The Avogadro Group, LLC

Source Emissions Testing and Emissions Specialists

Particulate Matter Source Emission Testing

Craig Thiry and Kevin Crosby The Avogadro Group, LLC Oregon – California - Arizona

Cemtek Users Group Conference 2012

The Need for Testing PM2.5, PM10 Total PM or Filterable PM

Compliance with various regulations

- Permit Limits driven by NSR, PSD
- MACT or NSPS emission limits
- Emission Factors for Quarterly Reporting (factors input to DAHS to calculate emissions)
- Correlation Tests for PMCEMS or PMCPMS (filterable PM only – what's particles in the stack)

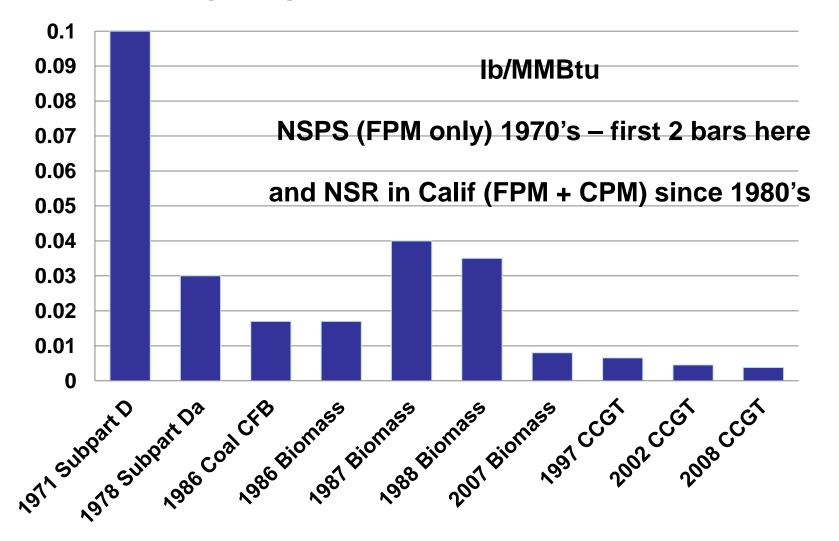
Data for Future Needs

- Baseline data for future permitting
- Emission inventories and inputs to AQ models

PM Measurement Challenges

- Lowering emission limits
- Addition of Condensable Particulate Matter (CPM) for some situations
- Bias in the measurement of CPM emissions (historical methods)
- Test methods may not measure low enough to quantify low-concentration emissions (see chart on next slide) Limits in 1970's as high as
 - 125 mg/m³ (125 mg in ~1-hour test run)
 - Limits Today much lower
 - 2 to 15 mg/m³ (actual results even lower)

Changing Emission Limits



What are we trying to Measure?

- Modern solid-fuel plants or gas-fired plants
 Low concentrations of mostly tiny
 particles (almost all is PM10 or PM2.5 or
 smaller)
- Require accurate data for:
 - Primary, Directly emitted PM2.5
 - Precursor gases to formation of
 Secondary PM2.5 (SO₂, NO_X, VOC, NH₃)

What are we trying to measure? Primary Particulate Matter

Primary PM2.5 Emissions

G

P

GG

G

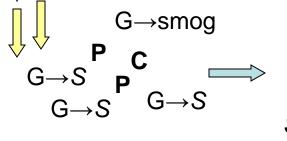
- Particles
- Condensable PM from some Gases just after release to atmosphere

Standard stack tests

– Easily measure

Particles and Gases
at stack conditions

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

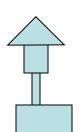


Ambient Monitor – collects all **P C** &S

Ambient PM2.5 commonly mostly secondary, and this determines NAAQS attainment



- Particles and Condensable Particles
- Gases kept separate as Precursors
 (use models to predict Secondary PM2.5 & smog)



