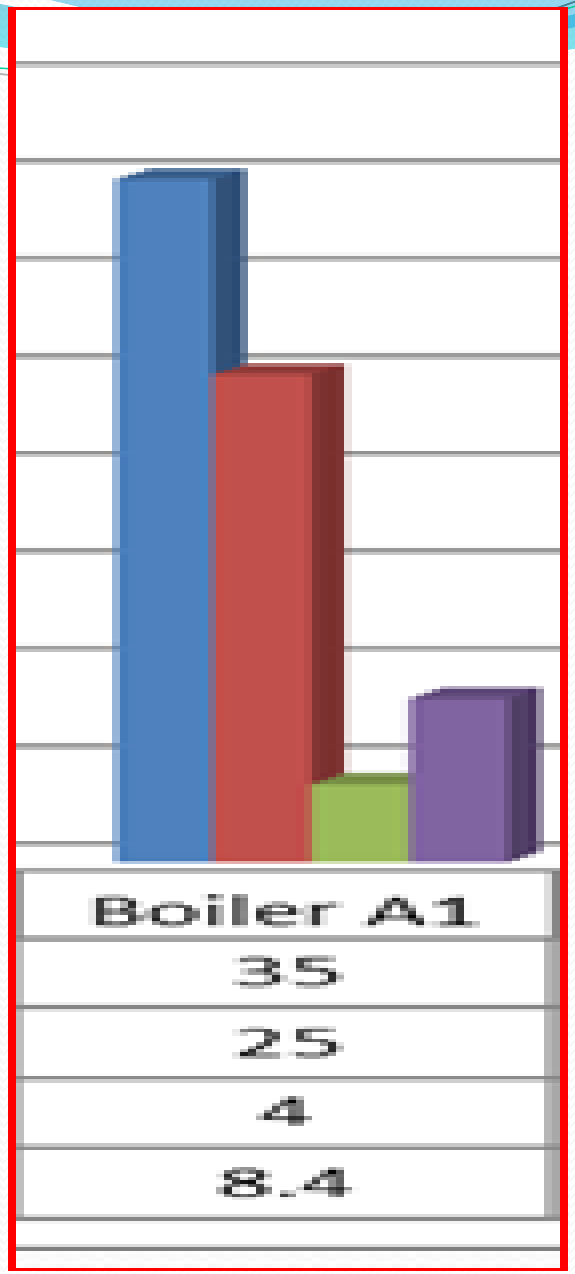
Status of New Source Testing Regulations & The Variability and Bias in Results From New PM/$PM_{2.5}$ Emission Test Methods

The Avogadro Group, LLC

Air Quality Consulting and Source Emissions Testing

ALL THESE TEST RESULTS ARE THE SAME POLLUTANT FROM THE SAME BOILER!!

Different test methods CAN = different results!



Recent Regulations - Topics

- Accreditation or Self-Certification as AETB to ASTM Standard D-7036
- QSTI, QSTO
- PGVP – Protocol Gas Verification Program
- SSAP – Stationary Source Audit Program
- EPA Methods changes

ASTM D7036 Standard: Source Testing Accreditation

The Avogadro Group, LLC

Air Quality Consulting and Source Emissions Testing

ASTM D7036-04 Acronyms

- Source Evaluation Society (SES)
- Qualified Source Test Individual (QSTI)
  Qualified Individual (QI)
- Qualified Source Test Observer (QSTO)
- Air Emissions Testing Body (AETB)
- Stack Test Accreditation Council (STAC)
- Emissions Collection and Monitoring Plan System (ECMPS)

Purpose of QSTI/QSTO

- **Begun by SES** before ASTM D-7036 came out… Anticipated a movement towards accreditation Purpose – to **Professionalize** emission testing
- Guarantee of thorough and practical **knowledge** of source testing methods
- Demonstrate an **understanding** of
  - Elementary physical Gas Laws, Chemistry
  - The basics of safety and hazardous material handling
  - primary theories of source testing (e.g., isokinetic and proportional sampling).
- Exemplify and demonstrate professional and **ethical** conduct as a QSTI

Main Components of QSTI/QSTO

- Qualifications
  - Experience must match ASTM D7036-04 standard
  - Pass at least one method group exam
- Application process – Document:
  - Experience with the methods
  - Two projects per methods group – description
  - Letters of reference – include 3
- Four emissions measurements groups
  - Group 1 – Isokinetic test methods (PM, flow, many of the basics)
  - Group 2 – Wet chemistry gaseous pollutant test methods
  - Group 3- Gaseous Pollutants Instrumental Methods + CEMS Performance Specifications - CEMS RA requirements of part 75
  - Group 4 – Hazardous metals test methods
  - And now Group 5 – Part 75 RATA only (subset of Groups 3 and 1)

Purpose of Accreditation

- Assure the Data Quality
- EPA has begun with revisions to 40CFR Part 75:
  - This rule became effective March 2012
    - This means Part 75 RATAs must be conducted by an accredited or self-certified AETB
  - Any AETB conducting RATAs of CEMS or Hg sorbent trap monitoring systems, or Appendix E testing must conform to the requirements of ASTM D-7036

Main Components of AETB

- The AETB must have a Quality System outlined in their Quality Manual that complies with D-7036
  - Continuous Improvement!
- Testing must be *overseen and supervised* by at least one on-site Qualified Individual (QI)
  - QSTI provides QI for the methods it covers
  - AETB must train and test to provide QI's for other methods

Main Components of AETB Continued

- At the time of a test, the AETB must certify compliance with D-7036 for the test methods used - this includes:
  - Certificate of accreditation or interim accreditation; **or**
  - Letter of self-certification signed by the AETB senior management and name, telephone number and e-mail of the AETB;
  - Name of the on-site QI and the date that the QI took and passed the relevant qualification exam(s)
  - The name and e-mail of the qualification exam provider

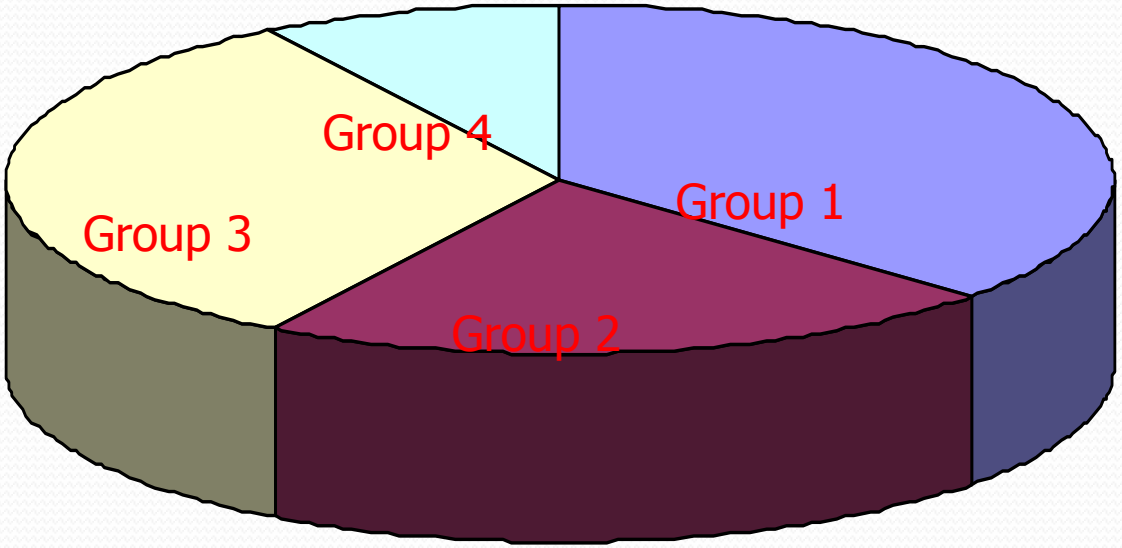
What to Ask For

- To ensure compliance with the Standard a Part 75 source (or Agency) should request that the AETB produce these items:
  - AETB's quality manual;
  - Results of external audits or internal audits performed by AETB within the last 12 months
  - Performance data
  - Training records

  OR provide a **letter of accreditation** (because that process includes all those items)

Status Today

- There are 21 companies with STAC interim or full accreditation, unknown # are claiming self-certified



- There are 404 QSTI's (mostly groups 1 & 3)
- There are 8 QSTO's

With Boiler MACT and Utility MACT, that is not many qualified testers in the country!!

The Avogadro Group, LLC

Air Quality Consulting and Source Emissions Testing

Protocol Gas Verification Program

Protocol Gas Verification Program (PGVP)

This program requires gas vendor participation:

- Annual "blind" audits of gases
- Vendor pays for the Audit
- Vendors must pay for their cylinders and audit by NIST
- **AETB provides the PGVP data** in their test report
- EPA Ambient group has their own independent audit as well.

