Condensable PM Test Method Improvement Workshop

Presentations

- Meeting Agenda
- Ron Myers - Introduction, Background and Philosophy
- Ray Merrill – QAPP development and Laboratory Results
- Naomi Goodman – EPRI funded stakeholder effort
- Bill Prokopy – Daimler Chrysler funded stakeholder effort
- Jorge Marson - Environment Canada funded stakeholder effort
- Ray Merrill – Chemistry Discussion
- Ray Merrill – Ron Myers - Meeting to assess and select hardware

Condensable Particulate Matter Test Methods Stakeholder Meeting
U.S. Environmental Protection Agency

February 9, 2007
8:30 a.m. to 4:30 p.m.
Research Triangle Park, NC
Room C114
Dial in Conference Number (919) 541-1590
If can not connect, call (919) 541-5545

Meeting Agenda

Time	Topic/Issue to be Discussed
8:30 am	Ron Myers (EPA) – Brief introduction
8:40 am	Ron Myers – Background of Modified M202 and supporting information • Goal: Single method with few options; however, EPA would consider options that do not change results • Options for wet stacks: Modified M202 vs. CTM 040 • Method should not require knowledge of source emissions beforehand (capture organic and inorganic fractions in same method)
9:00 am	Ray Merrill (ERG) – • Quality Assurance Project Plan (QAPP) development and revisions • Results to date
10:00 am	Stakeholder presentation – Naomi Goodman (EPRI)
10:30 am	Stakeholder presentation – William R. Prokopy (DaimlerChrysler Corporation)
11:00 am	Stakeholder presentation – Jorge Marson (Environment Canada)
11:30 am	Open floor for questions and discussion
12:00	Lunch
1:00 pm	Chemistry Discussion • Expected changes to M202 • Field and Reagent Blanks • Discussion (recovery of organic material, front half, etc.)
2:00 pm	Open floor for questions and discussion of Other Stakeholder projects.
2:30 pm	Ron Myers and Ray Merrill • Report on 1/18/2007 equipment meeting
3:00 pm	Open floor for questions and discussion of topics tabled during presentations
4:20 pm	Ron Myers – Wrap up and Blue Sky ideas for the future
4:30 pm	Adjourn

PM fines Test Method Workshop

Second workshop on an improved condensable particulate matter stationary source test method

Ron Myers
OAQPS/SPPD/MPG
2/9/2007

Housekeeping

- Meeting is informal – discussions open
- Everyone's input is valued
- Let others provide input
  - Try not to interrupt others
  - Try not to dominate discussion
- People on phone need to hear also
  - Speak up or come to mike
  - Speak slowly
- Limit extended discussion
  - I will move topic to Parking lot
- Limit “offline” discussions
- Cell phones off – they die in this bld.
- Facilities for relief

Presentation Topics

- **Morning**
  - **Background - Me**
  - **EPA QAPP development & results – Ray Merrill**
  - **10 min break**
  - **EPRI supplemental study – Naomi Goodman**
  - **Daimler Chrysler study – Bill Prokopy**
  - **Environment Canada - Jorge Marson**
  - **Open floor discussion**

Presentation Topics

- **Afternoon**
  - Chemistry Discussion – Ray Merrill
  - Open floor for questions and discussion of Other Stakeholder projects
  - 10 min break
  - Report on Hardware discussion meeting – Ron & Ray
  - Open floor for questions and discussion of topics tabled during presentations
  - Wrap up and Blue Sky ideas for future - Ron

Background

- PM2.5 Implementation Proposal
  - Inventories
  - Measurement
  - Controls
  - Monitoring
- Response Development
- John Richards dry impinger mod
- Initial laboratory assessment
- QAPP development
- Stakeholder Involvement

Method Development Philosophy

- **Objective is near field PM emissions**
  - **Primary Emissions**
  - **Solid or liquid at STP**
  - **Near ambient concentrations**
- **Gold Standard is dilution sampling**
  - **Avoids water chemistry artifacts**
  - **Approaches stack release conditions**
  - **Brings mobile source and stationary source measurement closer**

Method Development Philosophy
(continued)

- Use existing available hardware
- Existing "suite of options" not tenable
  - Requires little knowledge of gas matrix
  - Any options result in same mass
  - Some options may yield different mass
- Particulate defined by physics

Other EPA Activities

- Validation efforts for CTM-039
- ASTM method development
- Developing guidance for SIP process
  - Control Measures
  - Measurement issues
  - Monitoring issues
- Wet stack particle sizing

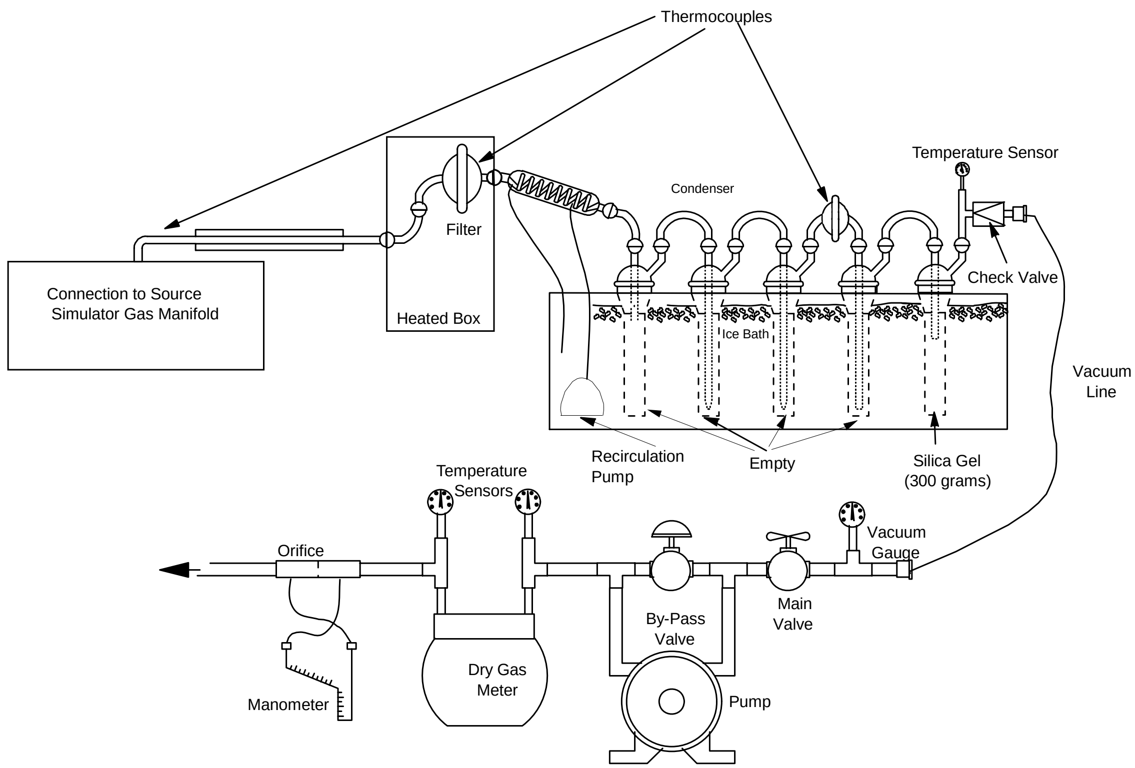
Open Discussion

- **QUESTIONS?**

M-202 Assessment and Evaluation QAPP Development & Revisions

- Round 1–Initial Tests
  - Train & conditions
  - Results
- Round 2–Replicate Tests
  - Train & conditions
  - Results

Round 1 Dry Impinger Train



Round 1 Conditions

- Operate heated portion of train at 160 ± 16°C (320 ± 32°F)
- Use a 50/50 mixture of NO/NO_2; O ppm NH_4; 12% CO_2; 8% O_2; 5% H_2O
- Use Method 5 and Method 23 glassware
- Use short stem impinger insert for dry method
- Operate condenser and impingers at ice water temperature
- Purge all trains with UHP nitrogen for ~1 hour (1 cubic meter)
- Recover samples following Method 202
- Use highest quality solvents
- Run paired tests for wet and dry impingers

Round 1 Test Matrix

Test	Method	SO_2 (ppm)
1	M-202	25
2	M-202	25
3	M-202	25
4	M-202	150
5	M-202	150
6	M-202	150
7	Dry Impinger Mod	25
8	Dry Impinger Mod	25
9	Dry Impinger Mod	25
10	Dry Impinger Mod	150
11	Dry Impinger Mod	150
12	Dry Impinger Mod	150

QAPP/Test Plan Revisions After August 1, 2006 Stakeholder Meeting

- Collect aliquot of aqueous impinger sample
  - Prior to residue dry down
  - Analyze for anions by Ion Chromatography
- Add ammonia to neutralize samples
- Dry samples and weigh residue
- Reconstitute samples in water for IC analysis

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Round 1 Results – Method 202 (Wet) Train

M0202 (Wet) Train	Moisture (g)	Total Water (g)	Residual Sulfate (CPM) (mg)
25 ppm SO_2 Run 1	27.4	397	13
25 ppm SO_2 Run 2	41	406	17
25 ppm SO_2 Run 3	44	391	10
150 ppm SO_2 Run 1	38	384	9.6
150 ppm SO_2 Run 2	31	376	9.5
150 ppm SO_2 Run 3	31	373	10.3

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Round 1 Results – Dry Impinger Train

Dry Impinger Train	Moisture (g)	Total Water (g)	Residual Sulfate (CPM) (mg)
25 ppm SO_2 Run 1	31	112	0.45
25 ppm SO_2 Run 2	41	168	0.85
25 ppm SO_2 Run 3	47	150	0.88
150 ppm SO_2 Run 1	41	141	0.93
150 ppm SO_2 Run 2	35	122	1.4
150 ppm SO_2 Run 3	58	98	0.5
150 ppm SO_2 Run 4	38	256	0.79
150 ppm SO_2 Run 5	36	220	0.48