Gaseous

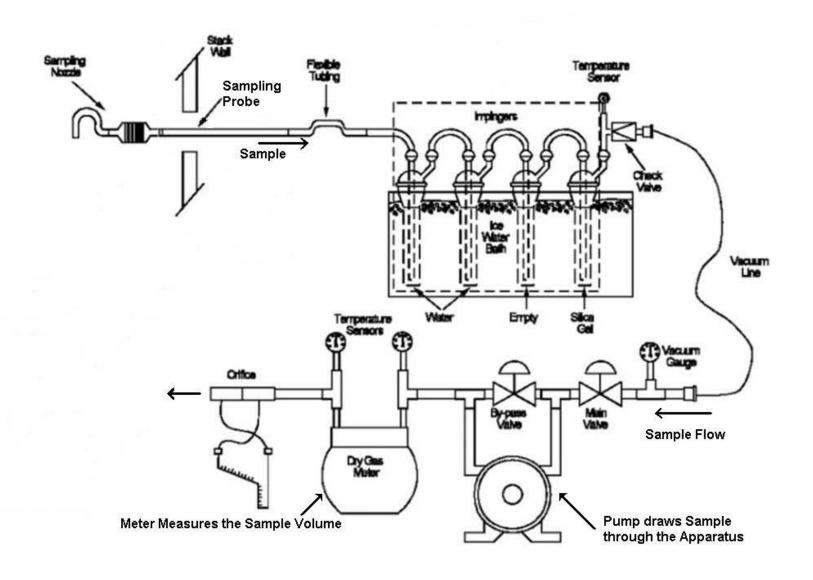
smog (O_3)

Typical sampling arrangement



Figure 2-7 Stack Platform Set-up with Modular Sample Case on Monorail

PM Sampling Apparatus Diagram In-Stack Filter and Impingers



"Traditional" methods

- Filterable PM collection is straightforward (not an issue or problem)
- Condensable PM collected by bubbling through water in impingers – works great!
 - this maximizes gas/liquid contact
- BUT Salts form from dissolved gases The salts become part of the CPM we measure (an *Artifact* of the test method)
- Example: Ammonia and SO₂ dissolve and form ammonium sulfate (NH₄)₂SO₄ which is measured as CPM – results biased high

Example of Traditional Method

Sample bubbled through impingers

Impingers stand about 18 inches tall. The photo shows a typical set of impingers, the first three with water and the 4th containing silica gel to dry the sample gas.

The next slide shows impingers "in action" with sample bubbling through them.





MAXIMIZED GAS-LIQUID CONTACT

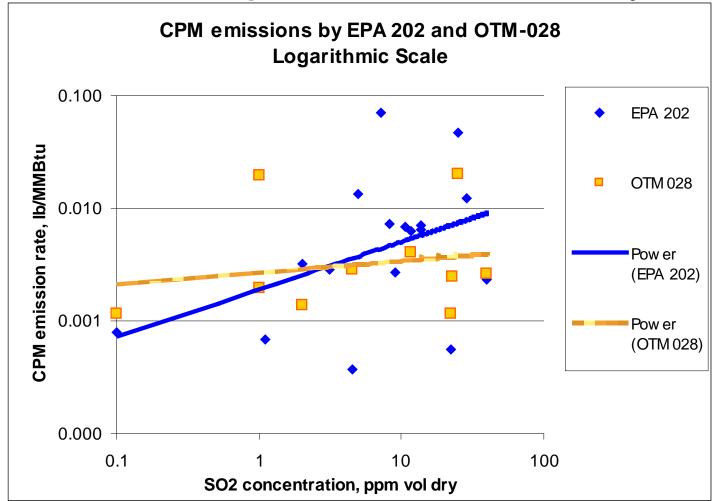
What to Do? "New 202"

- Promulgated December 2010
- Condensable PM collected by condensing into "dry" impingers – no bubbling through water – this minimizes gas/liquid contact
- Collects condensed aerosols or particles:
 - semi-volatile organic compounds
 - inorganic aerosols SO₃ + H₂O → H₂SO₄

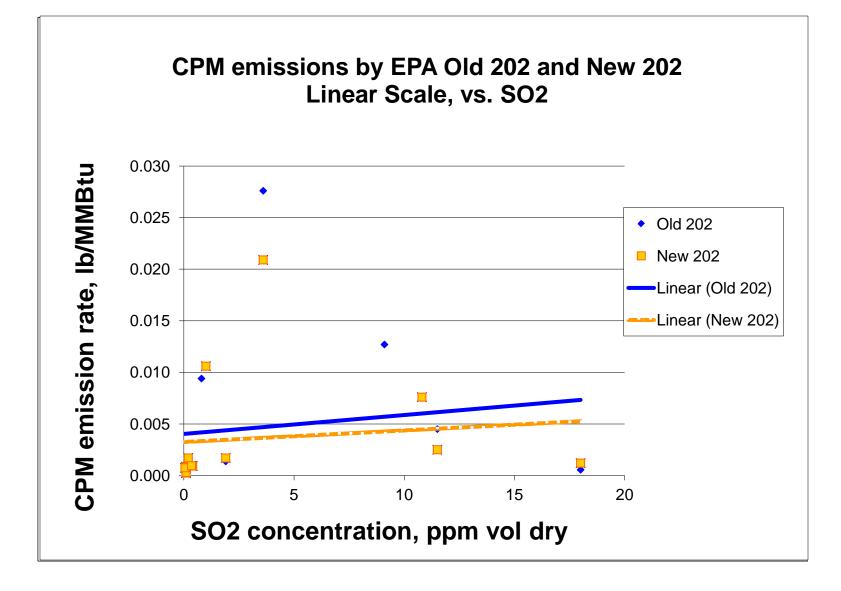
Hypothesis: the dry-impinger method will collect significantly less artifact