AETB and PGVP Information

Required for data entry to ECMPS, the EPA electronic reporting for Part 75 RATA results

The AETB provides this information for input to the software's cells

AETB info for Test Report

Air Emission Testing Body (AETB) data

Test Date	June 5, 2012
Project Name	Power Plant Company RATA Test
Project Number	120XX.2

For EPA's ECMPS

Entry to ECMPS (EDR) software:	
QI Last Name	*Tester*
QI First Name	*Joe*
QI Middle Initial	*B.*
AETB Name	The Avogadro Group, LLC
AETB Phone Number	925.680.4300
AETB Email	info@avogadrogroup.com
Exam Date	*August 25, 2010*
Provider Name	Source Evaluation Society
Provider Email	qstiprogram@gmail.com

Attachments:

- STAC interim accreditation certification letter
- Copies of your QSTI certificates

For EPA's PGVP:

Entry to ECMPS software:			
Calibration Gases	NO_X		
Gas Level Code	High	Mid	Zero
Gas Type Code	*NXC*	*NXC*	*Zero*
Vendor ID	*B32012*	*B32012*	*B32012*
Cylinder ID number	*CC284994*	*CC287792*	*CC159541*
Expiration Date	*02/10/2013*	*10/13/2012*	*03/02/2017*

Calibration Gases	O_2		
Gas Level Code	High	Mid	Zero
Gas Type Code	*OC2*	*OC2*	*Zero*
Vendor ID	*F22012*	*B32012*	*B32012*
Cylinder ID number	*CC44875*	*SG9134088BAL*	*CC159541*
Expiration Date	*06/16/2013*	*07/22/2013*	*(03/02/2017*

Note: Gas Type Code may be found on the Gas Certificate. Our usual codes:

"Zero" is zero N2 or zero Air (with certificate)

"NO" is NO alone in balance gas (there might be a NO_X or NO_2 uncertified value)

"NC" is NO and CO in balance gas (there might be a NO_X or NO_2 uncertified value)

"NXC" is NO (including certified NO_X or NO_2 value) with CO in balance gas

"OC2" is O_2 and CO_2 in balance gas

"SO2" is SO_2 in balance gas

"SN" is SO_2 and NO in balance gas

"SNC" is SO_2, NO and CO in balance gas

Balance gas is almost always N_2 in our gases. There are many other gas blends and codes.

Note: Vendor Code may be found on the Gas Certificate.

AirGas is code B32012 or B32011

Praxair is code F22012 or F22011

PGVP info for Test Report

Stationary Source Audit program

Stationary Source Audit Program (SSAP)

- EPA ran an audit program for many years – free audit samples
  - Audit samples would be requested by the regulatory agency, then analyzed with emission test samples
- SSAP is a way for the EPA to privatize audit samples
- An audit sample will now be **purchased** by the source (usually by the tester under contract) then analyzed with samples – so sources will bear the cost directly.
- SO_2, H_2SO_4, NO_X, Fluoride, HCl, Metals (Hg), VOC's, Dioxins/Furans, etc.
- The program was approved May 2011, no audits yet…
- Waiting for a second audit sample provider to be accredited

EPA method changes

Revised, Clarified, New…

- New – 16C for TRS – oxidize, measure with SO_2 analyzer (this has been done for years, now it's official)
- Clarification – proposal for many methods and specifications to get minor clarifications, corrections, typos fixed, etc.
- Revised – a few have been revised to provide needed flexibility or updates (no more requirement for mercury thermometers! Hooray, it's 21st century!)
- PM CEMS Performance Specification 11 (revisions and corrections proposed)
- These are just some examples – mostly important little improvements…

New methods coming? Examples…

- Performance Specifications (proposed)
  - HCl CEMS
  - Bag Leak Detection System
- Wet Stack PM2.5 Test Method and CEMS
  - In development for several years, progress continues (this is important for sources with wet scrubbers, etc.)
- Fugitive or Area-source emissions
  – VOC Passive Fenceline Monitoring – method continues strong development
  - Wind Blown Dust – method in early development
  - Fenceline Monitoring of Metals emissions – early development
- Digital Camera Opacity Technique – often approved

Other issues

- EPA's electronic reporting tool (ERT) continues to be revised (incremental improvements)
  - Used so far mostly to develop ICR test data bases
  - Being applied to more kinds of sources all the time
  - This represents the future of reporting test data.
- Change will continue – some will be improvements, some will be challenging…

Conclusion

- Continued progress toward Professionalization of testing – it's the future
- More stringent QA – improved data quality
  - critical for measurement of lower emissions
  - new plants will emit less and less – NSR, PSD, etc.
- Slow changes in methods, but we are working our way out of the 1970's
- Reporting to electronic to data bases will become a new normal

The Avogadro Group, LLC

Source Emissions Testing and Emissions Specialists

Variability and Bias in Results From New PM/$PM_{2.5}$ Emission Test Methods

Credit to: Kevin Donahoe
The Avogadro Group, LLC

WRBA – March 12, 2013
Portland, Oregon

Key Points

- What is particulate matter?
- What are we trying to measure?
- Methodology and Results
- Conclusions and Implications

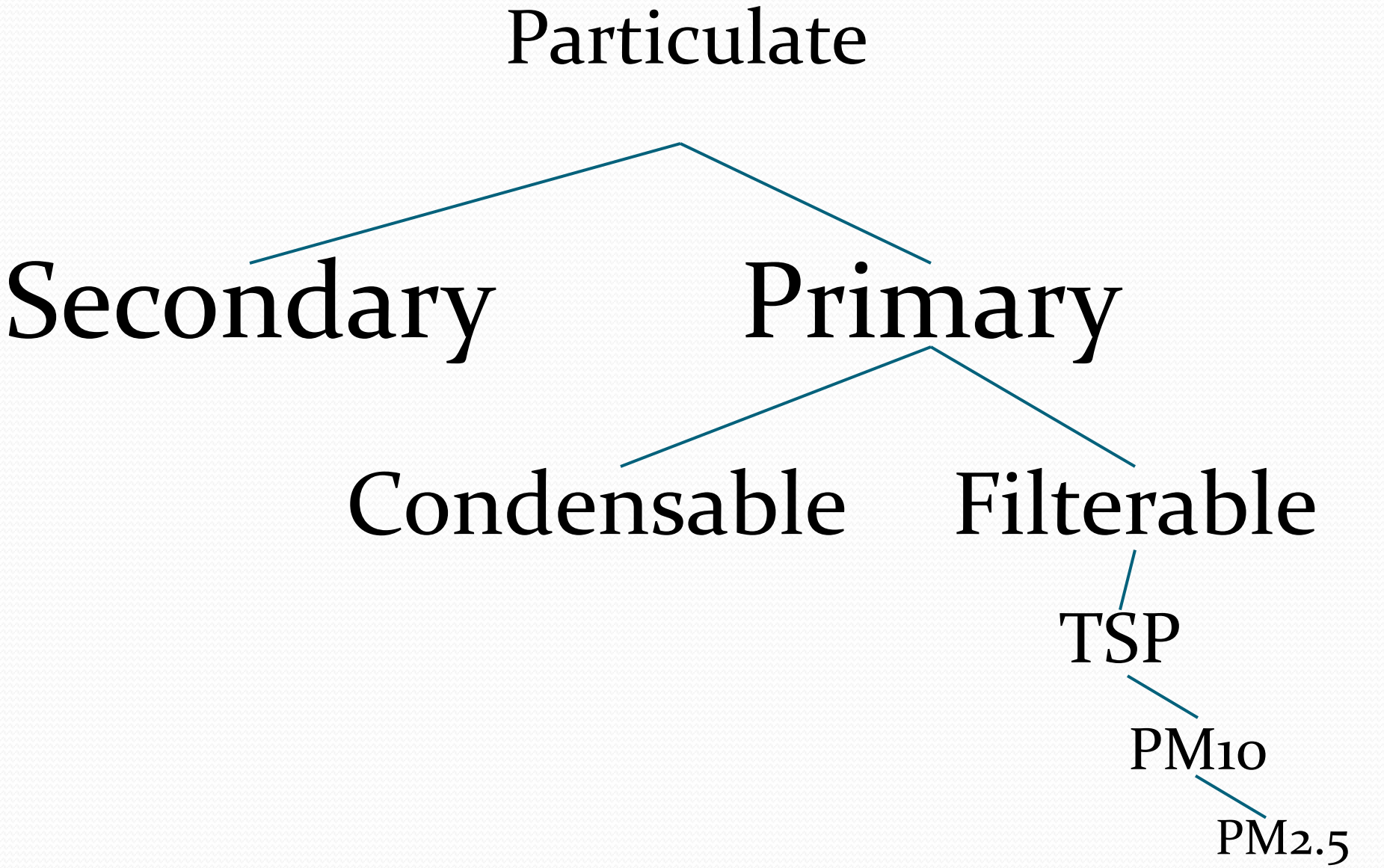
TAKE NOTE…

- A POLLUTANT IS NOT DEFINED BY THE CHEMICAL OR PHYSICAL CHARACTERISTICS OF THE POLLUTANT (e.g. PM2.5, CPM)
- IT IS DEFINED BY THE SAMPLING METHODOLOGY USED TO COLLECT THE POLLUTANT (and the sampler?)