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Preliminary Blank Observations

Blank Type	Residual Mass (mg)	Comments
Reagent Water	10.6	Doubly Deionized Water (16 µmho)
Wet Method (M202) FB	19.5	Doubly Deionized Water (16 µmho)
Dry Method FB	10.7	Doubly Deionized Water (16 µmho)
Empty Aluminum Pan Blank – unheated	-0.25	Pan was unheated, sat next to the pan below
Water Blank w/ Aluminum Pan	6.97	500 mL house DI (18 µmho) water evaporated in a 160 mL aluminum weigh pan
Water Blank w/ Aluminum Pan	8.24	Repeated evaporation in an aluminum weigh pan to confirm original results
Water Blank w/ Glass Beaker	0.35	500 mL house DI water evaporated in a 100 mL Pyrex beaker (18 µmho)
Purge Blank	0.31	50 mL DI (18 µmho) water + rinses evaporated in a glass beaker

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Round 1 Blank Data

Blanks	Field Blank Total Volume	Residual Sulfate (CPM) (mg)
Reagent Water	500	ND
Wet Method (M202) FB	415	ND
Dry Method FB	113.2	ND

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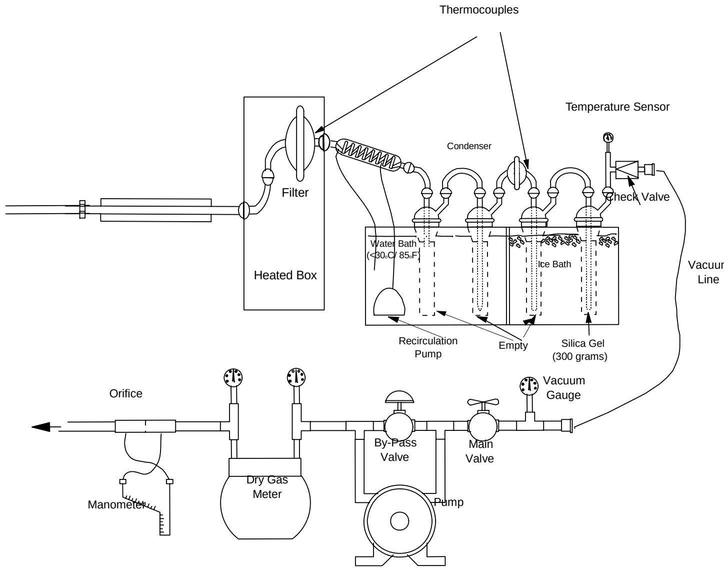
Round 2 Dry Impinger Train

Intro to Round 2 train

Test matrix: Eight replicate runs

Operational observations (qualitative)

Changes and reasons for changes (water distribution, others)



Round 2 Test Matrix

Same as Round 1, EXCEPT:

- 8 replicate runs (4 paired trains)
- 8 – 10% water
- 150 ppm SO_2 – all runs
- Increase collection temperature to reduce SO_2 gas solubility

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Round 2 Train Changes

- Heated portion of the train operated at

  160 ± 16°C (320 ± 32°F) same as Round 1

  Note: Heated portion of the train may be

  different depending on the regulatory

  requirement
- Remove one impinger to simplify train
- Water Drop out, First impinger, Cold Filter

  Ambient Temperature (80-85°F)
- Final Impinger and Silica Trap

  Ice Bath Ice water temperature

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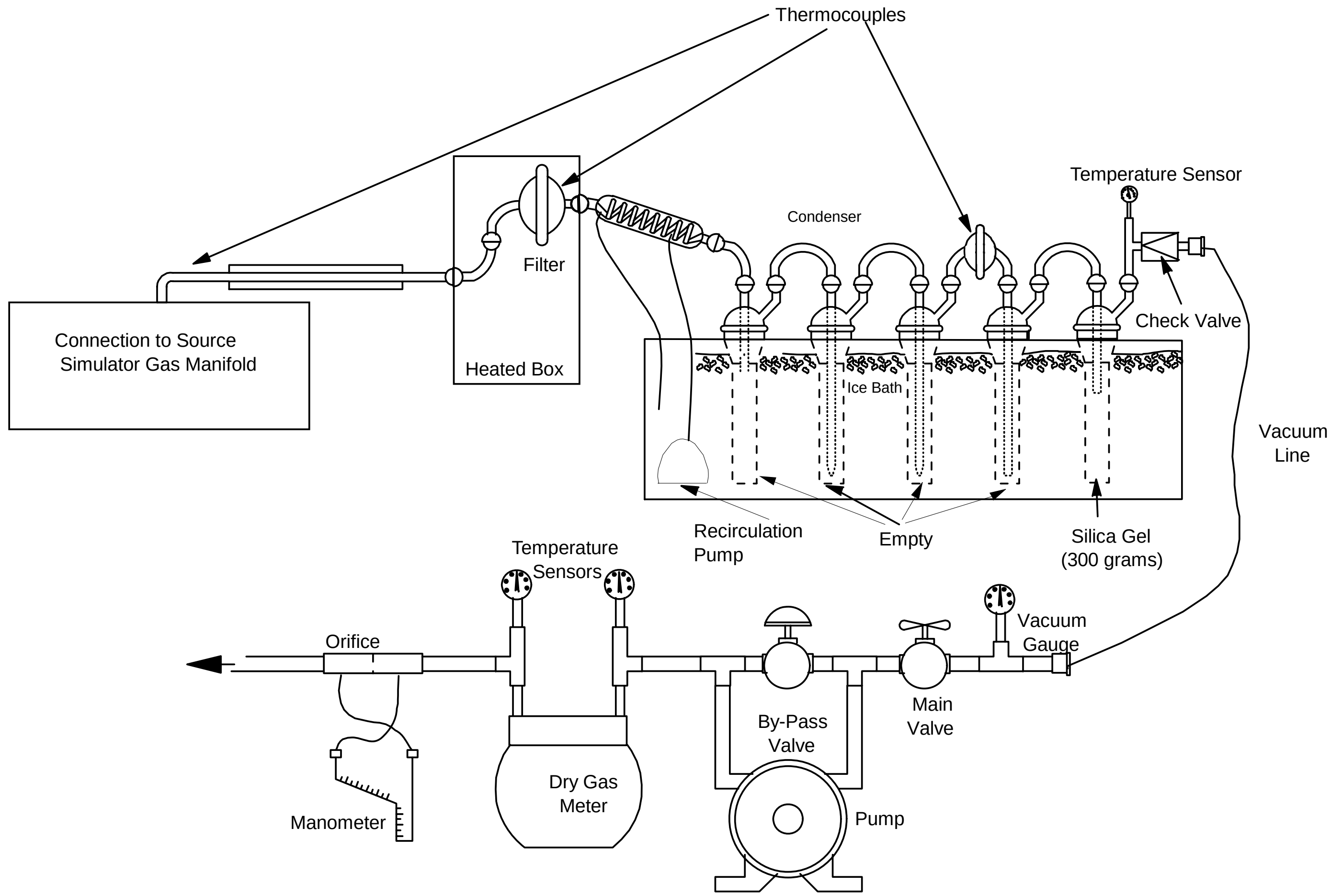
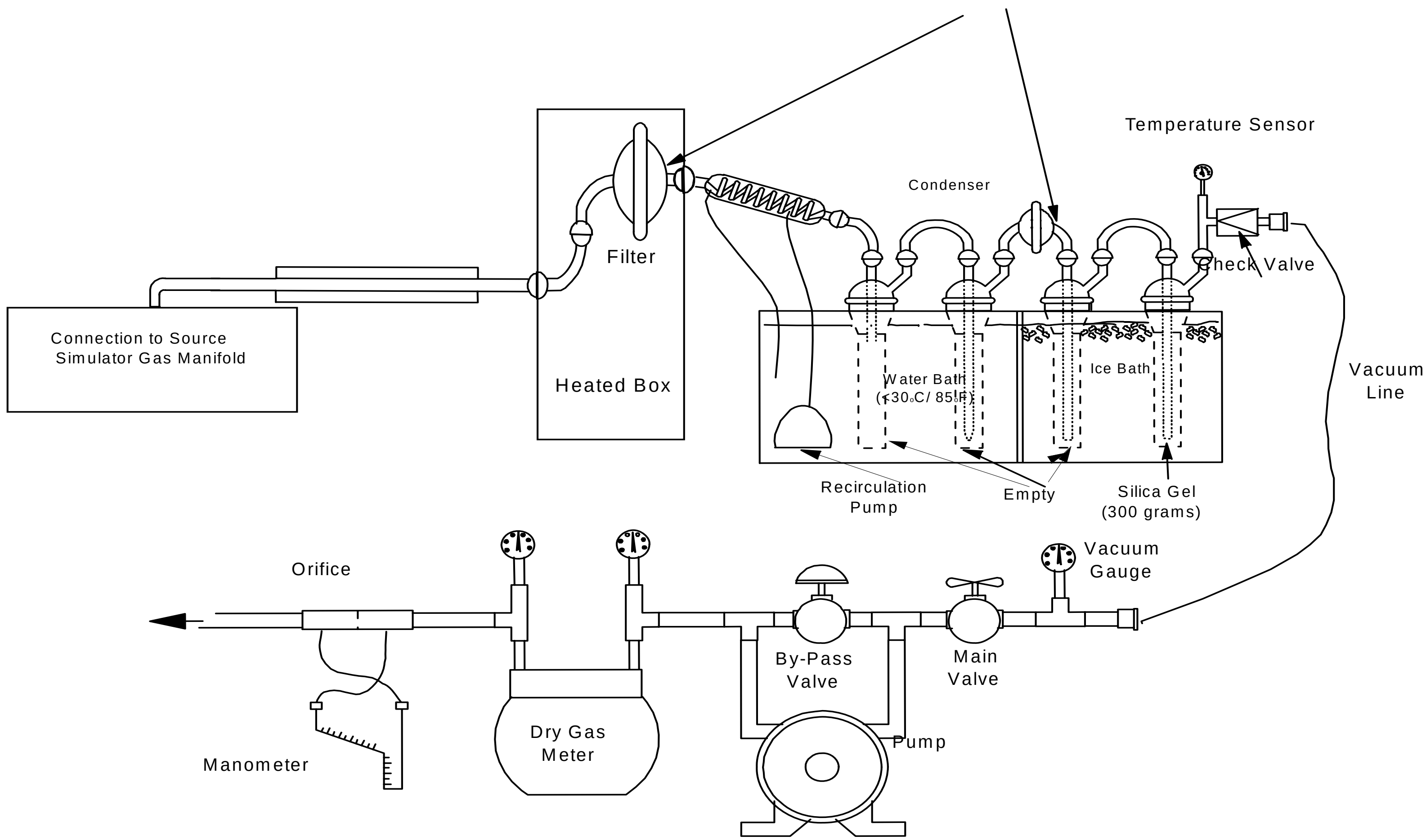
Dry Impinger Train Round 1



