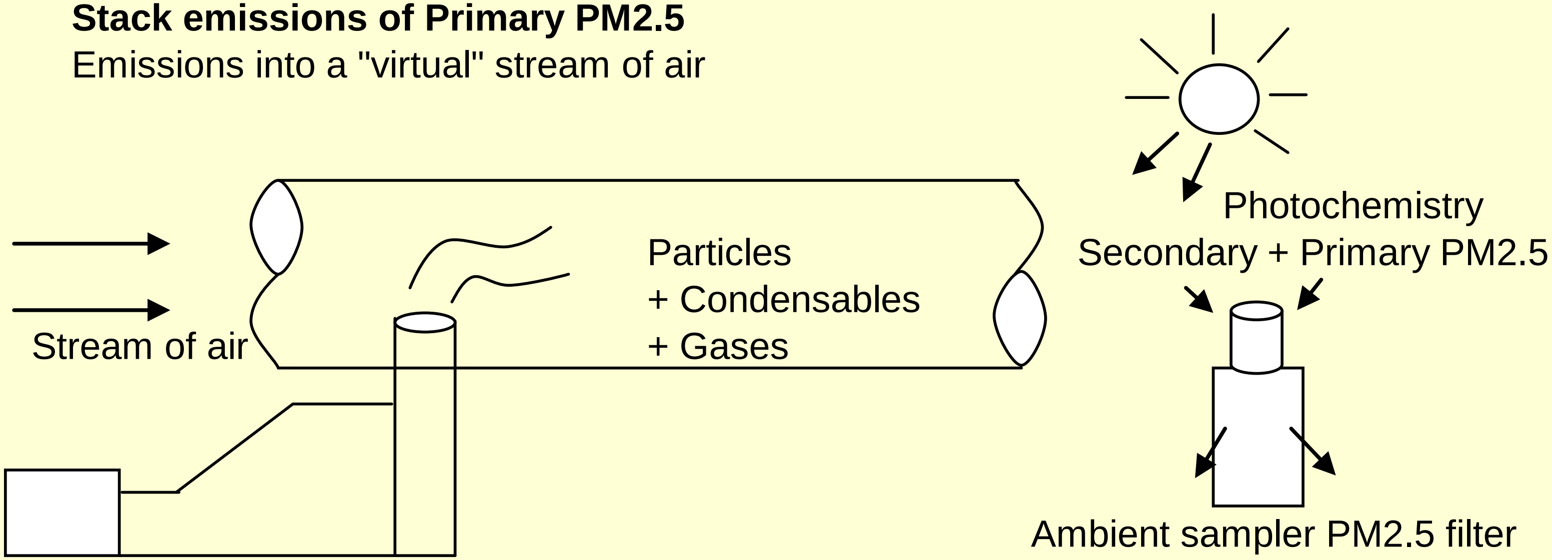


CPM Methods Comparison

- 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
  - our Hypothesis is not proven
- Is there a solution?

