Measurement of Condensible and Non-Condensible Particulate Matter

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2009 CAPCA Conference

Particulate Terms and Definitions

Primary Particulate Matter:

- Particles that enter the atmosphere as a direct emission from a stack or an open source. It is comprised of two components: Filterable PM and Condensible PM.

  (FR Vol.67, No.111, June 10, 2002)

Particulate Terms and Definitions
(Continued)

Secondary Particulate Matter:

- Particles that form through chemical reactions in the ambient air well after dilution and condensation have occurred.

(FR Vol. 67, No. 111, June 10, 2002)

Particulate Terms and Definitions
(Continued)

Filterable Particulate Matter:

- Particles that are directly emitted by a source as a solid or liquid at stack or release conditions and captured on the filter of a stack test train

(FR Vol. 70, No. 210, November 1, 2005)

Particulate Terms and Definitions
(Continued)

Condensible Particulate Matter (CPM):

- Material that is vapor phase at stack conditions, but which condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack

  (FR Vol.67, No.111, June 10, 2002)

Particulate Terms and Definitions
(Continued)

$PM_{2.5}$:

- Particulate matter equal to or less than an aerodynamic diameter of nominally 2.5 microns
- Includes both filterable and condensable particulate when applied to direct emissions from a given source

Detection Limits

Detection Limit Definition:

- The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero

  (40 CFR 136, Appendix B, Definition and procedure for the determination of the method detection limit Revision 1.11)

- Statistically determined value based on 7 or more replicate analyses

Detection Limits
(Continued)

Determination of pollutant emissions quite often involves two distinct operations:

1. Collection of the sample
2. Analysis of the sample to determine a concentration or mass quantity

- **A separate and unique detection limit is associated with each operation for collection and analysis**

Why Detection Limits Are Important

Sample Time (hrs)	**1**	**2**	**11**
Sample Volume (dscf)	**30**	**60**	**330**
Measured Mass (mg)	**0.23**	**1.47**	**6.88**
Reported Mass (mg)	**2**	**2**	**6.88**
Concentration (gr/dscf)	**0.0010**	**0.0005**	**0.0003***

*True Concentration

Detection Limit = 2 mg

Practical Limit of Quantitation

- The PLQ is approximately the smallest sample size that can be measured in a single analysis with 99% confidence that the measurement is within 30% of the true value. (EPA Method 301)
- Uncertainty increases as value approaches the detection limit

How do we measure $PM_{2.5}$?

Current EPA Methods

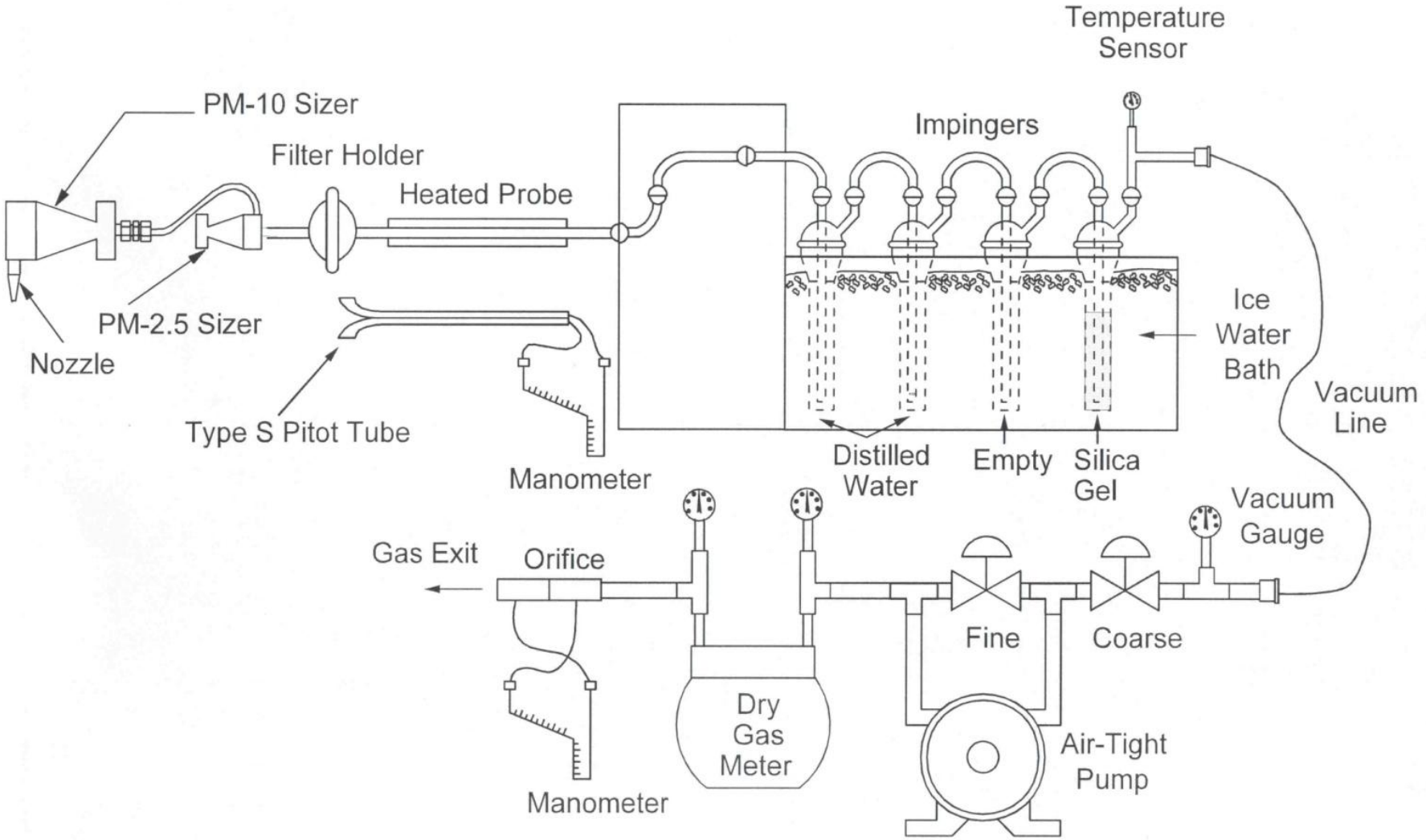
- OTM 27 (filterable PM) + Method 202 (CPM) – **dry sources**
- CTM 039 – dilution method (filterable + condensable PM) – **dry sources**
- Method 5 (filterable PM) + Method 202 (CPM) – **wet sources**