Dry Impinger Train Round 2



Round 2 Operational Observations

- Qualitative Observations
  - Separate or divided impinger box needed for 2 temperatures
  - Condenser cooled 320 °F gas to <85 °F efficiently
  - Less water was collected in the first two impingers
  - Water condensed on the surfaces of all the ambient temperature components
  - Water soaked the ambient temperature filter

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Round 2 Results – Water Distribution

Run	Knockout Impinger	1st ambient Impinger	Cold Impinger	Silica Impinger	Total Moisture (g)	Percent Moisture (%)
1	39	0	22.9	19.7	81.6	10.31
2	36	~0.1	25.8	20.5	82.6	10.26
3	24	0.7	24.9	17.9	67.5	8.64
4	23.8	.3	22.6	20.1	66.8	8.47
5	28.2	1.6	23	16.9	69.7	9.05
6	27.9	0.7	22.9	18	69.5	9.86
7	11.7	0.2	22.6	15.9	50.4	6.57
8	9.9	0.2	19.5	16.4	46.0	5.99

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Round 2 Results – CPM

Run	Organic (mg)	Inorganic (mg)	Filter (mg)	Total (mg)*
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 Deviation**	0.10	0.51	0.17	0.45
Estimated MDL**	0.31	1.54	0.49	1.36

*Negative weights were not used in blank correction
** Negative weights were used to determine standard deviation and MDL

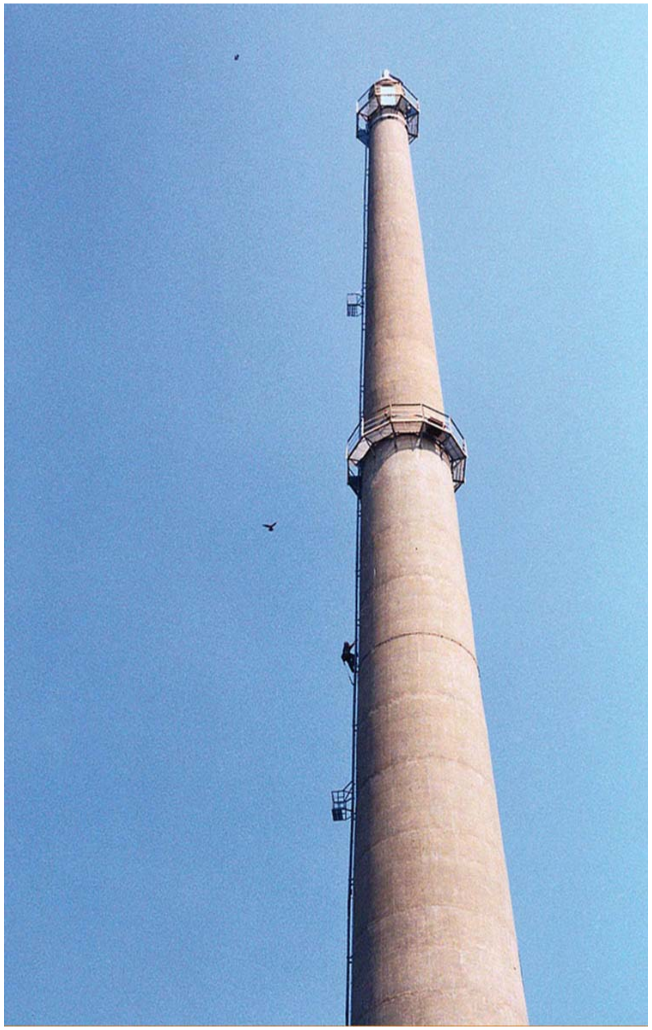
EPRI Additions to EPA Method 202 Test Plan

EPA Stakeholder Meeting, RTP
February 9, 2007

Naomi Goodman
Senior Project Manager, EPRI

Gary Blythe
URS Corporation

Characteristics of Coal-Fired Boiler PM and CPM



- Typical PM limits in recent permits
  - Filterable or not specified: 0.01 - 0.015 lb/mmBtu
  - Filterable and condensible: 0.01 – 0.04 lb/mmBtu
- Composition of CPM
  - >90% ammonium sulfate
  - <1% organic

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Objectives of EPRI Test Matrix Addendum

- Challenge dry impinger method with more extreme conditions, greater range of “coal” flue gases:
  - Higher flue gas moisture (15%)
  - Lower flue gas temperature (140^{o}F)
  - Higher SO_2 (500 ppmv)
- Verify complete capture of SO_3/sulfuric acid
- Test alternate methods
  - Provide backup if dry impinger method does not remove enough bias
  - Field-tested alternatives
- Impact of ammonia not addressed at this time

Dry Impinger Expanded Testing

- Flue gas mixtures in ERG test plan are similar to:
  - Subbituminous (PRB) coal with dry injection flue gas desulfurization (FGD)
  - PRB coal without FGD
- Will dry impinger method reduce bias sufficiently with higher moisture and SO_2?
- EPRI will support testing:
  - Four additional conditions
  - Triplicate runs at each condition (12 runs)
  - Run dry impinger and baseline Method 202 in parallel
  - Effect of longer test runs (2 hours)

Expanded Conditions Test Matrix (EPRI tests shown in yellow)

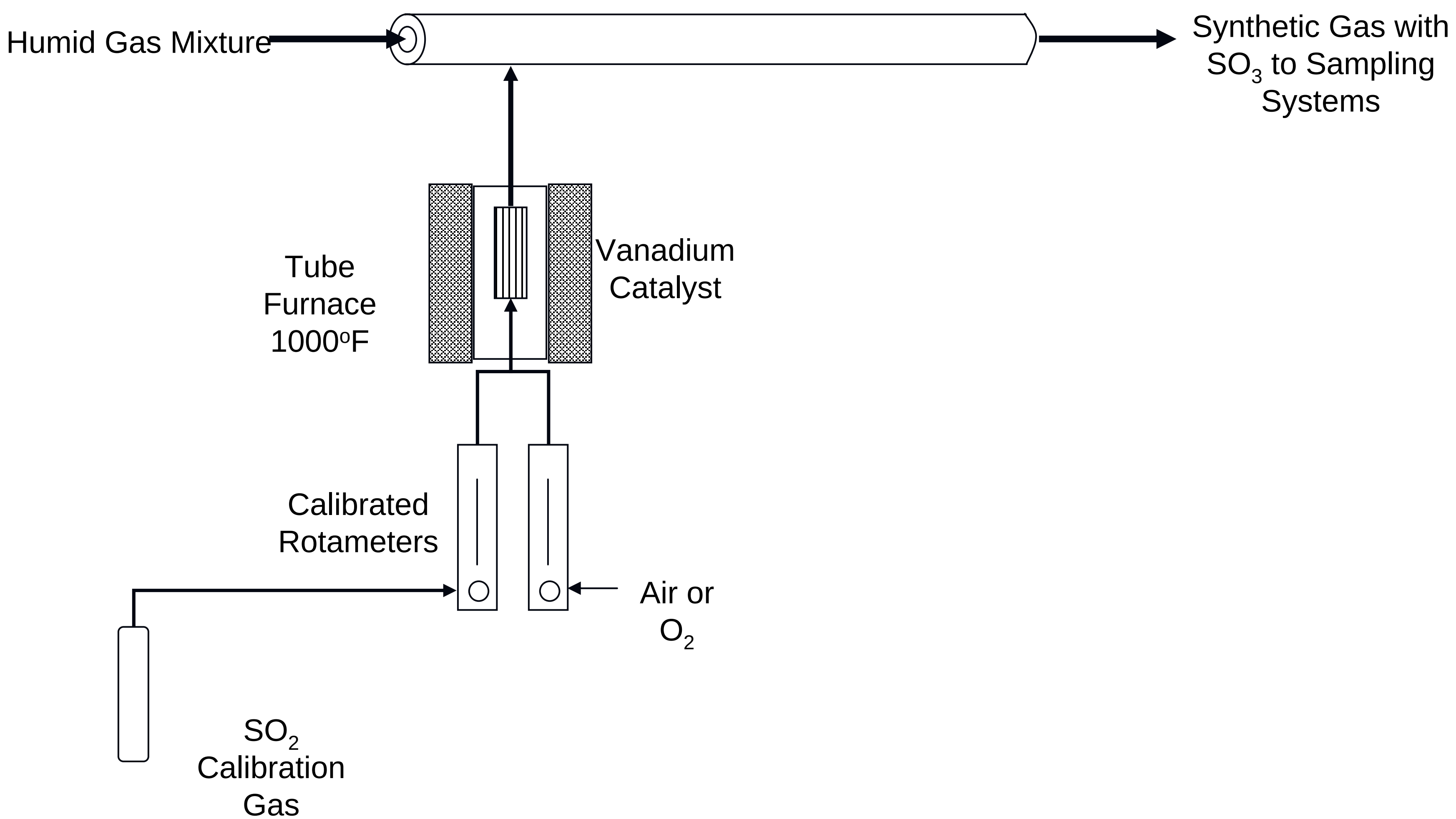
SO_2 (ppmv)	H_2O (%)	Inlet Temp (^oF)	Coal Flue Gas Simulated
150	8-10	300	PRB, no FGD*
500	8-10	300	Low S bit., no FGD
25	15	140	Low S, wet FGD
150	15	140	High S, wet FGD
500	15	300	Lignite, no FGD