Dilution Sampler Concept

Stack emissions of Primary PM2.5
Emissions into a "virtual" stream of air



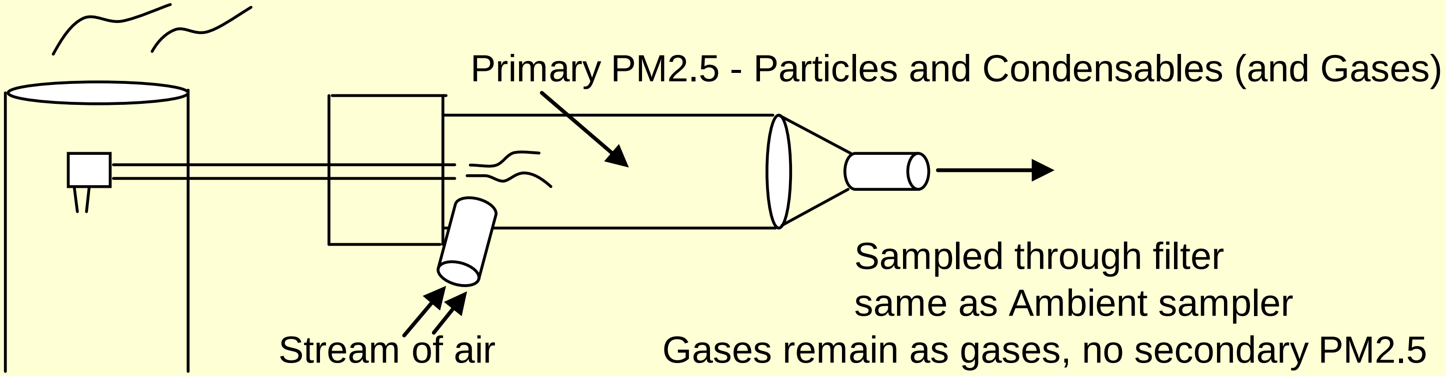
Stream of air

Particles
+ Condensables
+ Gases

Photochemistry
Secondary + Primary PM2.5

Ambient sampler PM2.5 filter

Stack sampling of Primary PM2.5 by CTM-039
Sample "emitted" into a stream of air



Primary PM2.5 - Particles and Condensables (and Gases)