How do we measure $PM_{2.5}$? (Continued)

Other Methods

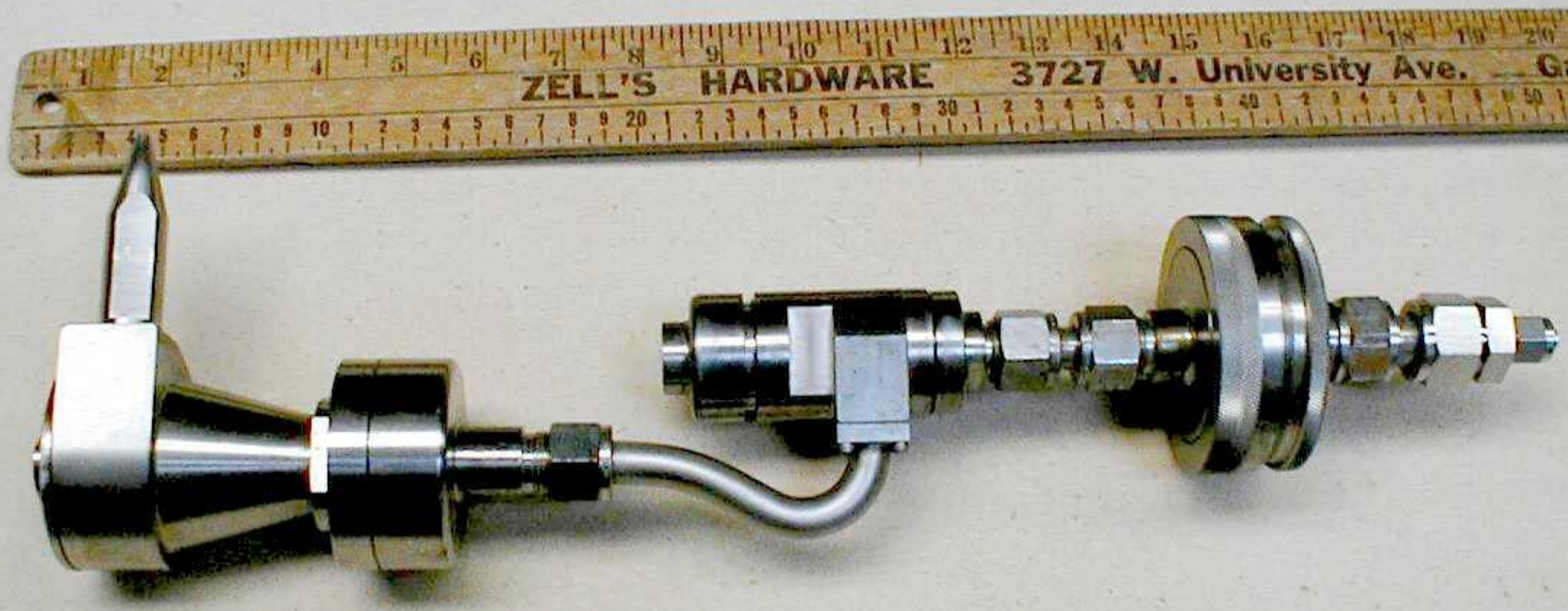
- CARB 501– (filterable PM) + Method 5 Impingers (CPM) **dry sources**
- GE Energy Compact Dilution Sampler – (filterable + condensable PM) **dry sources**

What is OTM 27?
Figure 1, Other Test Method 27



What is OTM 27?
(Continued)

- Measures filterable PM_{10} and $PM_{2.5}$ emissions in stationary sources
- Sample captured in cyclones and on in-stack filter
- Used concurrently with Method 202 to measure direct PM_{10} and $PM_{2.5}$ emissions


ZELL'S HARDWARE 3727 W. University Ave.