*Condition included in ERG Test Plan

Challenge Methods with Inorganic CPM

- Up to 24 runs with SO_3/sulfuric acid added to simulation gas:
  - 2 ppmv to simulate low S bit. or PRB with SO_3 conditioning
  - 10 ppmv to simulate high S, high SO_3 conditioning "slip"
  - Did not recommend higher SO_3 due to potential testing difficulty
- Test with 150 ppmv & 0 ppmv SO_2
  - Ensure that method effectively collects true CPM
  - Distinguish between "artifact" and actual collection of sample gas SO_3

Proposed SO_3 Injection Approach



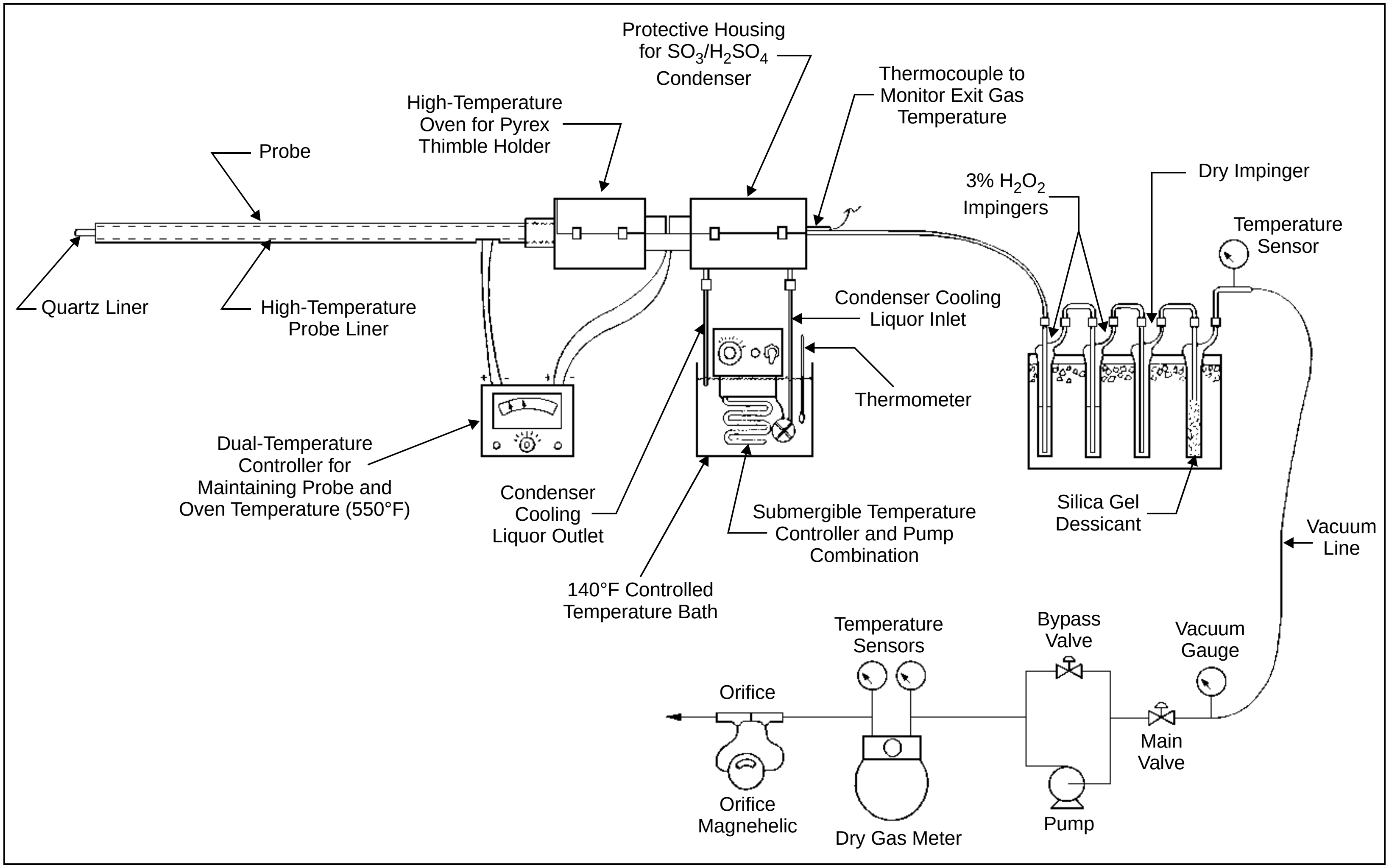
Alternate Test Methods

- Controlled Condensation System (CCS) correction
- EPRI Low-temperature Filter Modification to Method 202
- Testing matrix:
  - Test only conditions where SO_3 is added to synthetic gas matrix
  - Included in 24 tests previously mentioned

Controlled Condensation System Correction

- CCS developed by EPA in 1970s
- Unbiased measure of SO_3/sulfuric acid concentration
- In field, run CCS in addition to Method 5/202
- Use CCS to correct Method 202 inorganic CPM
  - Measure sulfate in impinger catch
  - Replace Method 202 sulfate with CCS mass
- Pros/cons
  - Provides complete correction of sulfate bias
  - Requires extra sample train
  - Difficult to traverse

Controlled Condensation System Method Train



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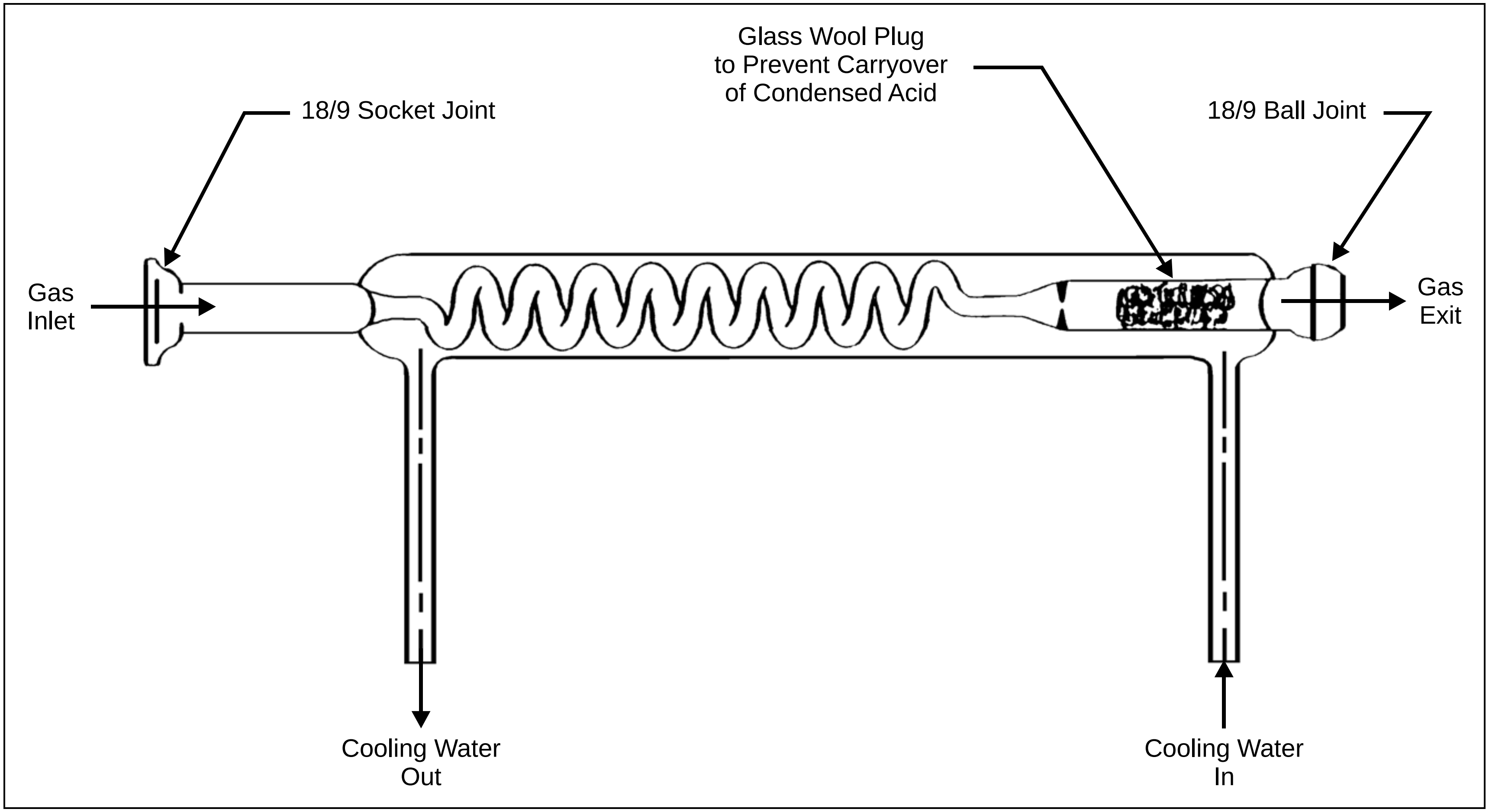
Controlled Condensation System - Condenser