Lab studies indicated 40 to 80% less sulfate artifact (as much as 85 to 95% for some high-SO₂ sources). **Does it really work?**

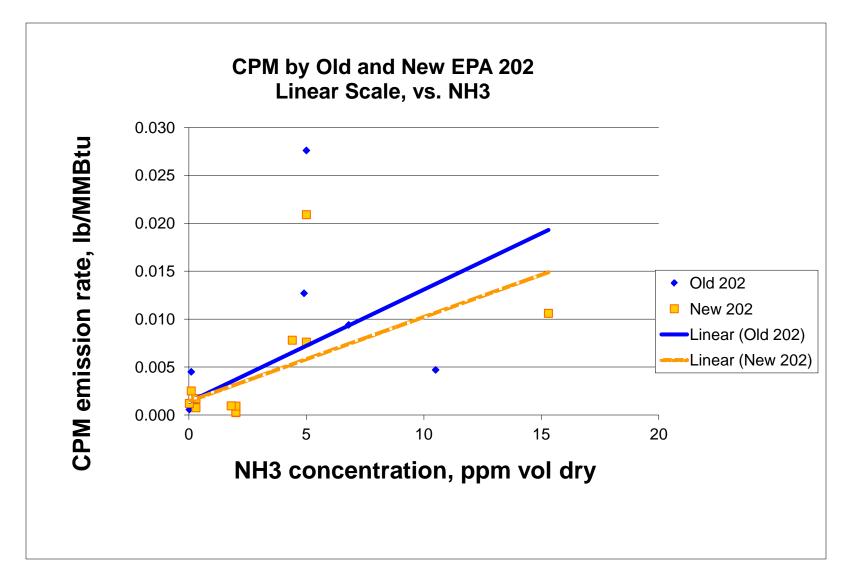
Results Comparison From Early Tests



These are results from a variety of sources, 2007 to 2009 with trend lines for each of the two methods. OTM-028 (draft 202) results were higher than Old 202 for low-emitting sources with low SO₂.

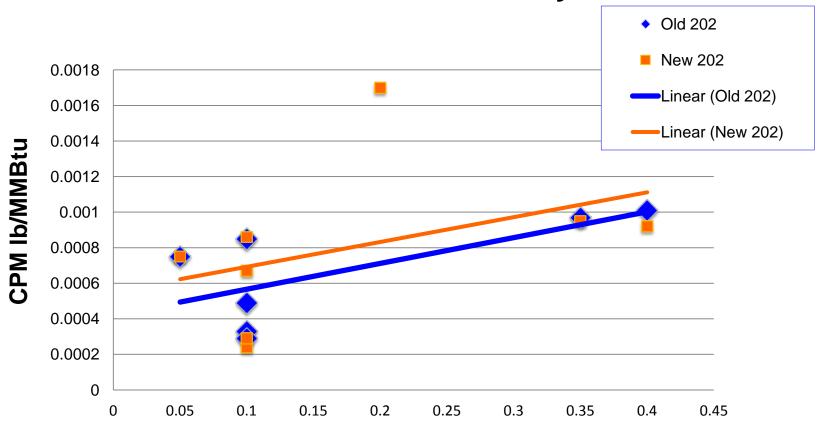


These are results from 2010 and 2011 distributed according to SO_2 . The New and Old 202 gave similar results and neither trended with SO_2 . There are results around 0.010 and around 0.001 throughout the range.