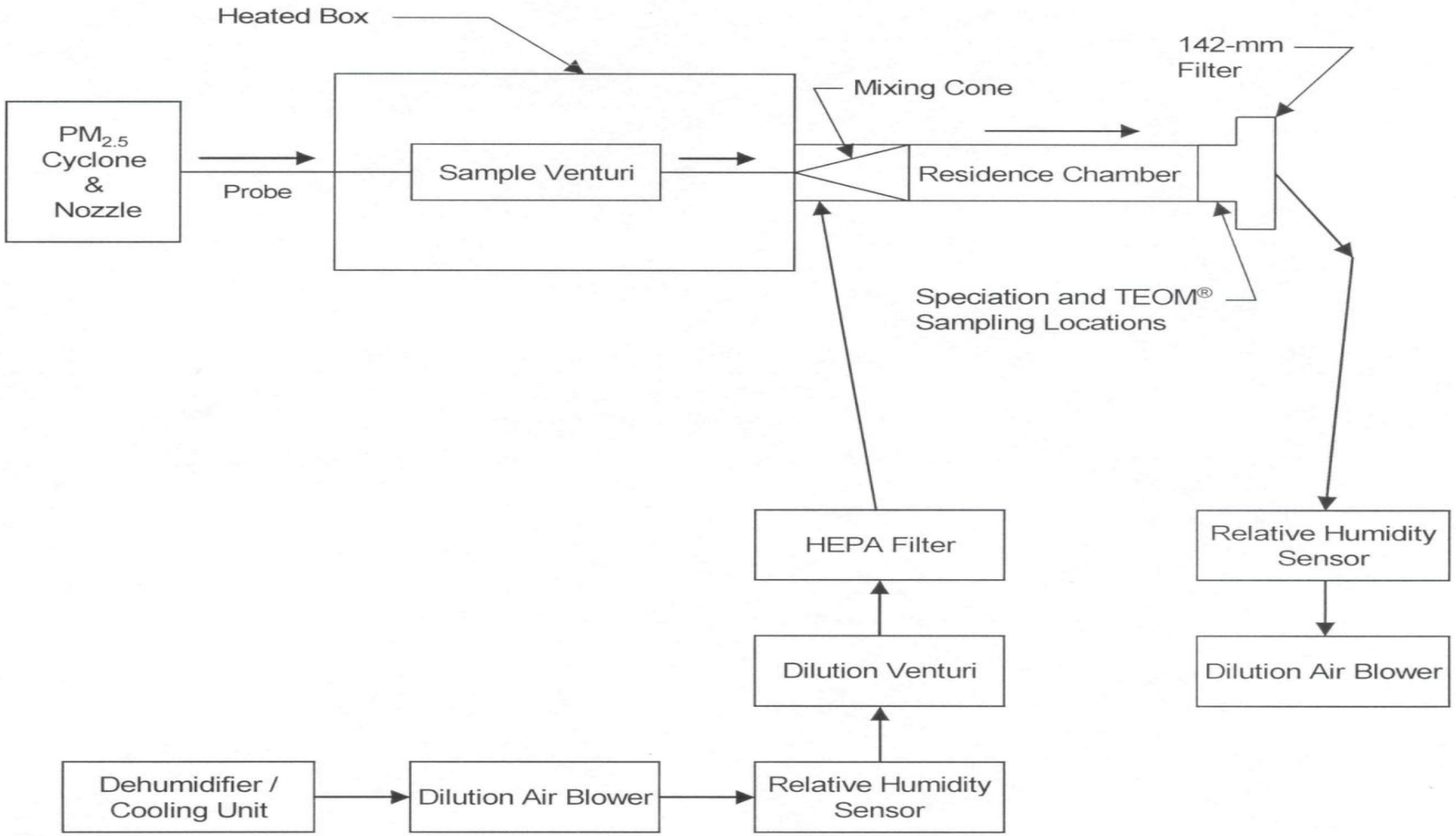
OTM 27 Limitations

- Not suitable for use in saturated or wet sources where entrained water droplets may be present.
- Requires a 6-inch diameter sampling port for simultaneous determination of PM_{10} and $PM_{2.5}$ emissions
- Sampling in small diameter ducts is challenging

OTM 27 Limitations
(Continued)

- Determining PM_{10} and $PM_{2.5}$ emissions simultaneously in low temperature sources can be difficult due to narrow overlap of acceptable flow rates for both cyclones
- Complex method – Requires an experienced sampling team to get good results

What is CTM-039?
Figure 1, Conditional Test Method 039



What is CTM-039? (Continued)

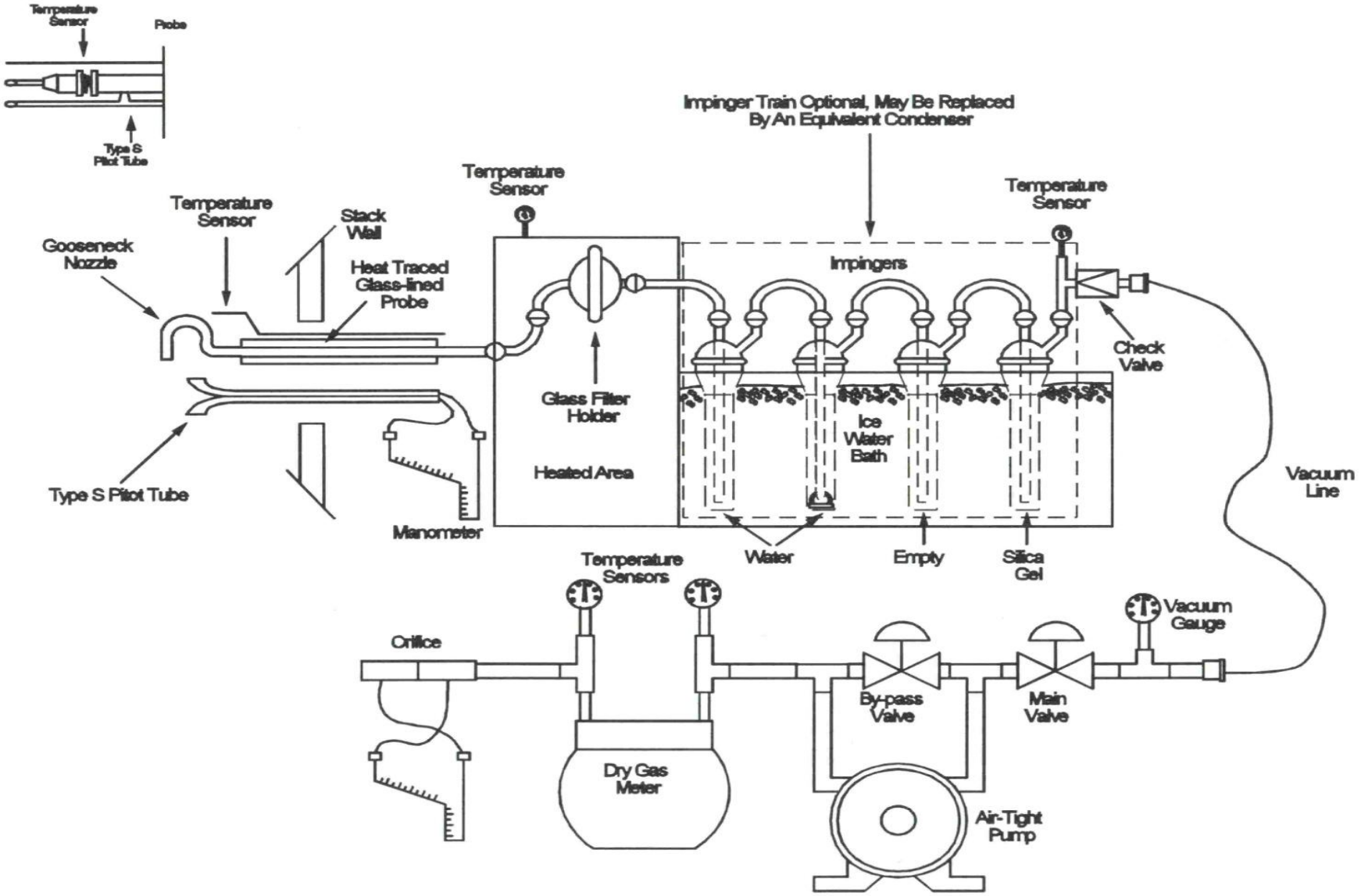
- Measures direct $PM_{2.5}$ emissions in stationary sources
- Sample captured on out of stack filter
- Uses dilution tunnel approach to mimic processes associated with formation of CPM