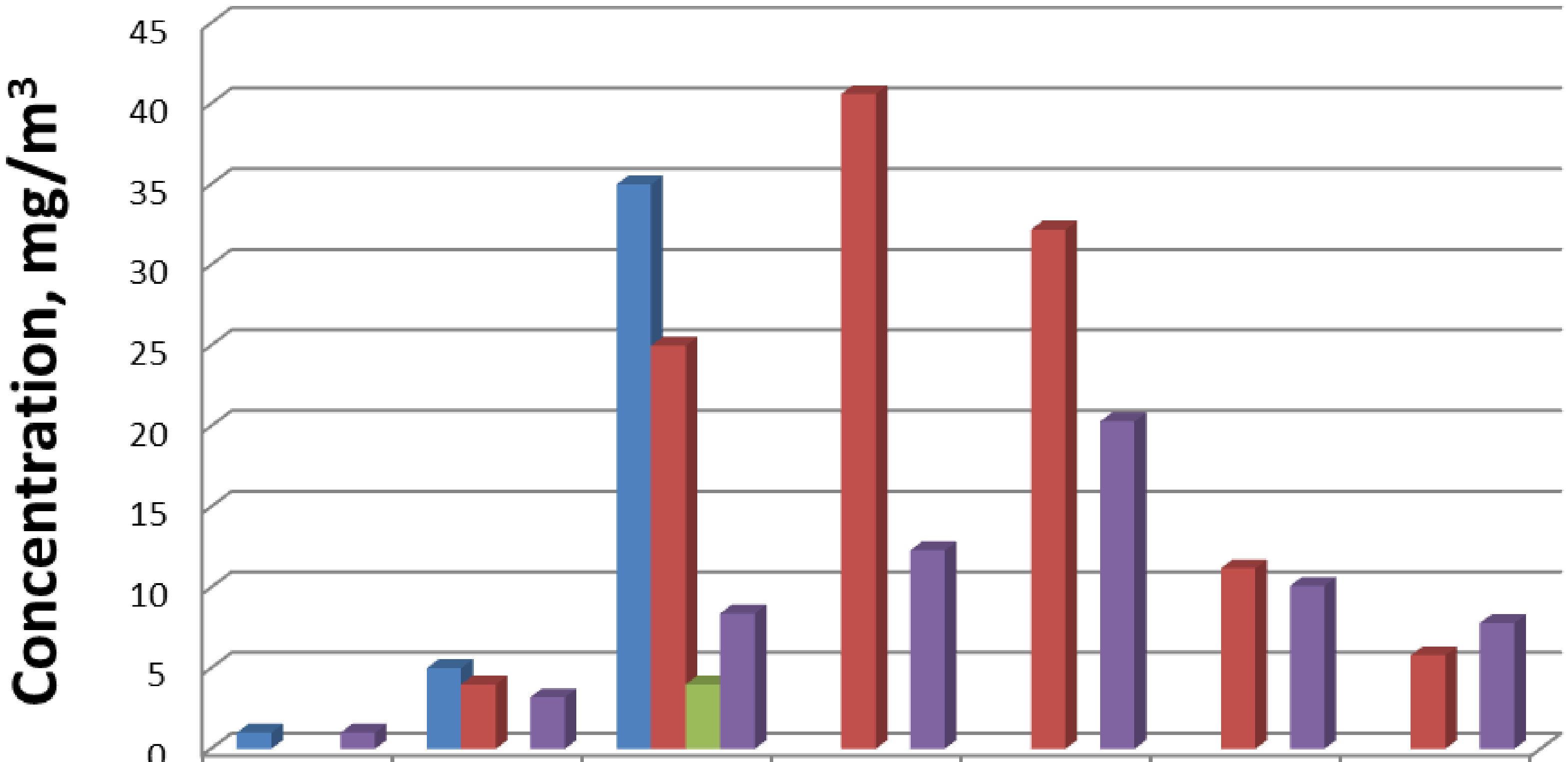
Stream of air

Sampled through filter
same as Ambient sampler
Gases remain as gases, no secondary PM2.5

Dilution Method CTM-039 (2004)

- Designed to emulate dilution of stack emissions in ambient air
- Can sample PM10 and/or PM2.5
  (using the same in-stack cyclones as 201A)
  Can also be used on wet stacks (without the 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 air sampling)
- Disadvantage: Expensive new equipment, Not widely embraced
- Case studies…