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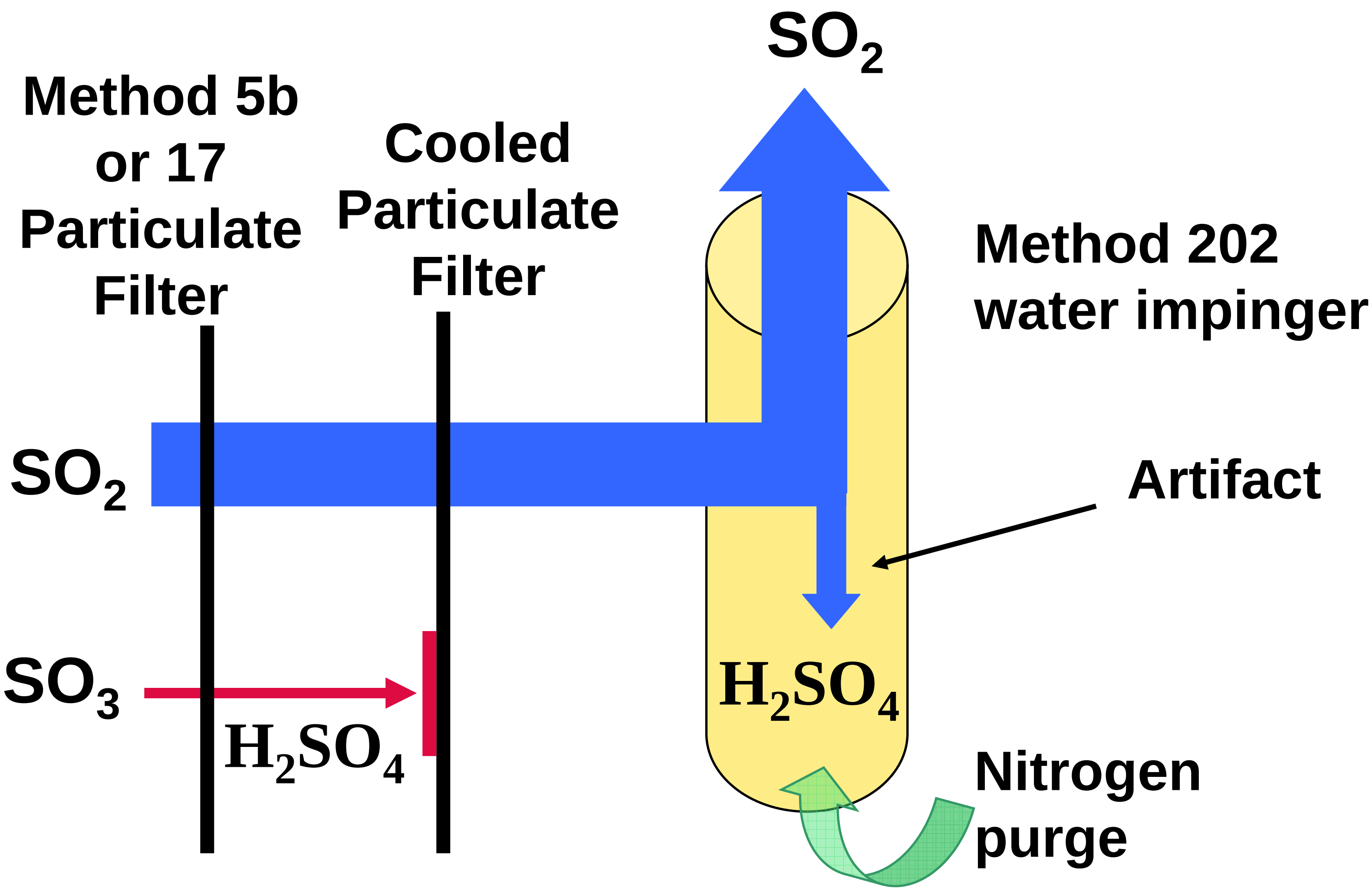
EPRI Low-temperature Filter Modification to Method 202

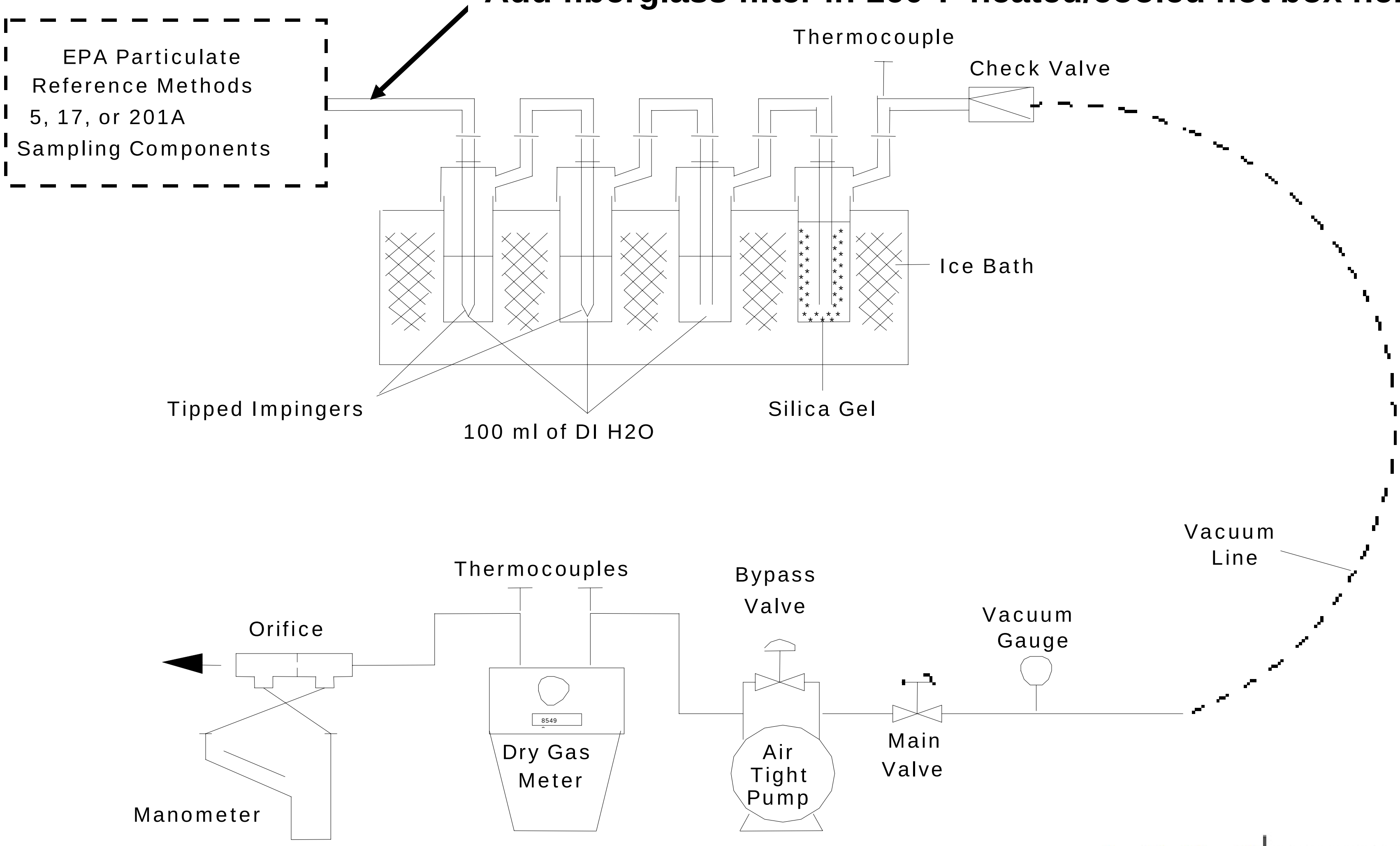
- Adds ~160°F filter between Method 5b or 17 particulate filter and Method 201/202 train.
  - Cooled filter collects all true SO_3/sulfuric acid
  - Measure artifact sulfate in impinger catch
  - Replace Method 202 sulfate with mass on cooled filter
- Pros/cons
  - Provides complete correction of sulfate bias
  - One sampling train
  - Easily modified from standard parts
  - Organic CPM may partition between filter and impinger – no impact on total CPM measurement

