PM_{fine} Quantification

Perceptions about Ammonia Slip, Acid Gases,
Condensable Particulate Matter and
Applicable Test Methods



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Presentation Topics

- Archaeology
- Philosophy
- Recent History
- Current Activities
- Future





History

PM-10 NAAQS

- Recognized condensable PM impact
 - Crustal PM was cause of most nonattainment areas
 - Condensable PM was a small consideration
- Condensable PM method proposed in 1990
 - Was a "Consensus Method" addressing several State specific compliance test methods
 - Incorporates several analytical options

1990 EPA Method 202

- Collects PM in impinger water
 - Similar to 1971 back half PM method
 - Nitrogen purge added
 - Added stabilization of Sulfuric Acid
 - Reflected several State/local methods
 - Allowed several options
 - Air purge
 - No purge
 - Analysis of some components





Method 202 (cont)

- Intent was to replicate ambient air emissions (see Quotes from NSPS)
 - PM is defined by the conditions
 - Temperature
 - Concentration
 - Pressure
 - All 1990 M202 options generated different emissions values

No Referee Method available in 1990



Measurement/Monitoring Drivers

- PM fines NAAQS
- Permits Program
- Enhanced Monitoring
- Consolodated Emissions Reporting Rule
- Significant emissions increase w/ CPM addition
- Industry "artifacts" concern





Assessment of 1990 Method 202

- Conducted Laboratory Study
- SO₂ bubbled through impingers
 - 300 ppm for 1 & 3 hours
 - 50 ppm for 6 hours
 - Nitrogen purge and no purge
- No ammonia





Method 202 Artifacts

| SO ₂ | Test | H ₂ O | Artifact Mass (mg) | | |
|-----------------|----------|------------------|--------------------|----------|--|
| ppm | duration | volume | No Purge | Purge | |
| 300 | 1 Hr | 400 ml | 180 ± 6 | 10 ± 0.5 | |
| 300 | 3 Hr | 800 ml | 400 ± 25 | 20 ± 5 | |
| 50 | 6 Hr | 1400 ml | 200 ± 10 | 20 ± ?? | |





Recent Activities

- Revised Method 201A & 202
 - Eliminated options
 - Reduced initial impinger water
 - Required purge
 - Required back up impinger
- Dilution Sampling for PM
 - Research Methods
 - **OAQPS** developed Method



Method 202 Improvement



Expand Lab Study

- Purge Only
- Expand SO2 conc
- Modify glassware
- Collaborate with stakeholders





Dry Impinger Method Performance

| Run | Organic (mg) | Inorganic (mg) | Filter (mg) | Total |
|---------|--------------|----------------|-------------|-------|
| 1 | 0.11 | 2.23 | -0.34 | 2.34 |
| 2 | 0.15 | 2.88 | -0.06 | 3.03 |
| 3 | 0.09 | 1.37 | 0.00 | 1.46 |
| 4 | 0.30 | 1.91 | 0.00 | 2.22 |
| 5 | 0.16 | 1.54 | 0.07 | 1.77 |
| 6 | 0.33 | 2.19 | -0.17 | 2.52 |
| 7 | 0.08 | 1.18 | 0.30 | 1.56 |
| 8 | 0.02 | 1.87 | 0.17 | 2.06 |
| Blank | -0.02 | 0.21 | 0.00 | 0.68 |
| Average | 0.16 | 1.90 | 0.00 | 2.12 |
| Std Dev | 0.1 | 0.51 | 0.17 | 0.45 |
| MDL | 0.31 | 1.54 | 0.49 | 1.36 |

Important PM_{2.5} Method Dates

- Final PM Implementation Rule
 - April 25, 2007
 - FR Vol 72, No 79, pg 20586
- Proposed Test Methods
 - March 25, 2009
 - FR Vol 74, No 56, pg 12970
- Final Test Methods
 - December 21, 2010
 - FR Vol 75, No 244, pg 80118





Residual PM Testing Concerns

- Method 202 > SO₃
- Ammonia reactions
- CPM still dominates PM_{2.5} emissions
- Permit limits exceeded