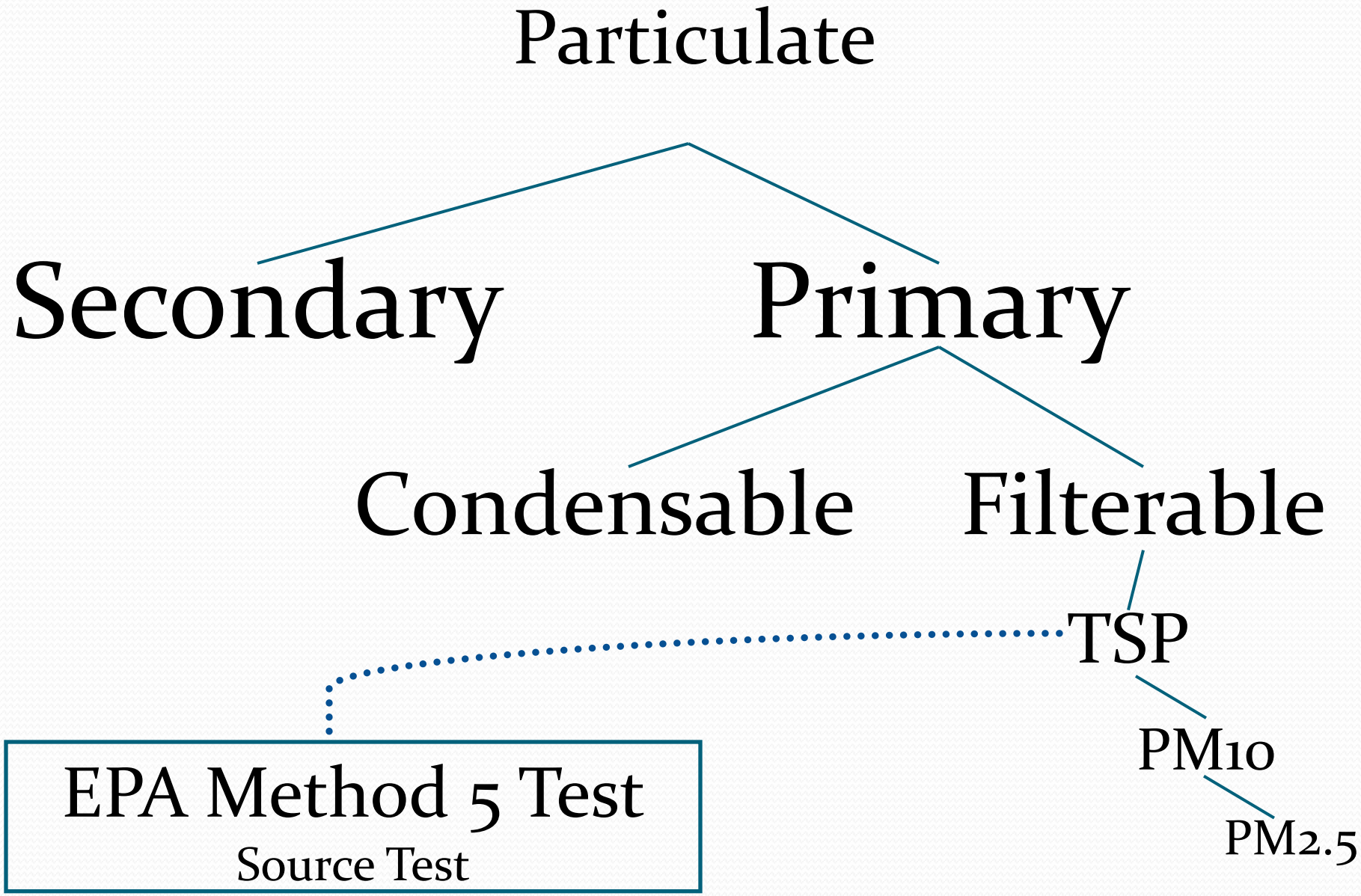
What is Particulate Matter?

- **Primary Particulate**
  - **Filterable PM** (*primary front half*)
    - Solid or liquid material at stack conditions – TSP, PM_{10} , & $PM_{2.5}$
    - Methodology well-established – no problems
  - **Condensable PM** (*primary back half*)
    - Vapor or gas at stack conditions
    - Condenses and/or reacts upon cooling and dilution in ambient air to form solid or liquid PM immediately after stack discharge
    - Precursors are organic and inorganic
    - Common measurement bias involves inorganic (e.g. ammonia and SO_2)
    - **All assumed to be in the $PM_{2.5}$ size fraction**
    - Source testing methods attempt to duplicate complicated formation process
- **Secondary Particulate**
  - Forms by chemical reactions in atmosphere downstream of release point, but not immediately
- **Question: Can we separate the two?**

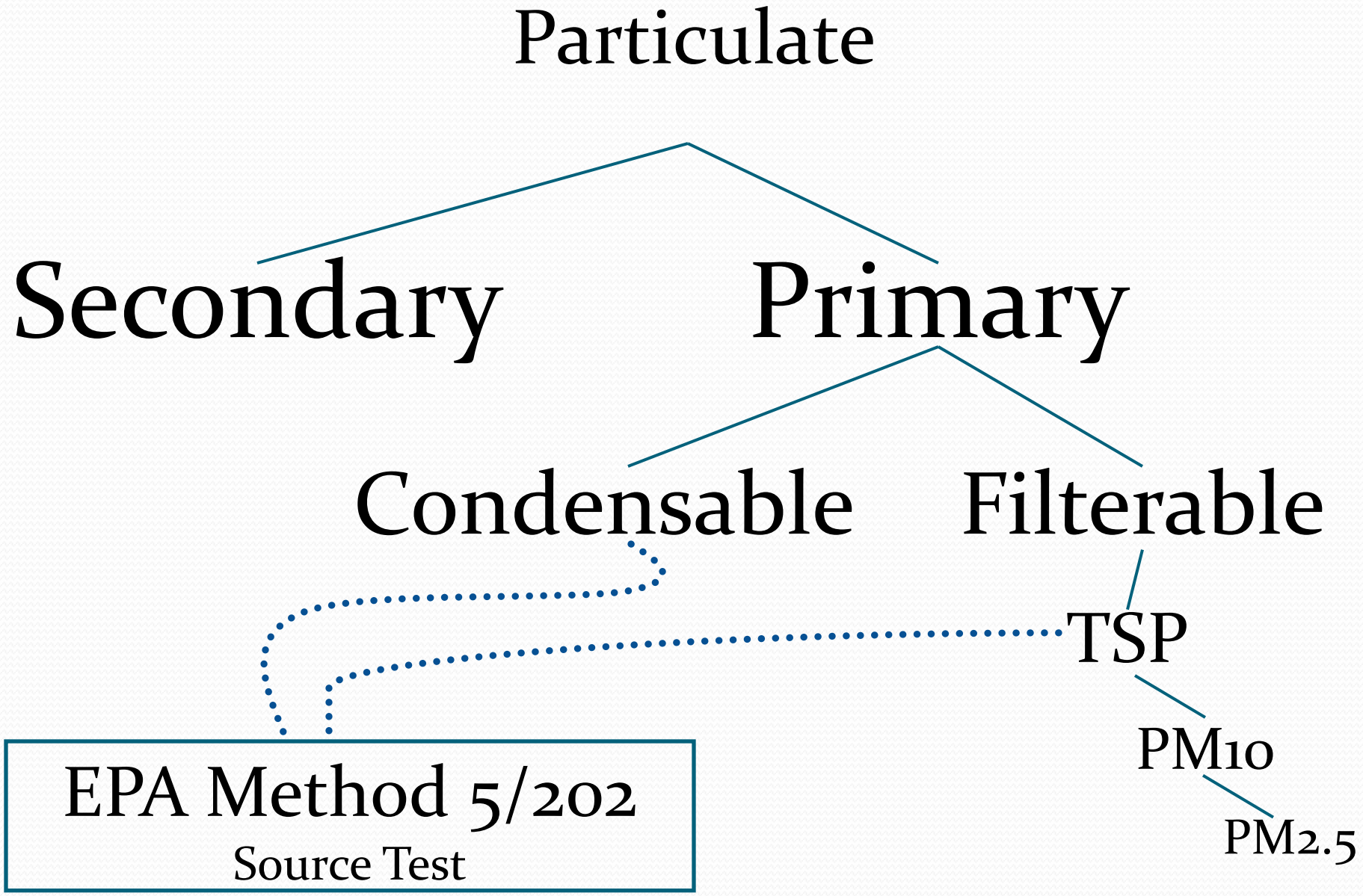
What is Particulate Matter?