EPRI Modification to Method 202



EPRI Low-temperature Filter Train

Add fiberglass filter in 160ºF heated/cooled hot box here



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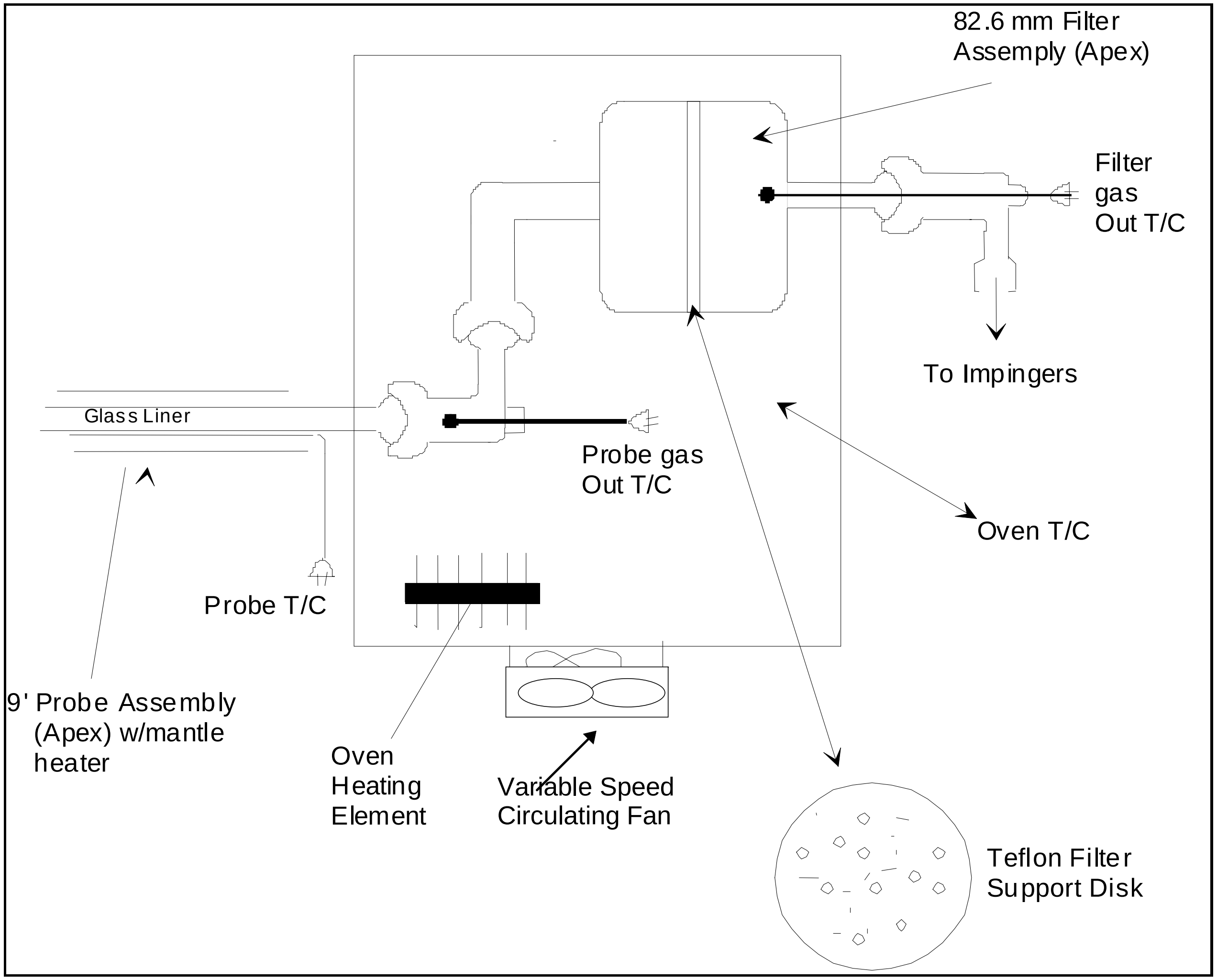
EPRI Low-temperature Filter Apparatus



Questions?

Contact Naomi Goodman at 650-855-2193 or
ngoodman@epri.com

Stakeholder Contribution Condensable Particulate Matter Study

Comparison of Methodologies
Wet vs. Dry - Organic Application

Presented by
William R. Prokopy
at
U.S. Environmental Protection Agency
February 9, 2007

Introduction

- Bill Prokopy – DCC Regulatory Planning/Compliance & Energy
- Representing the Auto Alliance – an industry trade association for automotive manufacturers formed in 1999
- Alliance Focus – Commitment to improve environment & safety

Organic Application

- Process – HOBS gear cutting machines.
- Metalworking Lubricant – Ultrasol 787
- Control Device – Monroe Oil Mist Collector

ULTRASOL 787 - Ingredients

- Hydrotreated Napthenic Oil 30-40%
- KOH 0.1-5%
- Paraffin 5-10%
- Concentrate diluted approximately 1:10 with water

(All concentrations by weight)

Sampling Conditions

- Stack – rectangle stack, 3 ports, 83^{o} F,

9,000 scfm, 1% moisture, no cyclonic flow,

- 12 traverse points, 8 samples collected from each method.

- Rooftop conditions – 12^{o}F to 28^{o}F, barometric pressure 29.36 in Hg. to 30.75 in Hg.

Method Parameters

Wet Method

- Probe/Filter @250^{o}F.

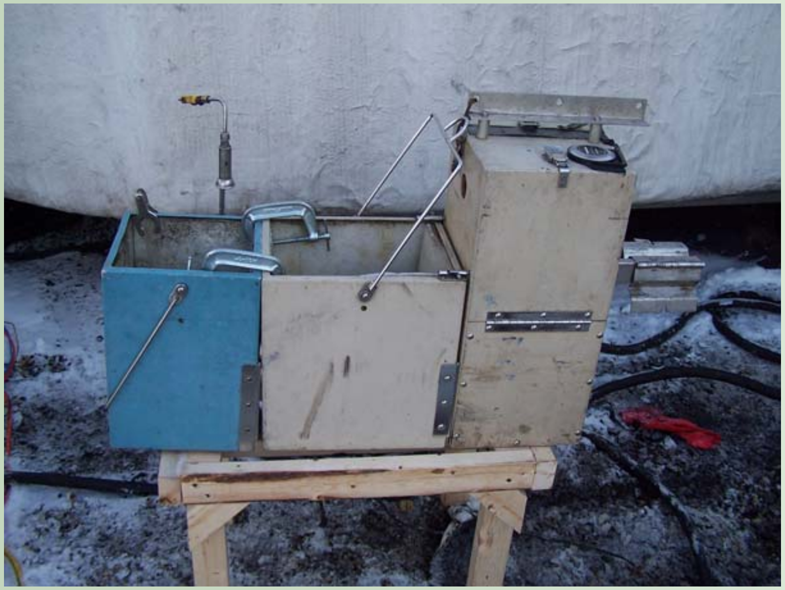
Dry Method

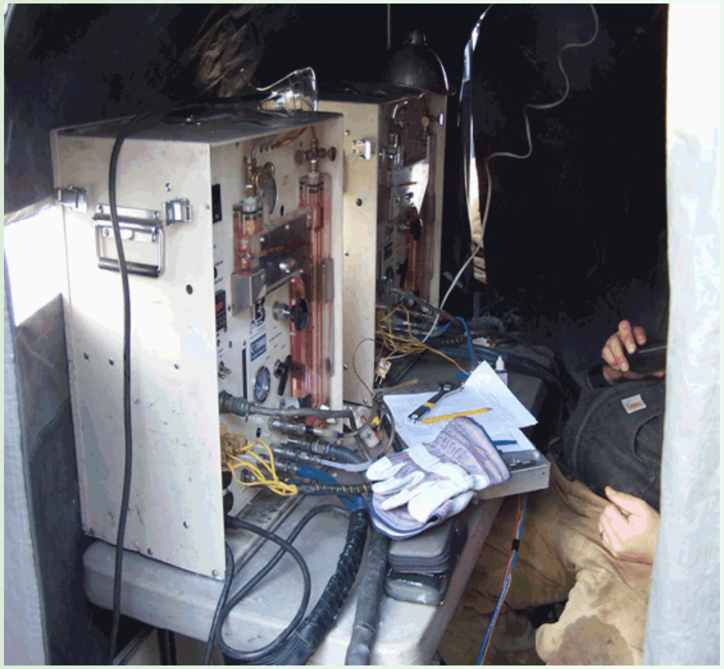
- Primary Filter/Probe @ 85^{o}F, Secondary filter at approximately 30^{o}F.
- Dry method – replaced moisture impinger with windshield washer fluid.
- Dry condenser (no recirculated)

*No adjustments to either methods samples. i.e. degassing, pH adjustments, etc.

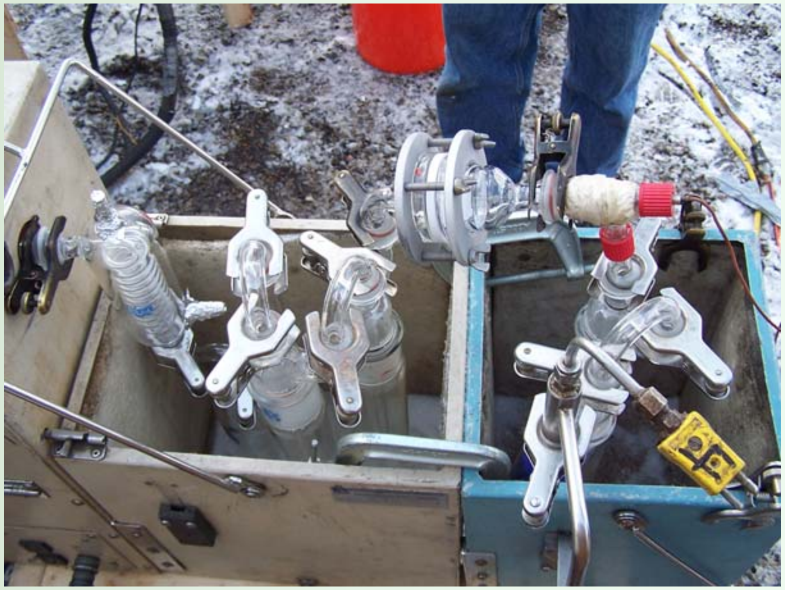
Sampling Location

Equipment Set-up





Equipment Set-up (Dry Method)



Dry Method

Simultaneous Testing

Technical Difficulties

Trailer – Sample Preparation

Data incomplete

Method 202 improvements

Theoretical considerations regarding Condensable Particulate Matter (CPM) emission testing.