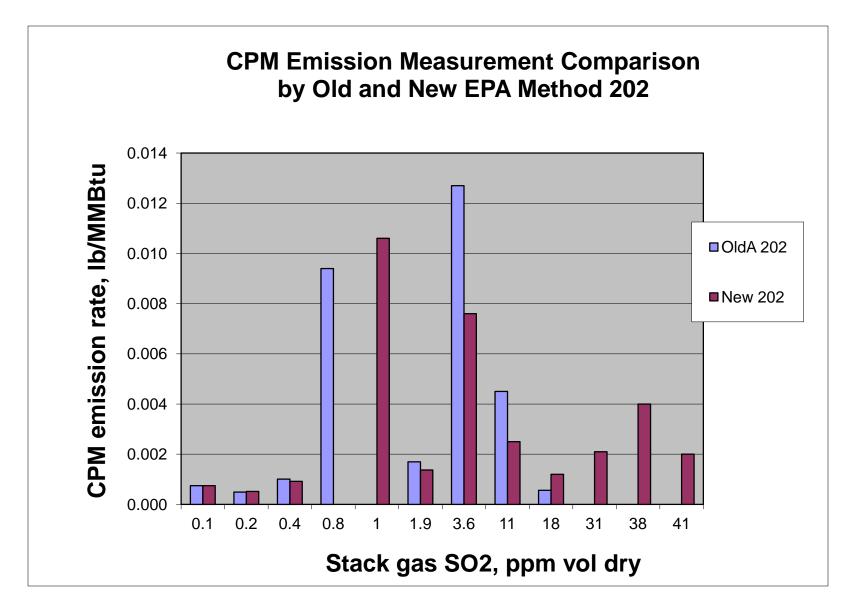
These are results from 2010 and 2011 distributed according to NH_3 . The New and Old 202 gave similar results generally trending with NH_3 . The data points around 0.010 have both high NH_3 and SO_2 . The data points around 0.001 have NH_3 of 2 ppm and below, no matter the SO_2 .

CPM Emissions by Old and New EPA 202
Gas-Fired Plants Only

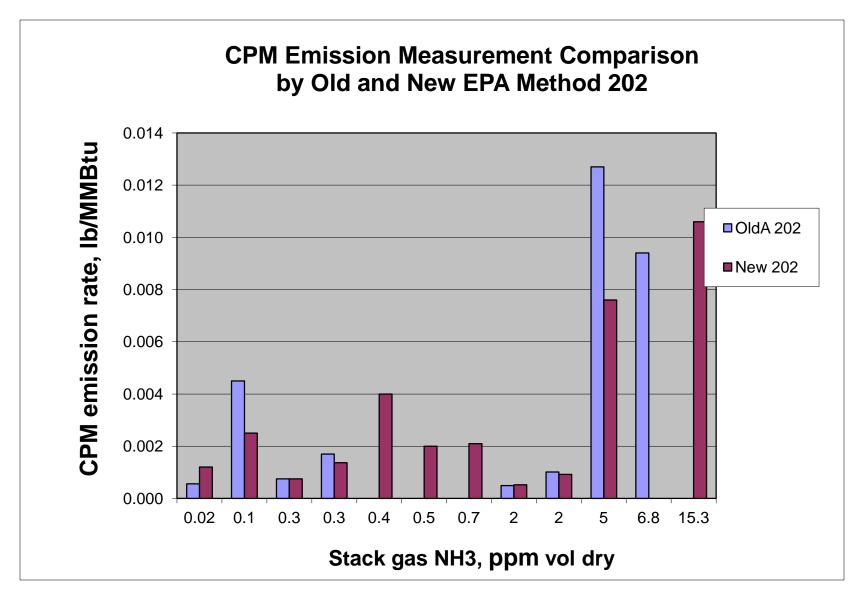


SO2 Concentration, ppm vol dry

Data from just gas-fired boilers and gas turbines; some of the SO2 concentrations shown are estimated. Little difference Old/New Method.



Results are arranged according to SO_2 concentration, X-axis is not linear. These are from a variety of sources with more variables than just the SO_2 concentration. The highest SO_2 sources did not have the highest results.



These are the same results as the previous slide, arranged by NH_3 . The data points with the highest SO_2 had low NH_3 , so are middle and left in this graph.

Progress so far

- Initial tests often had results higher than the old method
- Method can easily cost a 20% premium over the old method
- Improved technique and reagents have solved this problem
- Equipment improvements may eventually save labor
- Lab technique will always take more labor

The Hypothesis is NOT PROVEN by our data

- there is only slightly less artifact for low emitters

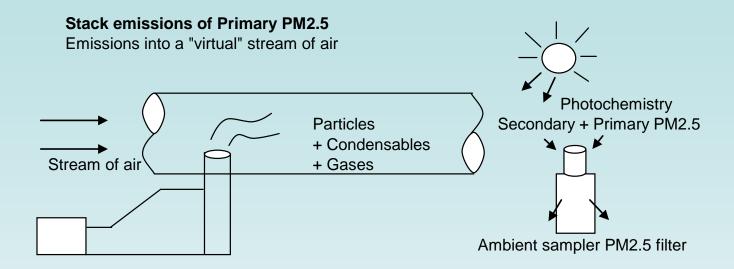
Can we Improve the Situation?