Example Measurement Issue

- Coal fired utility boiler
 - Catalytic Reduction for NO_X
 - Permit limit for NO_X & PM₁₀
- Failed annual PM compliance test
 - PM₁₀ was 5x limit
 - CPM was 95% (NH₄)SO₄
 - NH₃ slip measured at 57 ppm
 - SO₃ measured at 0.4 ppm



Stack test consultant concluded PM was primarily "artifact"

Resolution of Measurement Issue

- Retested with several test method changes
 - Increased sample rate
 - Increased condenser temperature ...
 - Same results
- Replaced catalyst bed 2 years early
- Reduced NH₃ slip to 1 ppm
- CPM emissions reduced by 90%
 - New Plant Manager hired
- New Test Contractor hired



Next Example Measurement Issue

- Biomass Boiler
 - Noncatalytic reduction during O₃ season
 - FF for PM control
- PM (M5 & 202) test results
 - w/o NH₃ injection 0.004 #/mmBtu
 - w/ NH₃ injection 0.02 0.04 #/mmBtu
- CTM 039 results 0.007 #.mmBtu



- Sampling issues
 - Water
 - Filter



Interest in CTM 039 Increasing

- National Academy encouraged use of dilution sampling
- EPA developed system
 - Potential benchmark for "artifact" elimination
 - Potential for use with extended sampling times
 - Development of speciation profiles
- EPA continues to encourage further development

Typical Research Test Method



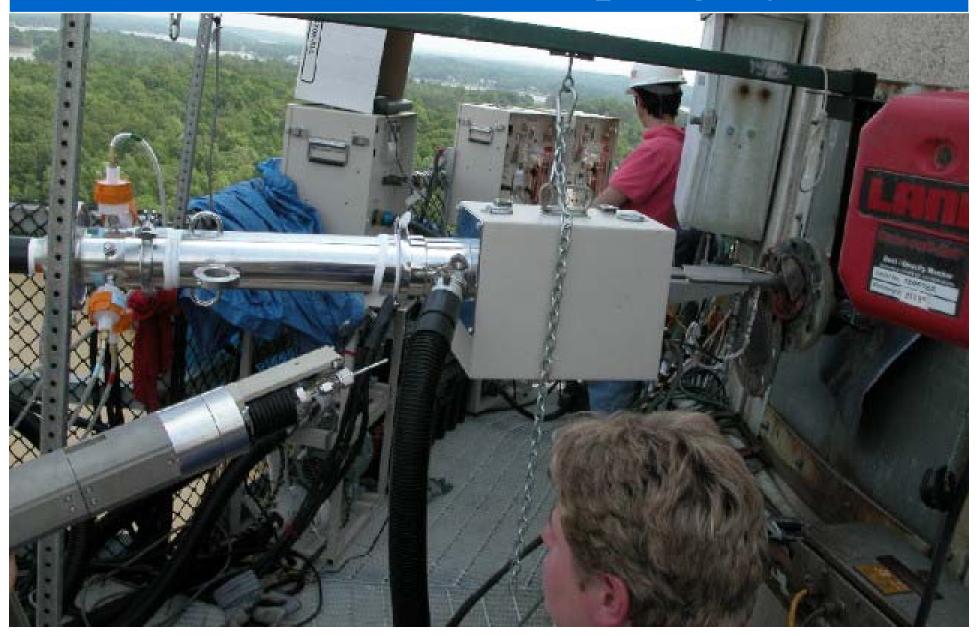




OAQPS Dilution Sampling System



OAQPS Dilution Sampling System



Video of OAQPS DST

This link will take you to the 2 min video of the OAQPS Dilution Sampling System.
You need to have Windows Media Player to view this slide of the presentation.





Future

- PM condensables are increasingly important
- Continued concerns by industry
- Several methods are available to accurately quantify condensable PM
- Continuous Monitoring Systems are on the Horizon
 - Several CPM control technologies available





Open Discussion

• QUESTIONS?