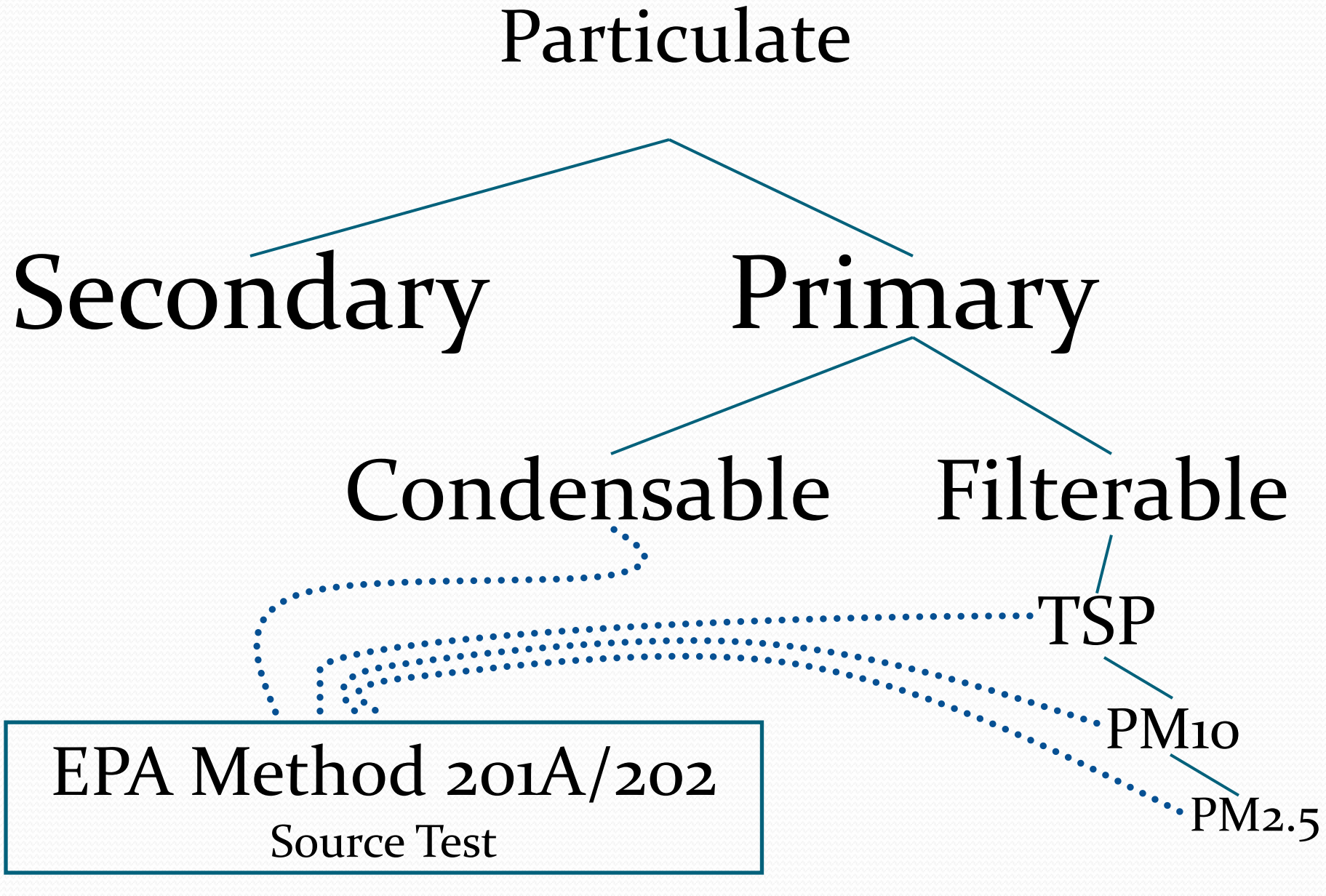
What is Particulate Matter?



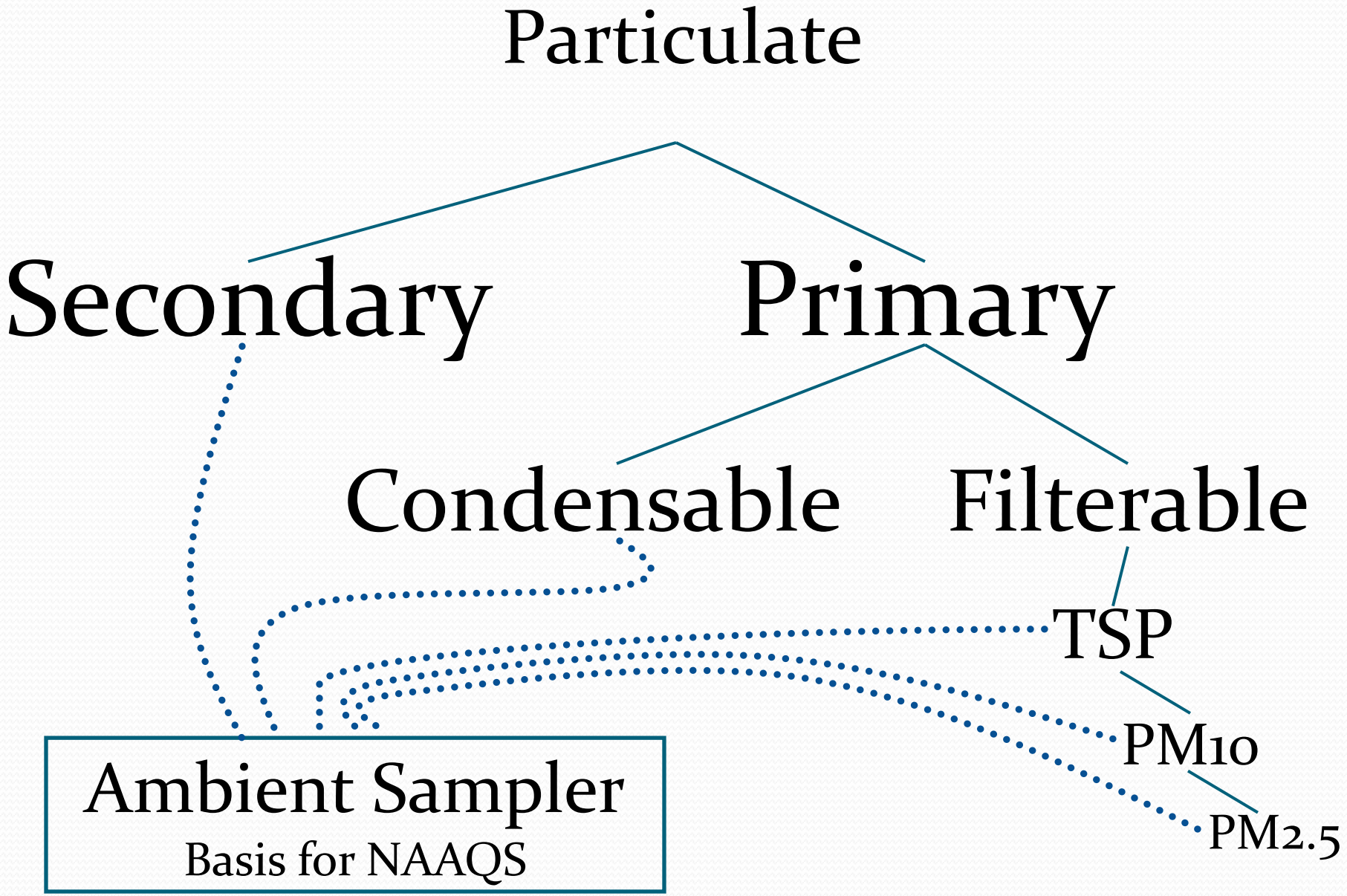
What is Particulate Matter?



What is Particulate Matter?

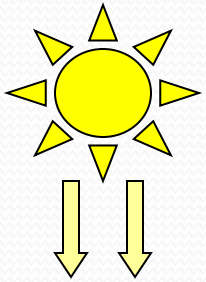


What is Particulate Matter?

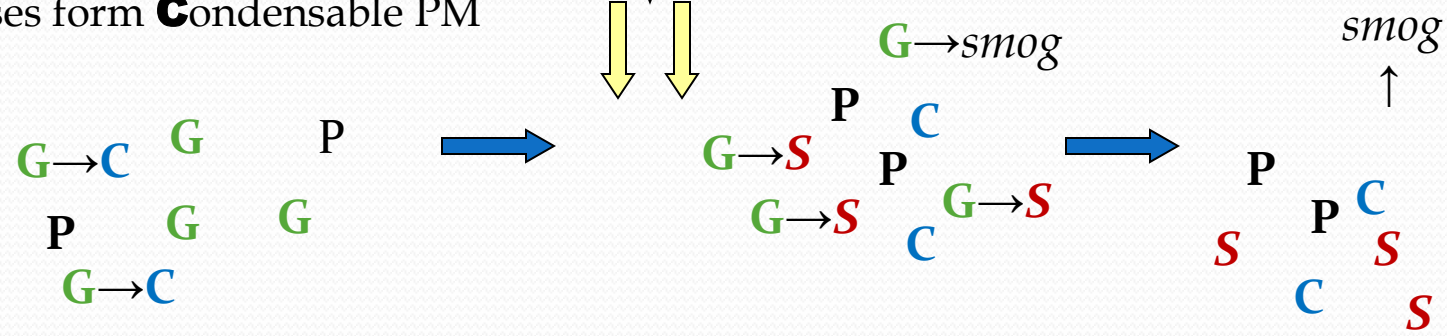


What are we trying to measure?