CTM-039 Limitations

- Not suitable for use in saturated or wet sources where entrained water droplets may be present.
- Equipment is complex and cumbersome
- Still under development and evaluation

What is EPA Method 5?

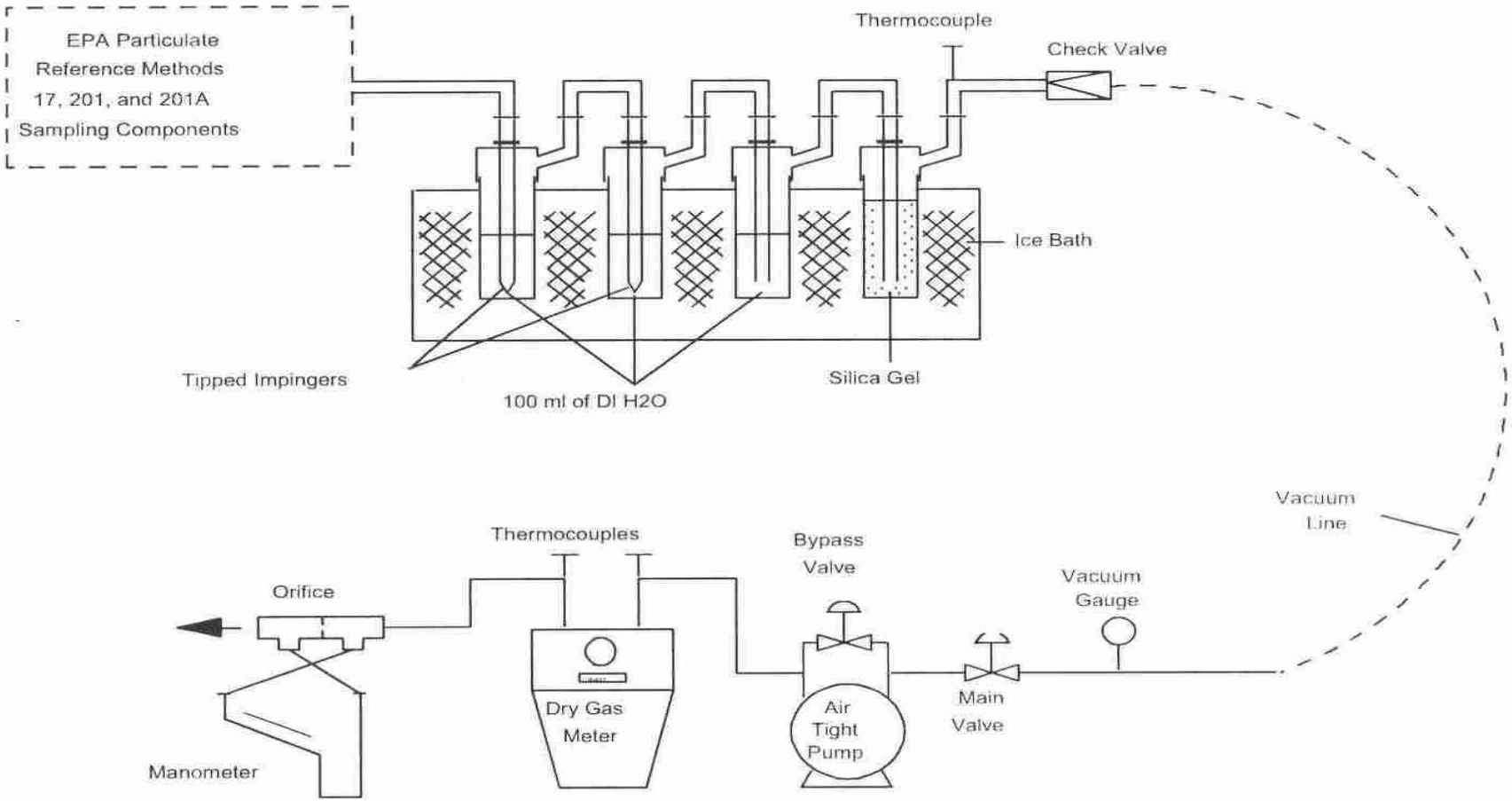
Figure 5-1, EPA Method 5



What is EPA Method 5? (Continued)

- Measures filterable PM in stationary sources
- Sample captured on out of stack heated filter maintained at a specified temperature
- Temperature of filter determines particulate captured

What is EPA Method 202? (Figure 202-1, EPA Method 202)



What is EPA Method 202? (Continued)

- Measures condensible PM in stationary sources
- May be used in conjunction with EPA Methods 5(x), 17, 201A, and OTM 27
- Sample captured by bubbling flue gas through de-ionized, distilled water, in chilled impingers

What is EPA Method 202? (Continued)

- Impingers are purged with nitrogen or air after sampling if pH of impinger water is less than 4.5
- The organics are extracted and measured separately from the inorganic fraction of CPM


2000 ml
PYREX
Di-chlor
ethane
ed Water
0
0

What are the concerns with EPA Method 202?