By Jorge Marson, Environment Canada

February 2007

Sulfate artifact issue

- Further dry impinger testing was put on hold. Preliminary conclusions:

  artifact < 2 mg/m^3 for:

  50 ppm < SO_2 < 250 ppm

  5% < moisture < 20%

- Focus widened to other aspects of Method 202

CPM issues

1. **Capture**: what compounds?
2. **Retention**: N_2 purge losses?
3. **Solvent removal**: potential losses
4. **Weighing**: end point
5. **Comparability**: vs. CTM 39

CPM capture, hydrocarbons

- Condensation is determined by concentration and vapor pressure (VP) ratios
- 0-100 ppm methane equivalent, hydrocarbon CPM range of interest
- VP > 1 mmHg data ready available,

  but much higher than the CPM range of interest

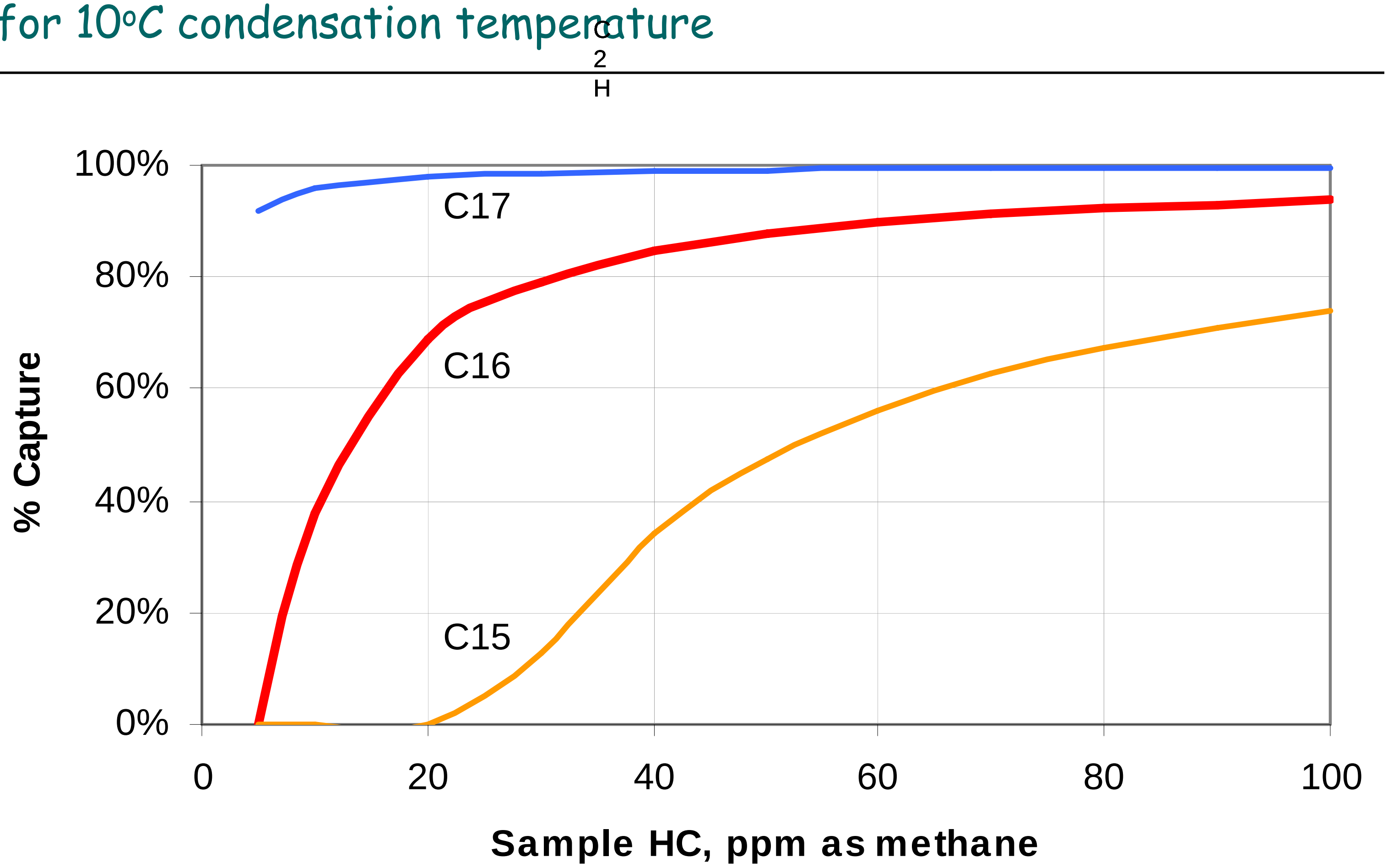
Capture (cont.)

- 0.0004 mmHg < VP < 10 mmHg point data available for alkanes, alkenes, polycyclic, and miscellaneous hydrocarbons
- Point data fitted to continuous function by Antoine equation:

  $\log p = A - B/(C + {}^{o}C)$

M 202 Alkanes Capture

for 10°C condensation temperature

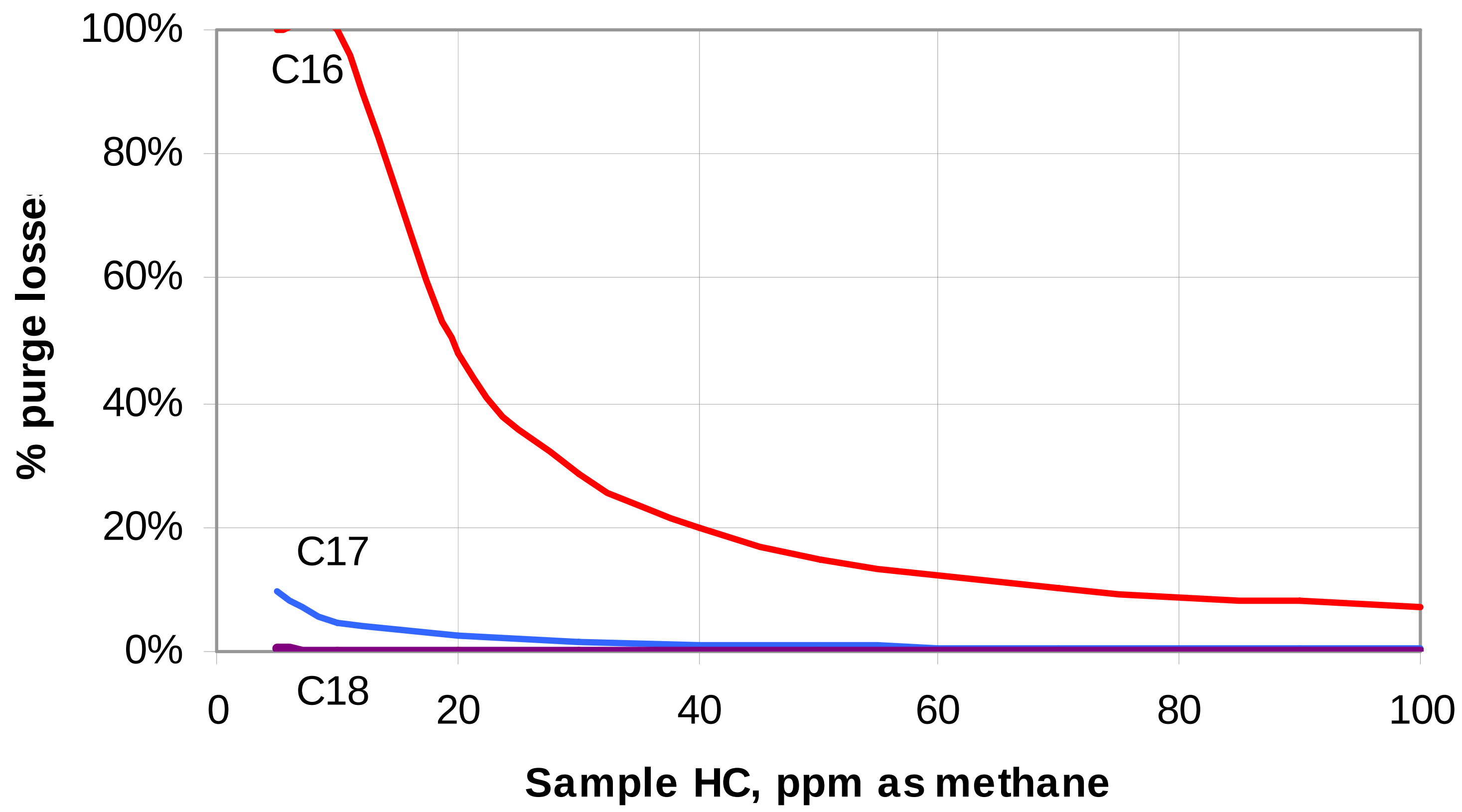


Retention

- Estimated for a purge volume equal to the sample volume: 1.2 Rm^3
- Assumes that the nitrogen exhaust is saturated with sample CPM (conservative)