Primary $PM_{2.5}$ Emissions
- **P**articles
- Some **G**ases form **C**ondensable PM

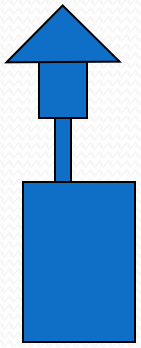


Photochemistry – other Gases (precursors) to **S**econdary $PM_{2.5}$ and to smog (ozone, etc.)



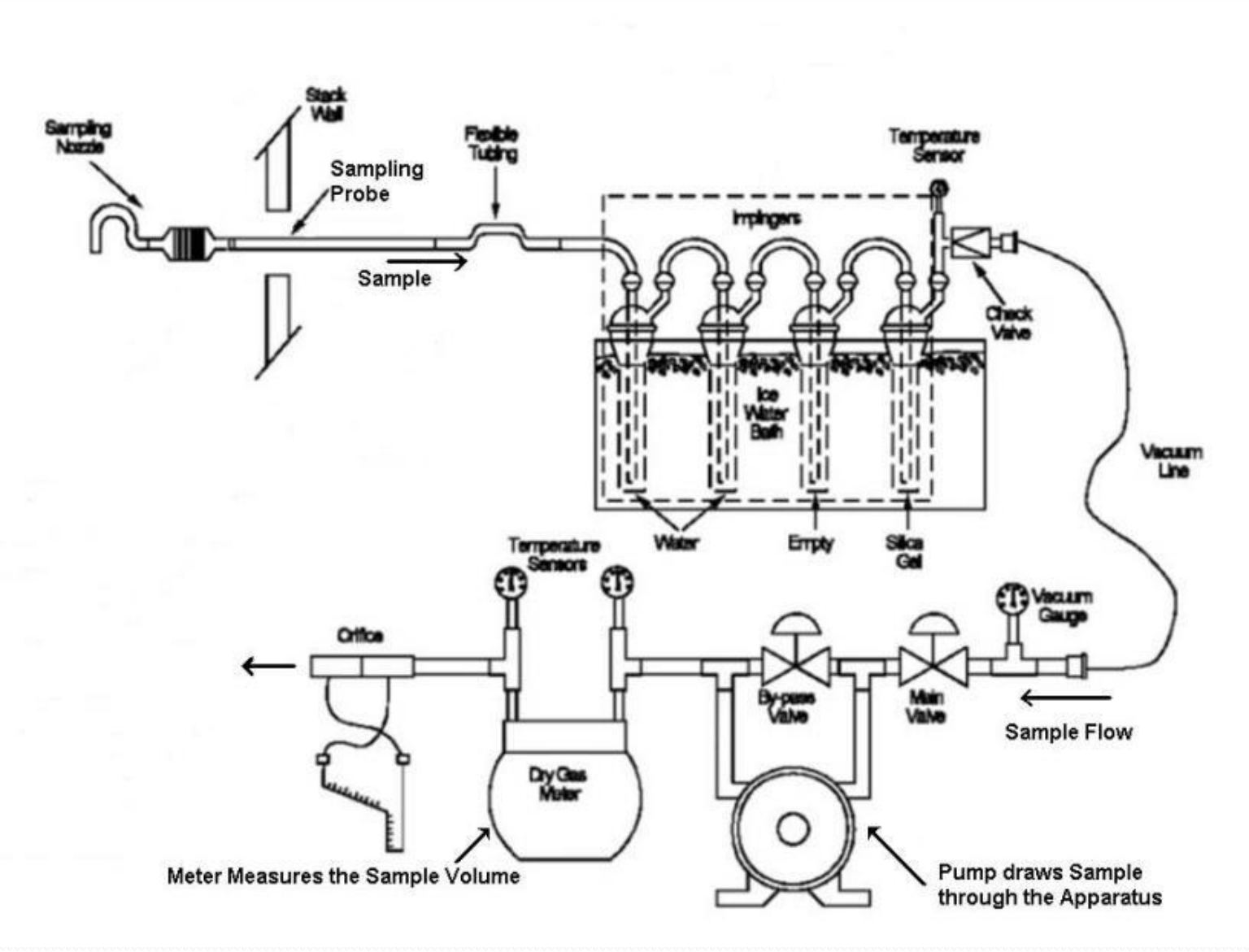
Under stack conditions
We measure
Particles &
Gases

Ambient Monitor
Collects
Particles,
Condensables &
Secondary



Primary $PM_{2.5}$ Emissions
- Particles (solid, liquid)
- Condensables

Old EPA 202 Test Method



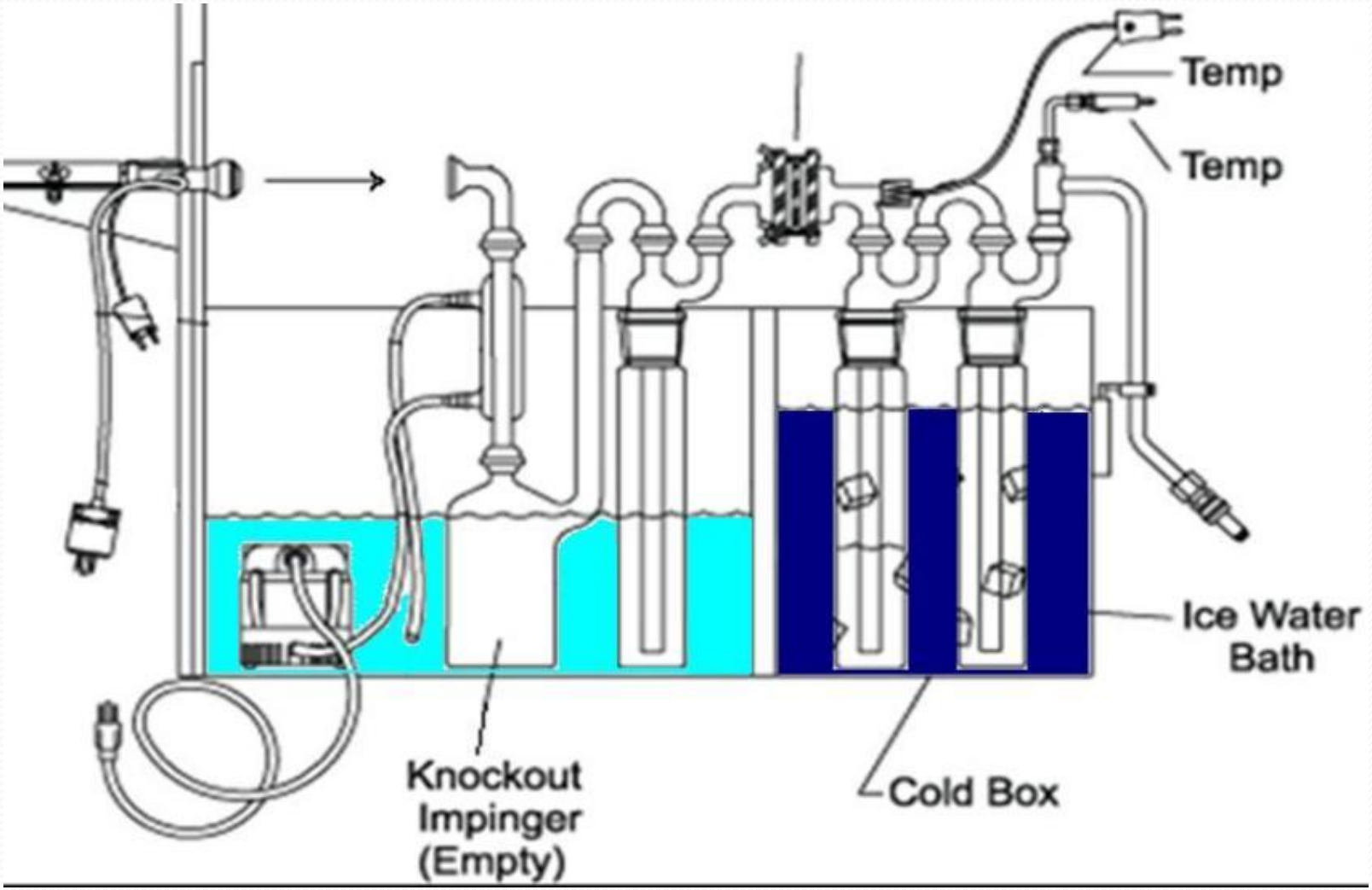
Old EPA 202 Test Method

Why "Old" EPA 202 is problematic

- Does not accurately emulate stack release
  - Gases bubbled through water dissolved into solution
    - Dissolved gases form salts that may or may not form naturally when released to atmosphere
    - Although some back-half PM may actually be CPM or primary $PM_{2.5}$ emissions, much can be an artifact of the method
- Nitrogen purge works very well for high SO_2 sources – but is only optional!
- Other optional analytical procedures varied results between sources/testers