- Multiple options in method mean results may not be directly comparable with other Method 202 tests
- High Method Detection Limit *(MDL = 6 mg)*[1] and high Limit of Quantitation *(LOQ = 20 mg)*[1] can make it difficult to generate accurate data using a typical one-hour run time

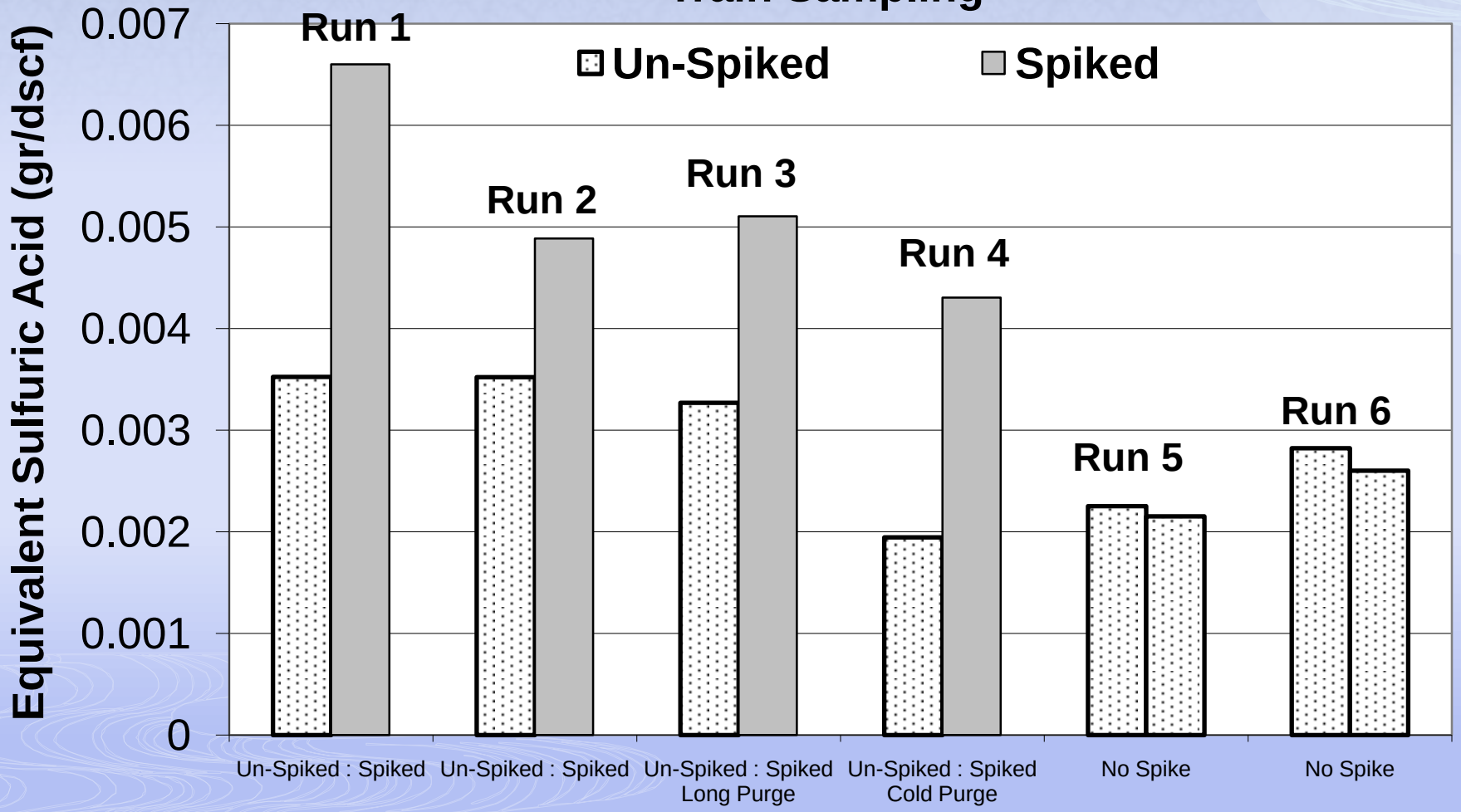
[1] NCASI Technical Bulletin No. 852

What are the concerns with EPA Method 202? (Continued)

- If SO_2 is present in the flue gas, a positive bias is imparted to the emission estimates due to oxidation of SO_2 to SO_4^{-2} (method induced artifact)
- An NCASI study published in NCASI Technical Bulletin No. 852 confirmed the potential for bias if SO_2 is present in the flue gas

Results of SO_2 Spiking of Sampling Train (NCASI Technical Bulletin No. 852)