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

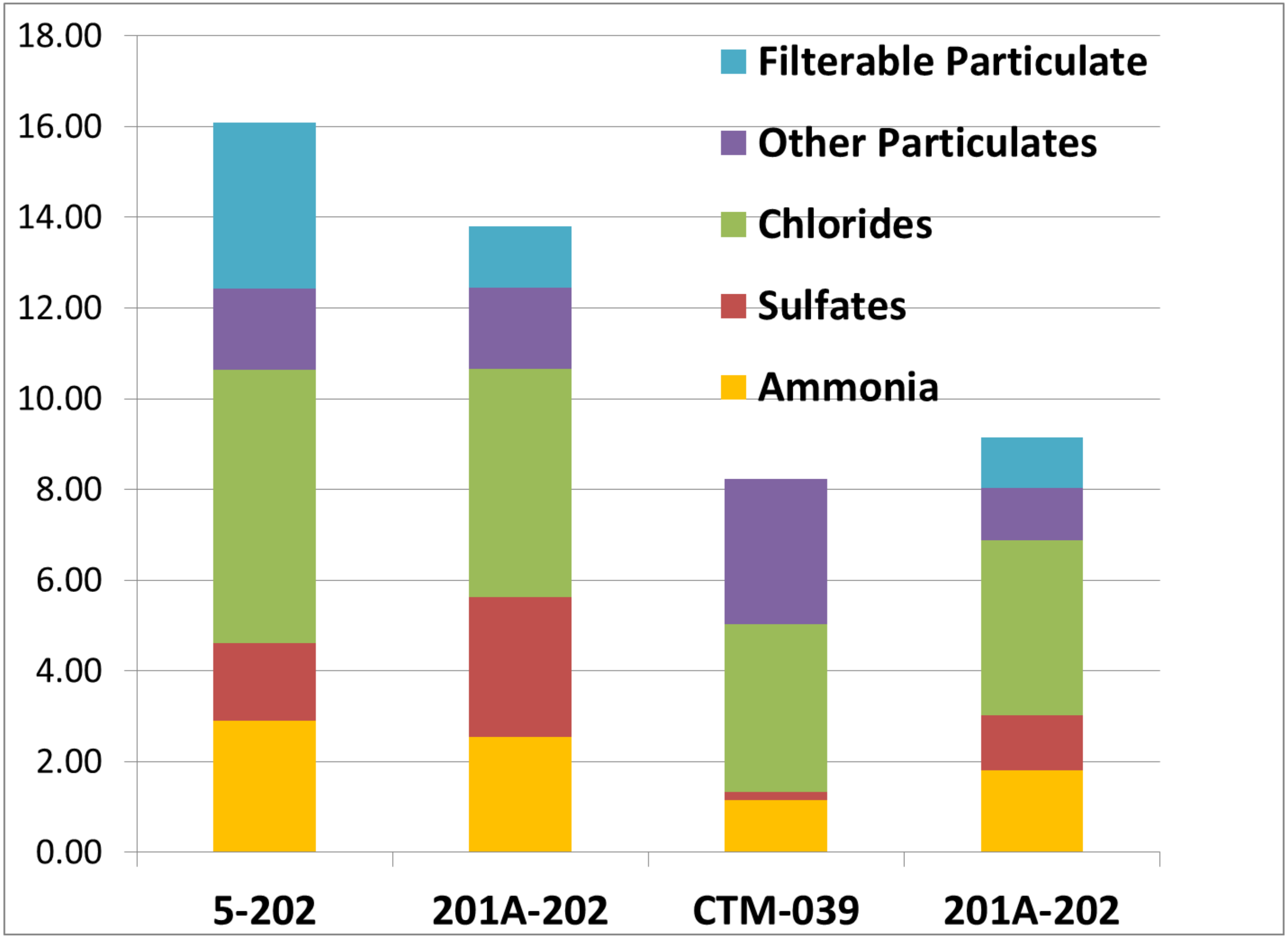
Methods Comparison for CPM

- Combined-cycle GT with SCR – too close to detection limit to tell
- Foundry – SO_2 and semi-volatile organics
  Old 202 highest, New 202 lower (probably captured less SO_2),
  CTM-039 lowest (apparently captured even less SO_2, but all the methods captured the semi-volatile organics)
- Boiler A – Biomass, SNCR, baghouse – SO_2 and NH_3 were present
  New 202 lower, captured less SO_2 artifact
  - measured emissions still above permit limit
  New 202 with ammonia turned off (NO_X over limit)
  - eliminated ammonium sulfate artifact, nice low result
  CTM-039 with ammonia on – unit passed, even test A2!
- Boiler B – Biomass-coal, SNCR, baghouse - SO_2 and NH_3 plus HCl
  CTM-039 helped some at higher emission levels
  - But its results were similar to Method 202 at low emission levels…

Methods Comparison for CPM

- CTM-039 can greatly reduce artifact from NH_3 and SO_2 in some cases (boiler A passed test using this method!)
- CTM-039 can have a higher blank background (there is more surface area of apparatus to rinse and recover sample from)
- So its Detection Limit can be a bit higher than for 201A-202
- Let’s look closer at the Boiler B case study to illustrate other issues…

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



Case Study Comparison

- CPM residue analyzed for Sulfate, Chloride and Ammonium ions
  - reducing levels of SO_2, HCl and especially NH_3 lowers CPM
- Series 1 shows the difference between 5-202 and 201A-202 was mostly in the FPM rather than CPM
  (as expected – Filterable PM10 < PM)
- Series 2 shows CTM-039 was found to greatly reduce artifact ammonium sulfate,
  But ammonium chloride remained!
- Do actual ammonium chloride particles form?
  The results indicate actual CPM formation from NH_3 and HCl -
  But 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? Or is it real emissions? *More study needed*
- Results will depend on which method is used, and on the concentrations of NH_3, SO_2 and HCl

Case Study Experience

- New Method 202 gets better CPM results in some cases, barely any better in others
- Dilution such as CTM-039 can help CPM results greatly in some cases
- We have learned how to run CTM-039 very well
  - any new method takes experience to run well
- We know enough so far to understand that it might not be “the solution” for all cases
  – especially with NH_3 and HCl forming NH_4Cl

Conclusions

- The test method defines the results
  - Not all can/should be used everywhere – choose wisely, discuss with your testers
  - Match carefully to the stack gas conditions
  - Consider likely test results when designing emission controls and fuels and other commodities used
- The wet stack methods may become important tools for FPM
  - one of them will help FPM only
  - the other includes dilution, so may also help CPM

  Funding will make the methods better, and get them sooner
- Nuances of testing technique can be critical, and make more difference at lower emission limits
- Use very **competent testers** to get the best results
  - cheap results are <u>not inexpensive</u>

Questions ???

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