New "Dry" 202 (formerly OTM-028)

(uses condenser, dry impingers and backup filter)

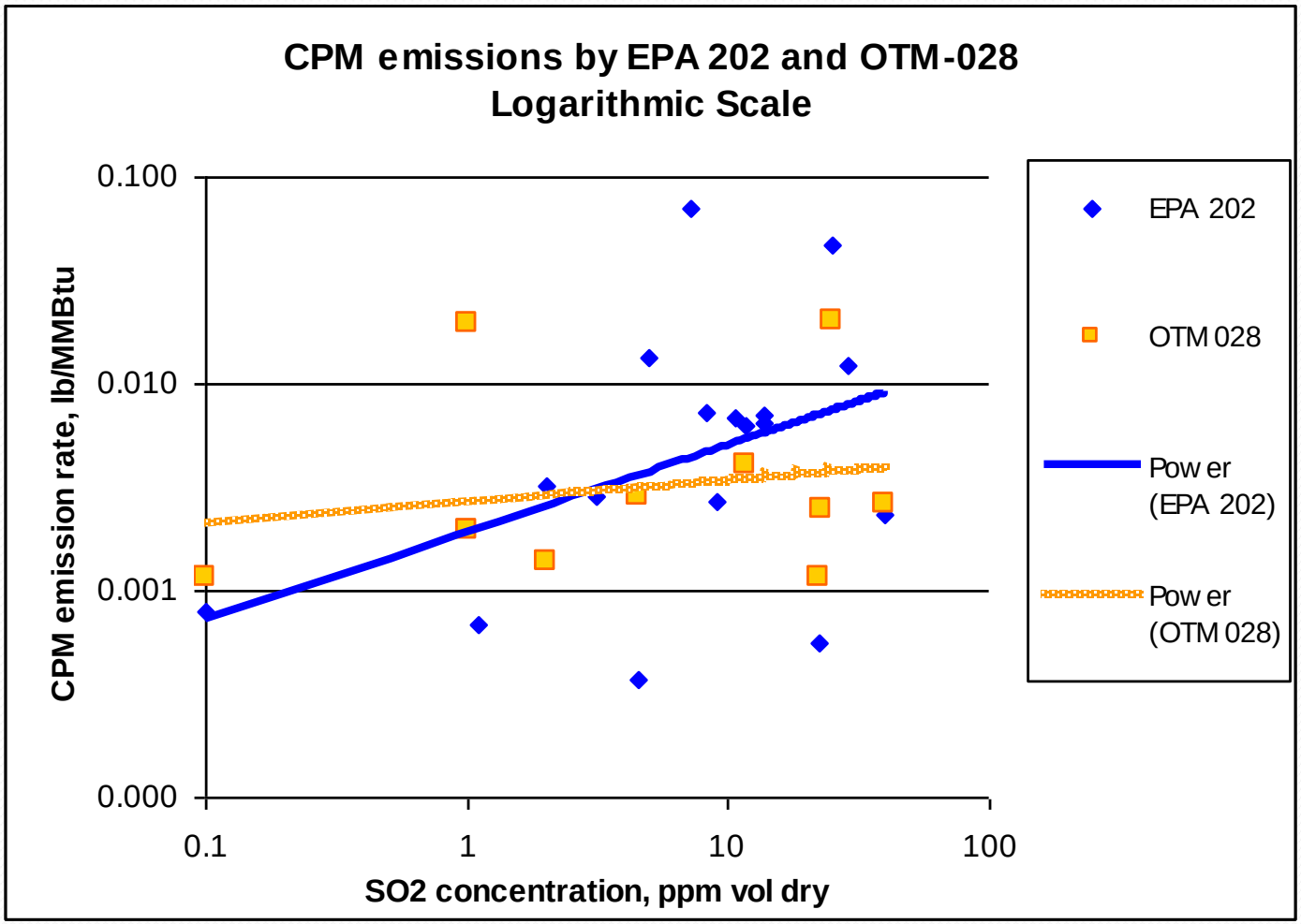


New "Dry" 202 (formerly OTM-028)

New "Dry" Method 202 (OTM-028)

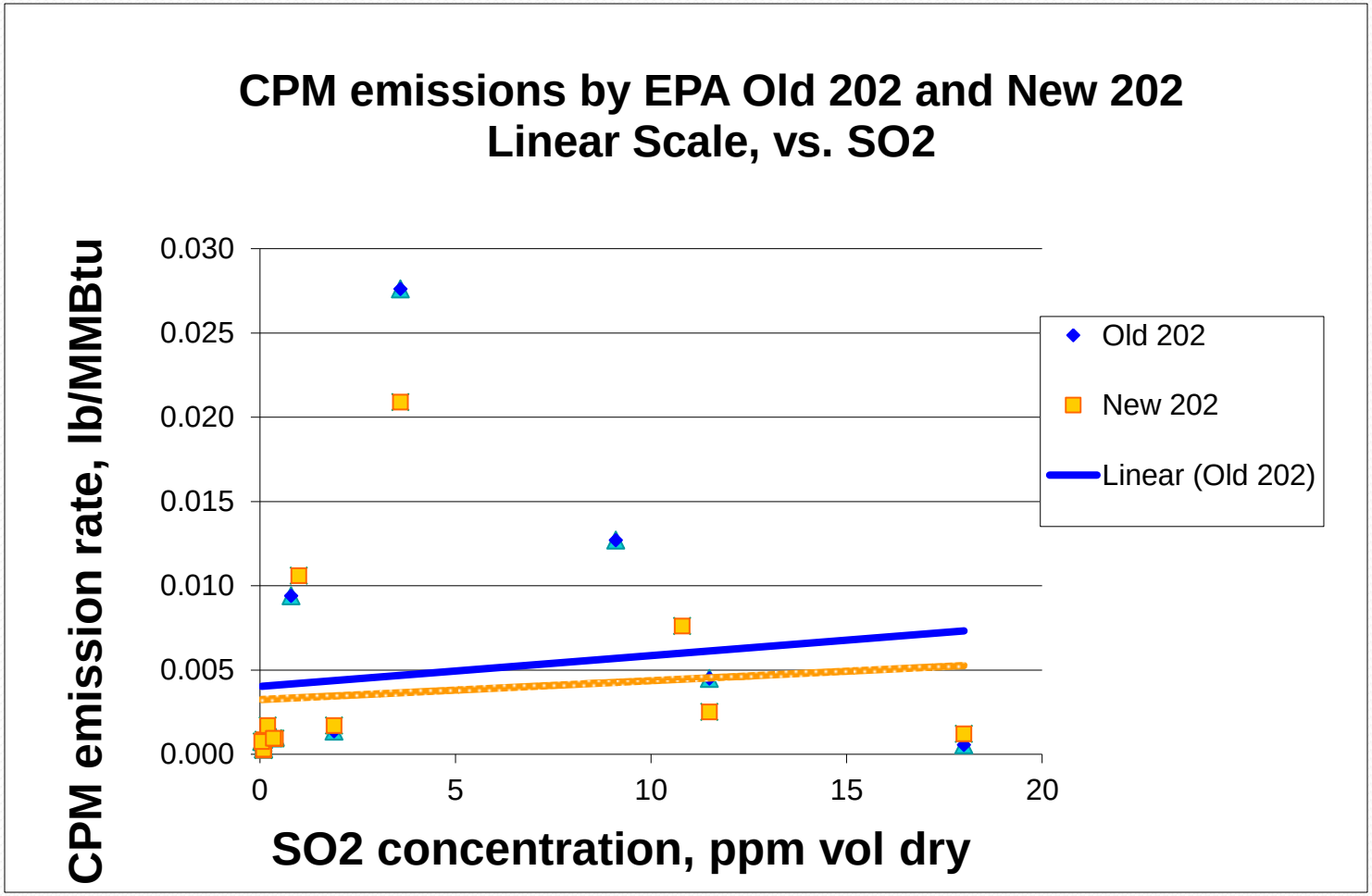
- **Objectives**
  - Less artifact
  - Fewer variables (eliminate options)
  - More consistent results
- **Procedural Changes**
  - Water-insulated condenser coil
  - First impinger is short-stem dropout variety
  - First two impingers are dry at beginning of test run
    - Condenser and impingers cool sample to 85 °F or lower
    - Gas does not bubble through excess water or condensate
    - Condensables recovered from coil, dry impingers and CPM filter
  - CPM filter added after 2nd impinger
  - Mandatory nitrogen purge to remove dissolved SO_2
  - Impingers after filter are not recovered (moisture content only)
  - Extraction solvent - $MeCl_2$ is replaced with hexane
  - Glassware is baked