Figure 8.1.1 Results of Spiked and Un-Spiked Paired-Train Sampling

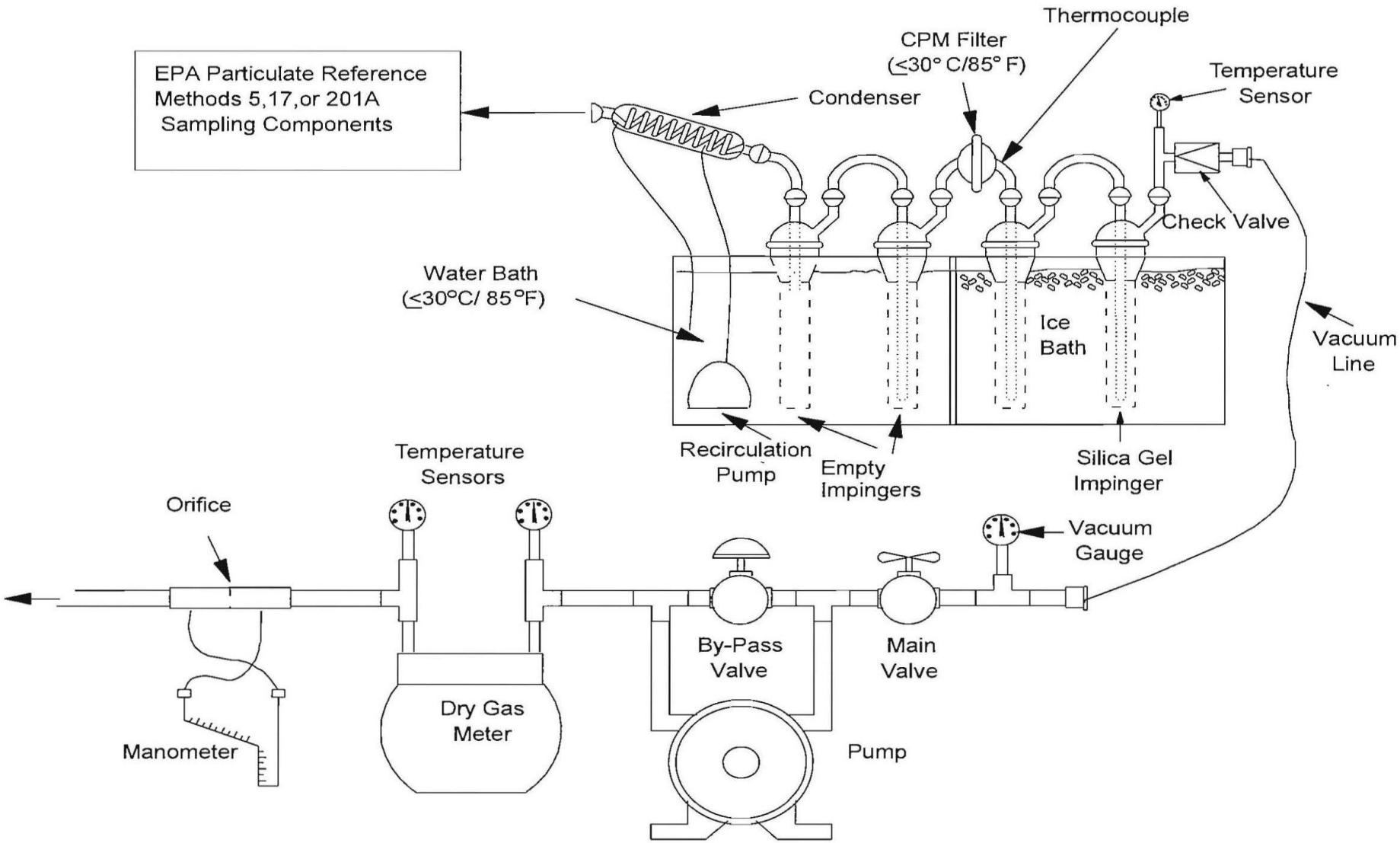


Current Thinking on CPM Measurement

- EPA has acknowledged the SO_2 bias issue with Method 202 and is sponsoring research on a modified version of Method 202
- Modified version called the "Dry Impinger Method" and currently classified as Other Test Method 28 (OTM 28)

http://www.epa.gov/ttn/emc/prelim/otm28.pdf

What is OTM 28? (Figure 1, OTM 28)



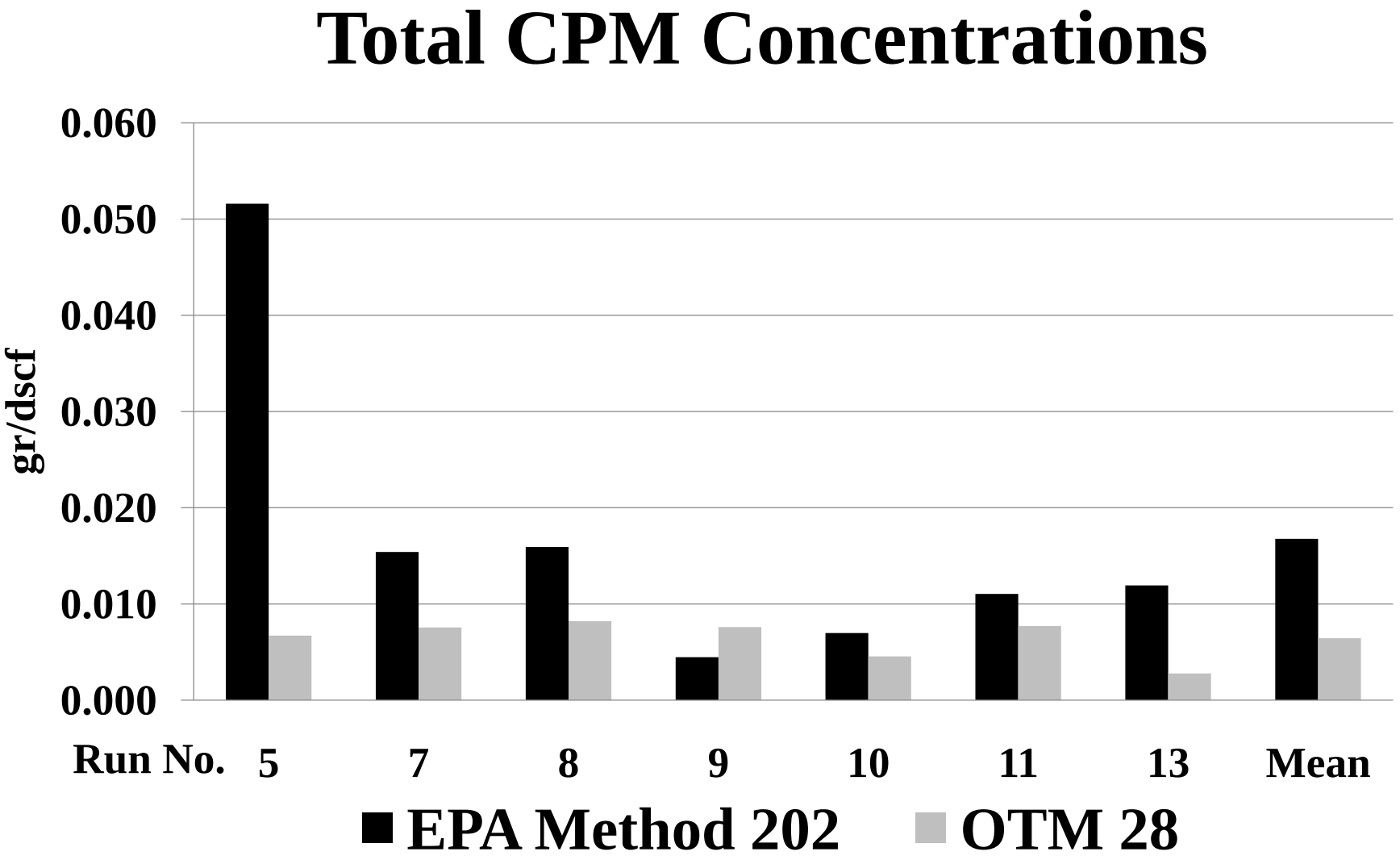
What is OTM 28? (Continued)