- Reduce Ammonia Slip (below about 2 ppm)
- Correct the results for ammonium salts
 - some have suggested using controlled condensation test results for the inorganic fraction
- Use a **Dilution** method (measure filterable and condensable together)
 - EPA "conditional test method" CTM-039

Controlled Condensation

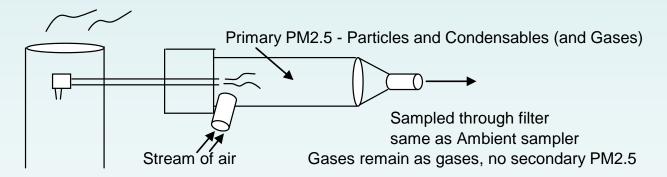
- ASTM is working on a standard method
- EPA has accepted NCASI Method 8A for some uses (CTM-013)
- CC accurately measures SO₃ and SO₂ from almost any type of source (even when NH3 is high)
- SO₃ would count as CPM; SO₂ would not!
- Example Gas Turbine SO₃ ~ 15 to 50% of Total SO_X so using this might reduce the inorganic CPM significantly from what we measure with Old or New 202. Would be even more beneficial for Coal-fired power plants with SCR.

Dilution Sampler Concept



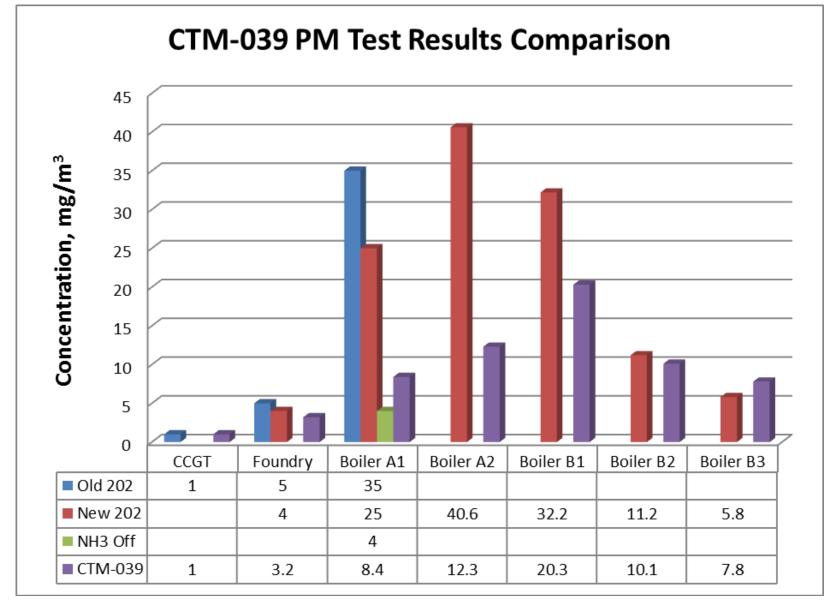
Stack sampling of Primary PM2.5 by CTM-039

Sample "emitted" into a stream of air



CTM-039

- Designed to emulate dilution of stack emissions in ambient air
- 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)
- Shows promise the results of comparative studies are encouraging
- Disadvantage: Expensive new equipment



A result of 1 mg/m3 (CCGT) is about the same level as a blank sample. Boilers were solid fuel with SNCR. Boiler A was tested once by New 202 with the ammonia injection off. CTM-039 can reduce artifact and therefore provide lower results in some cases.

Conclusions

- The Hypothesis is true only in certain cases, usually at higher concentrations
- New 202 is sometimes a slight improvement from the Old 202 for low-concentration sources
- New 202 might not be worth its extra cost
 except in some cases (sometimes every little bit helps)
- Other alternatives (such as CTM-039) will cost even more - but may provide more representative results for some cases
- Results will depend on which gases are present (NH3, SO2, SO3, HCl) and in what relative concentrations
- The Method used will define the Results
- Quality Testing is critical!

Questions???

Craig Thiry

Business Development Director

The Avogadro Group, LLC