Early Tests: OTM-028



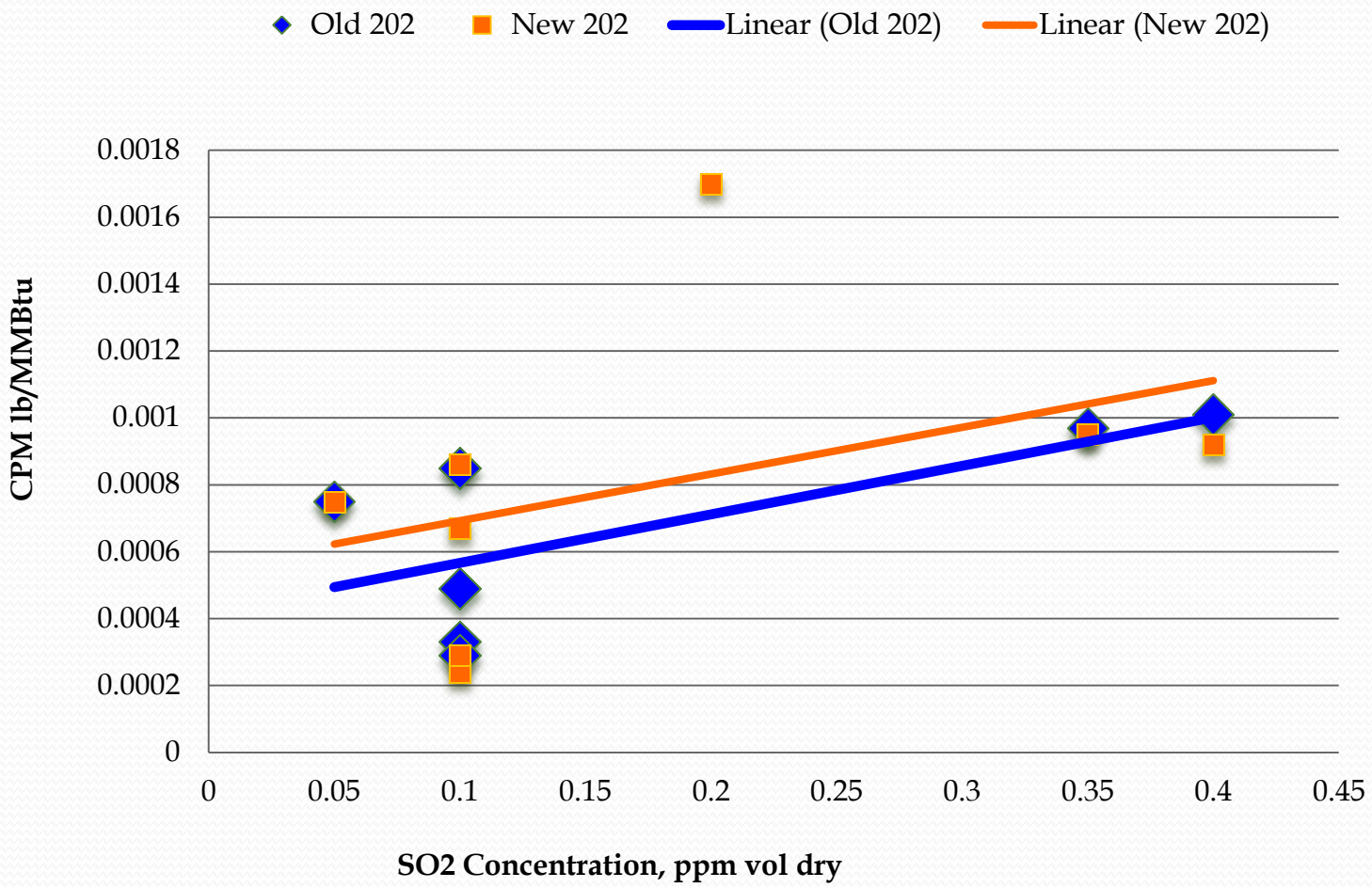
These are results from a variety of sources, 2007 to 2009 with trend lines for each of the two methods. OTM-028 (draft 202) results were higher than Old 202 for low-emitting sources with low SO_2.

More Recent "Dry" Impinger Results



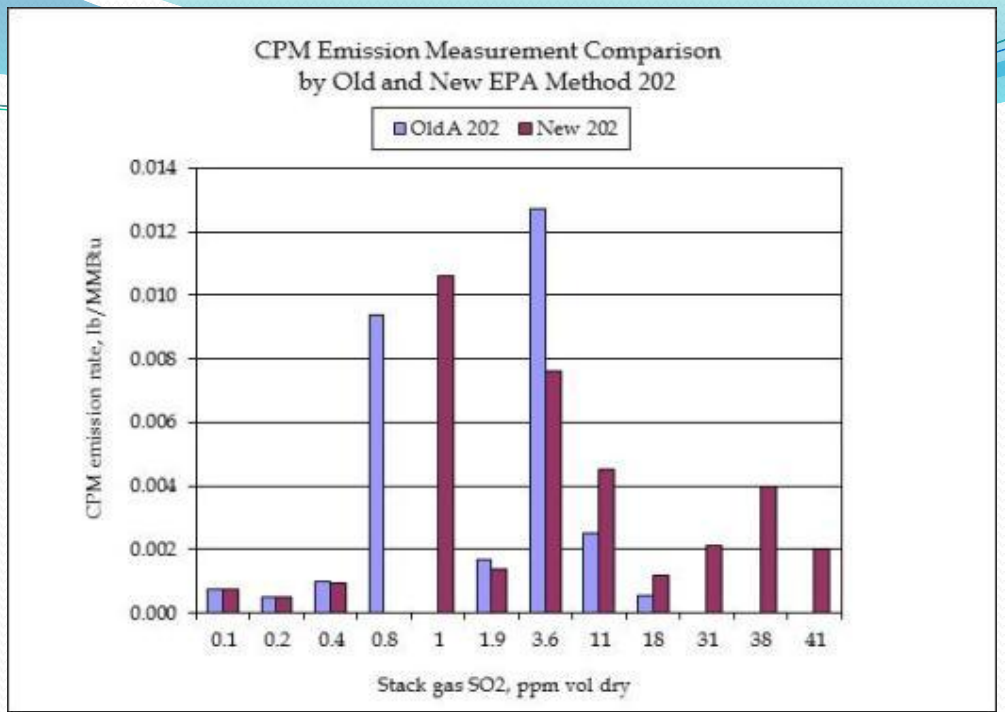
These are results from 2010 and 2011 distributed according to SO_2. The New and Old 202 gave similar results and neither trended with SO_2. There are results around 0.010 and around 0.001 throughout the range.

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

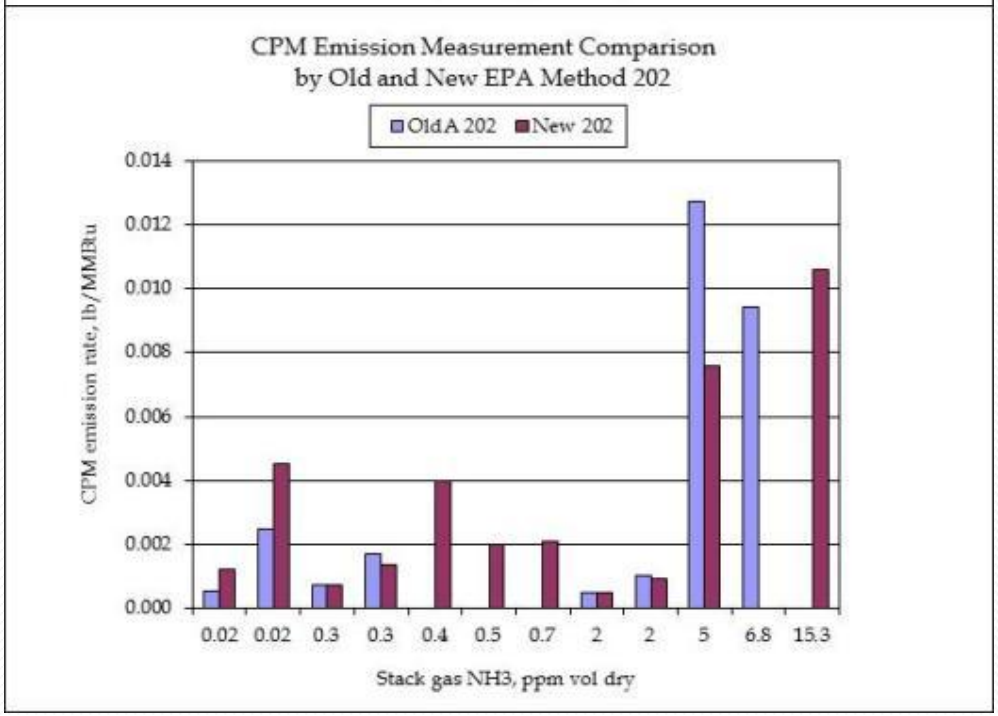


Data from just *gas-fired* boilers and gas turbines; some of the SO2 concentrations shown are estimated. Little difference Old/New Method.