- Measures condensible PM in stationary sources
- May be used in conjunction with EPA Methods 5(x), 17, 201A, and OTM 27
- Contact between flue gas and condensed water minimized
- Sample captured on Teflon® membrane filter and in glassware between the Teflon® membrane filter and the front half filter

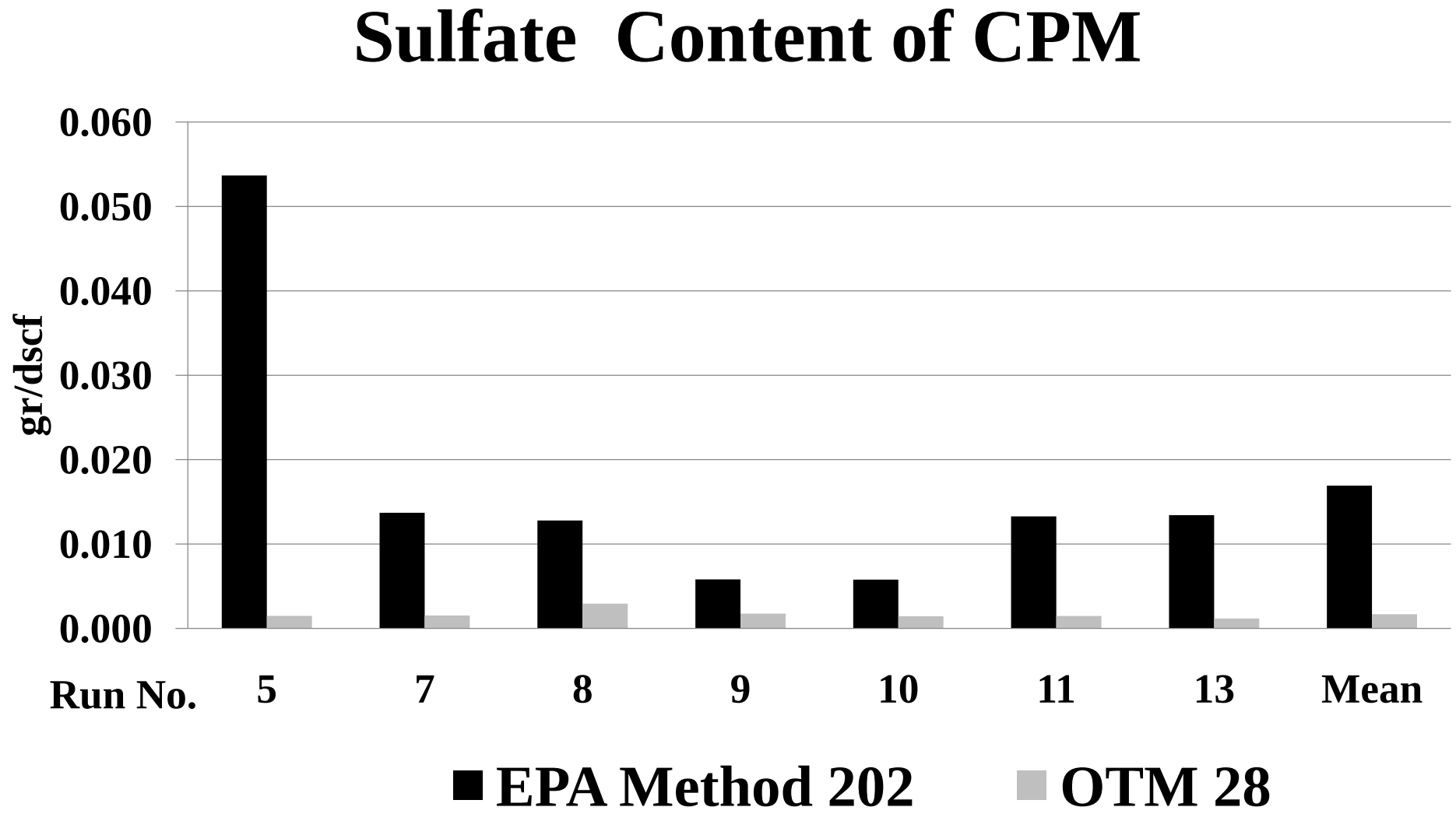
Method 202 and OTM 28 Comparison Study

- A comparison study was carried out on a DCE recovery furnace using EPA Methods 202 and OTM 28 in a parallel train
- CPM measurements between the two methods were compared
- CPM inorganic samples analyzed by ion chromatography for: sulfate, nitrate, chloride, ammonium, sodium, and calcium

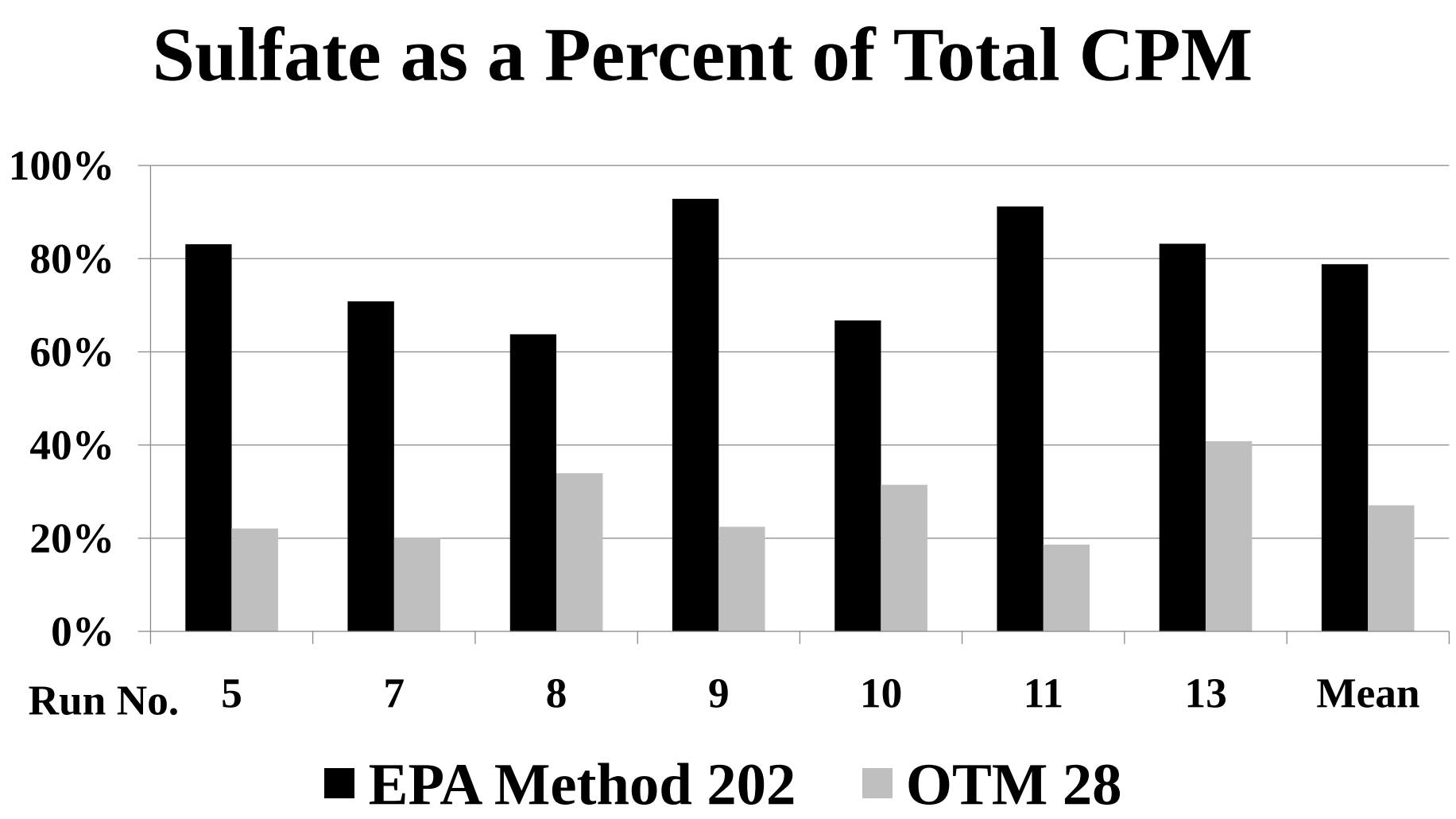
How do Method 202 and OTM 28 compare for total CPM?



How do Method 202 and OTM 28 results compare for sulfate content?



How does sulfate content compare to total CPM for Method 202 and OTM 28?



Conclusion

- EPA Method 202 exhibits significant positive bias when SO_2 is present in the flue gas
- When OTM 28 is used the sulfate fraction of CPM is much lower as compared to EPA Method 202

Regulatory Status

- EPA proposal to promulgate OTM 28 as the reference method for measurement of CPM emissions published in Federal Register March 25, 2009
- OTM 28 will replace current Method 202 and be titled Method 202
- No revisions to permits required

Regulatory Status
(Continued)

- EPA proposal to promulgate OTM 27 as the reference method for measurement of filterable PM_{10} and $PM_{2.5}$ emissions published in Federal Register March 25, 2009
- OTM 27 will replace current Method 201A and be titled Method 201A
- No revisions to permits required

Method Detection and Quantitation Limits

Method	Method Detection Limit (mg)	Quantitation Limit (mg)
EPA Method 5	2	6
EPA OTM 27 (PM)	4.7	14.8
EPA OTM 27 (PM_{10})	3	8
EPA OTM 27 ($PM_{2.5}$)	2	5
EPA Method 202	6	20

NCASI Technical Bulletin No. 852

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