CPM vs. SO_2



CPM vs. NH_3

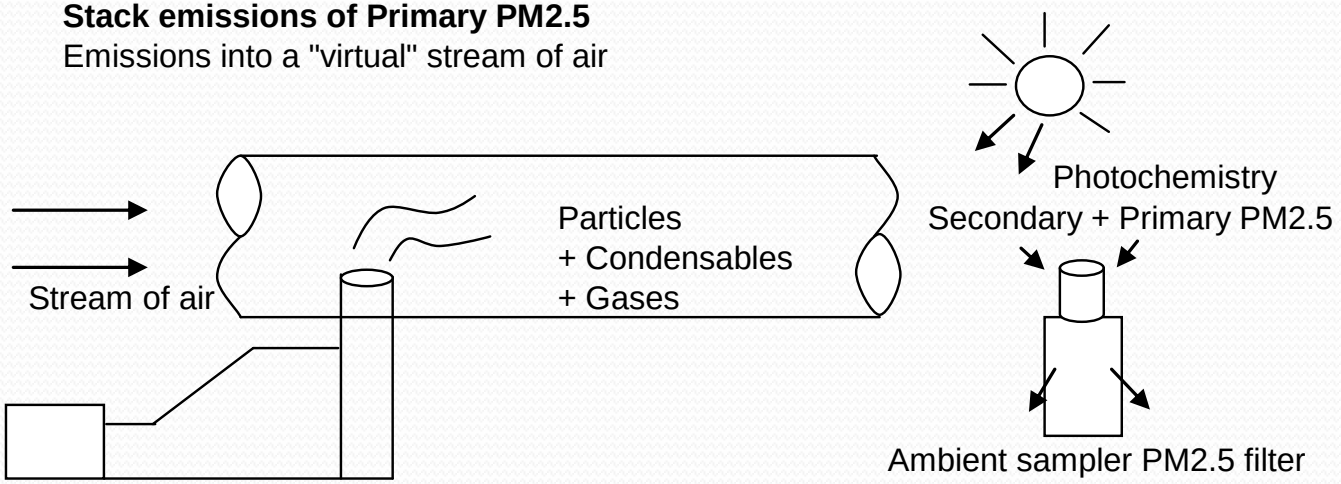


Is the new method better?

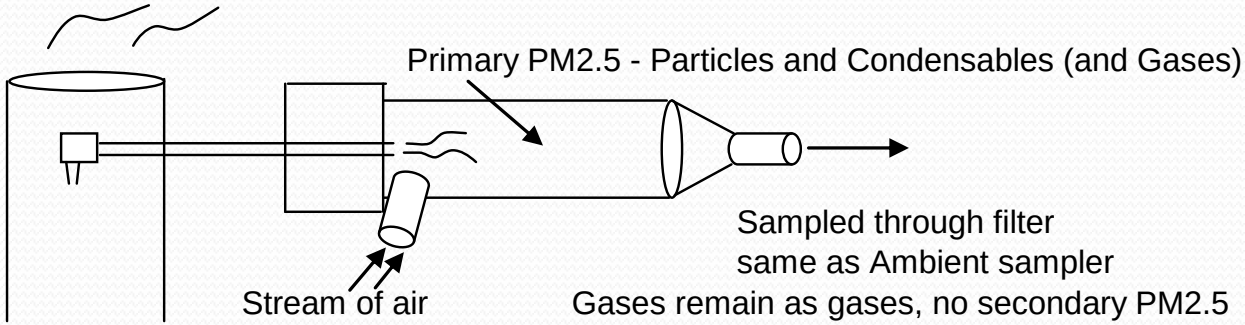
- **Did EPA meet its objectives?**
  - Results seem less variable
  - Less artifact at high SO_2 sources; inconclusive at low SO_2 sources
  - More recovery fractions add potential for contamination or bias
- **Can we improve the situation?**
  - Improve blank levels, update lab procedures
    - More fractions add complication to analysis
  - 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
    - ASTM dilution method

Dilution Sampler Concept

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



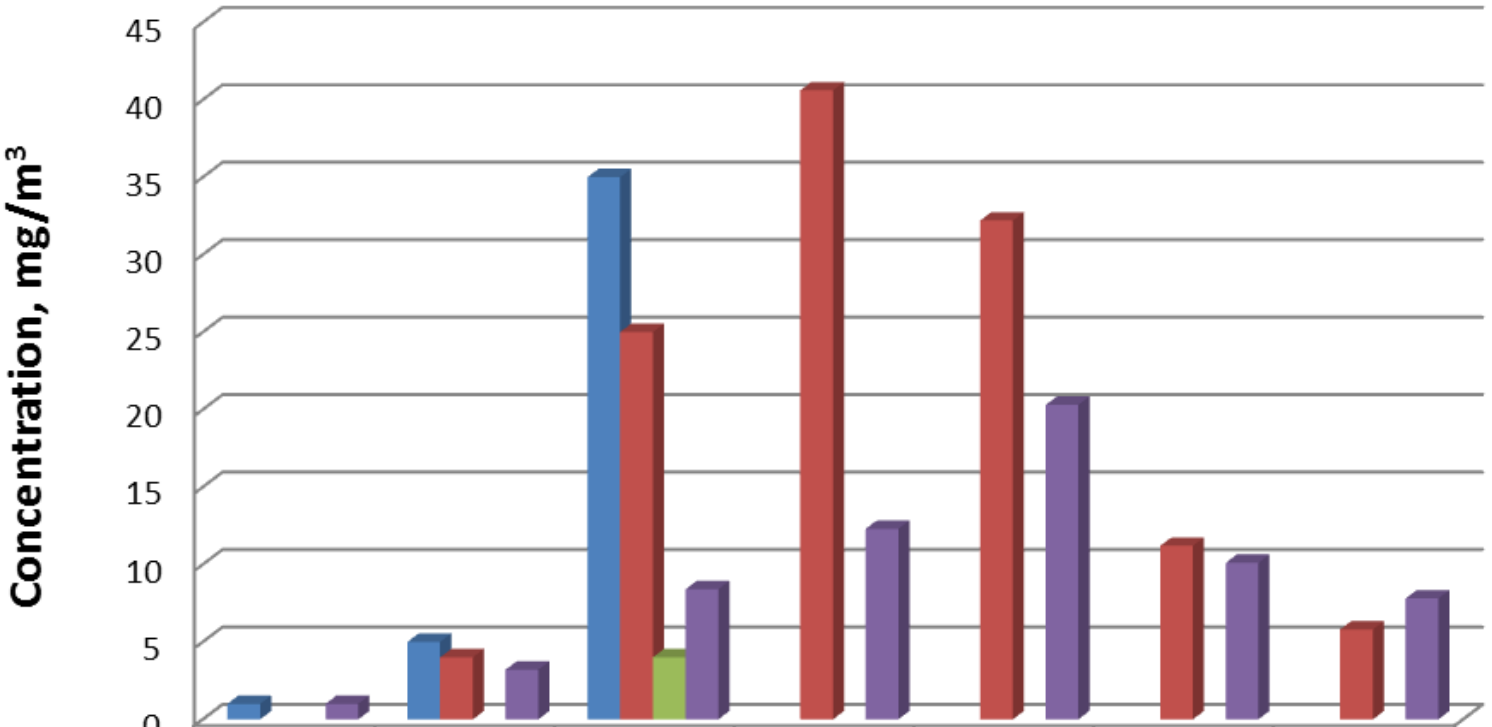
Stack sampling of Primary PM2.5 by CTM-039
Sample "emitted" into a stream of air



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 – no secondary collection
- Shows promise – the results of comparative studies are encouraging
- *Disadvantage: New, Rare, Expensive, Bulky*

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

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 new method is advantageous only in certain cases, usually at higher concentrations of SO_2 or other CPM precursor gases
- New 202 is sometimes only 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 (NH_3, SO_2, SO_3, HCl) and in what relative concentrations
- The Method used will define the Results
- Quality Testing is critical!

Questions ???

The Avogadro Group, LLC

Source Emissions Testing and Emissions Specialists

Portland, OR – Phoenix, AZ - Antioch, California – Medford, OR

Craig Thiry
Business Development Director
Email: cthiry@avogadrogroup.com
Phone: (925) 680-9065

Kevin Donahoe
Portland District Manager
Email: kdonahoe@avogadrogroup.com
Phone: (925) 331-7583