M 202 Sample Losses During Purge

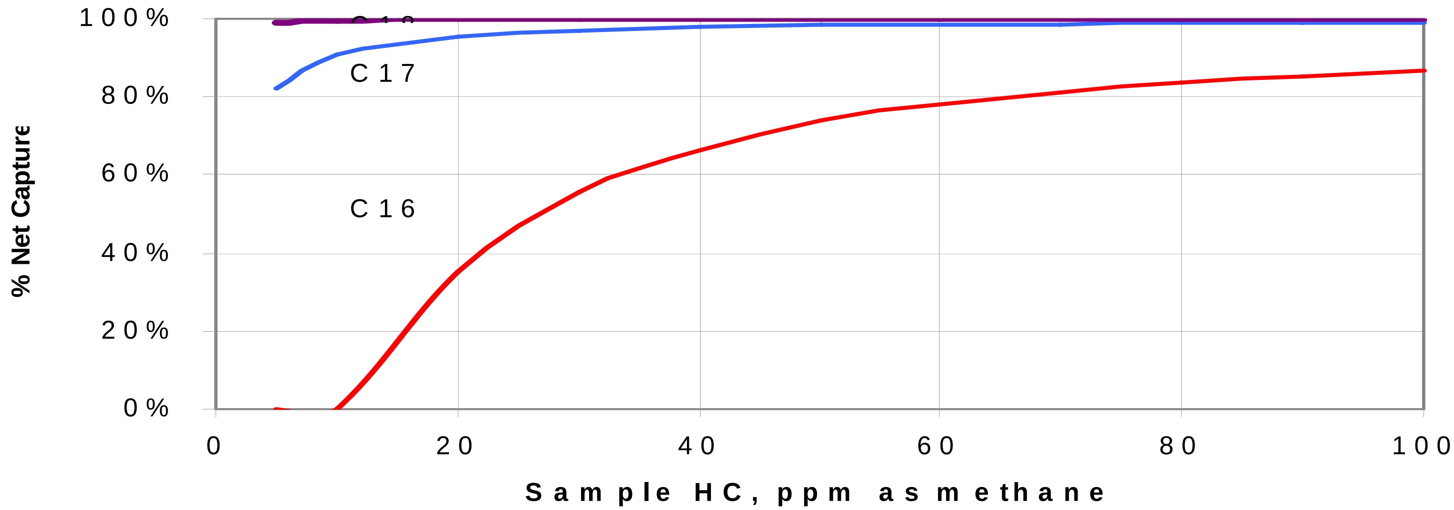
for 10°C 1.2 Rm³ nitrogen purge

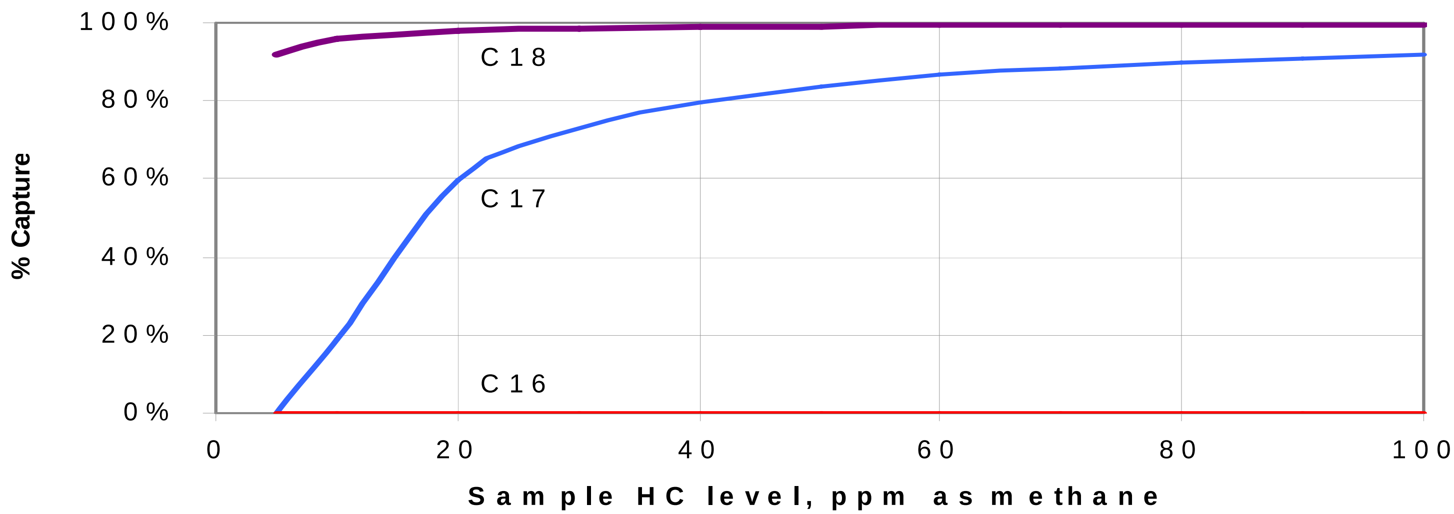


Comparability with CTM 39

- M 202 and CTM 39 net capture compared for 0-100 ppm alkane samples
- 10°C condensation temperature for each train
- CTM 39 operated at 20:1 dilution

M 202 net capture (above) vs CTM 39





Comparability

- The CTM 39 dilution step shifts the alkanes cutoff from C_{16} to C_{17}
- The CTM 39 dilution air should be as close to 0 °C as it is practical, to avoid greater differences with M 202

Solvent removal and weighing

Which CPM compounds may dissolve in the condensate, and what are the losses when the residue is dried at 105°C ?

- Water evaporation is approximately 20 times slower than methylene chloride (MC), at ambient temperature
- CPM losses occur when the solvent has almost fully evaporated

Is two stage drying ($Temp_1$ – $Temp_2$) necessary to avoid CPM losses?

Capture and loss modeling for additional compounds

- Less accurate than alkanes modeling
- Based on Perry's Section 3
  VP tables (~ 1,600 organic and inorganic compounds)
- Low VP extrapolated from 1 – 5 mmHg range via Classius-Clapeyron
  (linear log p = 1/T plots)
- Target CPM range 0 – 20 mg/Rm^3
- Losses estimated from actual solvent evaporation tests, relative vapor pressure and molecular weight

Capture and loss modeling Summary results

- 11% of the database compounds produce CPM at 20 mg/m^3, with 80% average capture efficiency.
- 8% of the database compounds still produce CPM at 5 mg/m^3
- A few inorganic and various heavy organic acids and polyalcohol are likely to dissolve in the condensate
- The number of CPM compounds lost, as function of residue drying temperature, is shown in the next table

CPM losses

as function of residue drying temperature

Temperature °C	Number of Compounds lost	20 ml pan drying hours
22	0%	57
40	5%	20
60	26%	8
80	57%	3 (~ to MC)

Recommendations

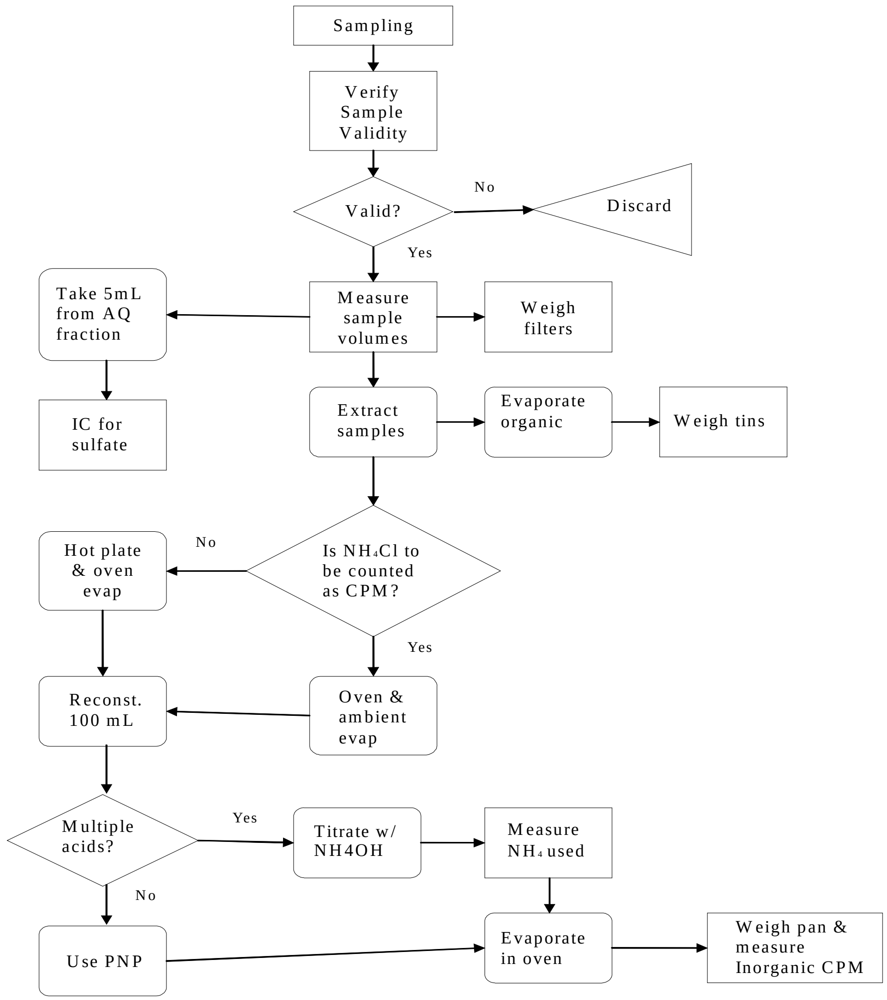
- The M 202 condensate residue should be dried at room temperature, or only slightly higher
- The MC and aqueous CPM residues should be determined as in M 315 (rather than the <0.5 mg variance in 6 hour criterion)
- Modeling results should be confirmed by lab testing with MC-soluble and water soluble CPM compounds of suitable VP.

Thank you

M-202 Dry Impinger Sample Recovery and Analysis

- Method 202 Flow chart
- Recovery and analysis will eliminate options
- Dry Impinger Method Flow Chart
- Blank Reagents
- Other issues

Current Method 202 Sample Recovery and Analysis



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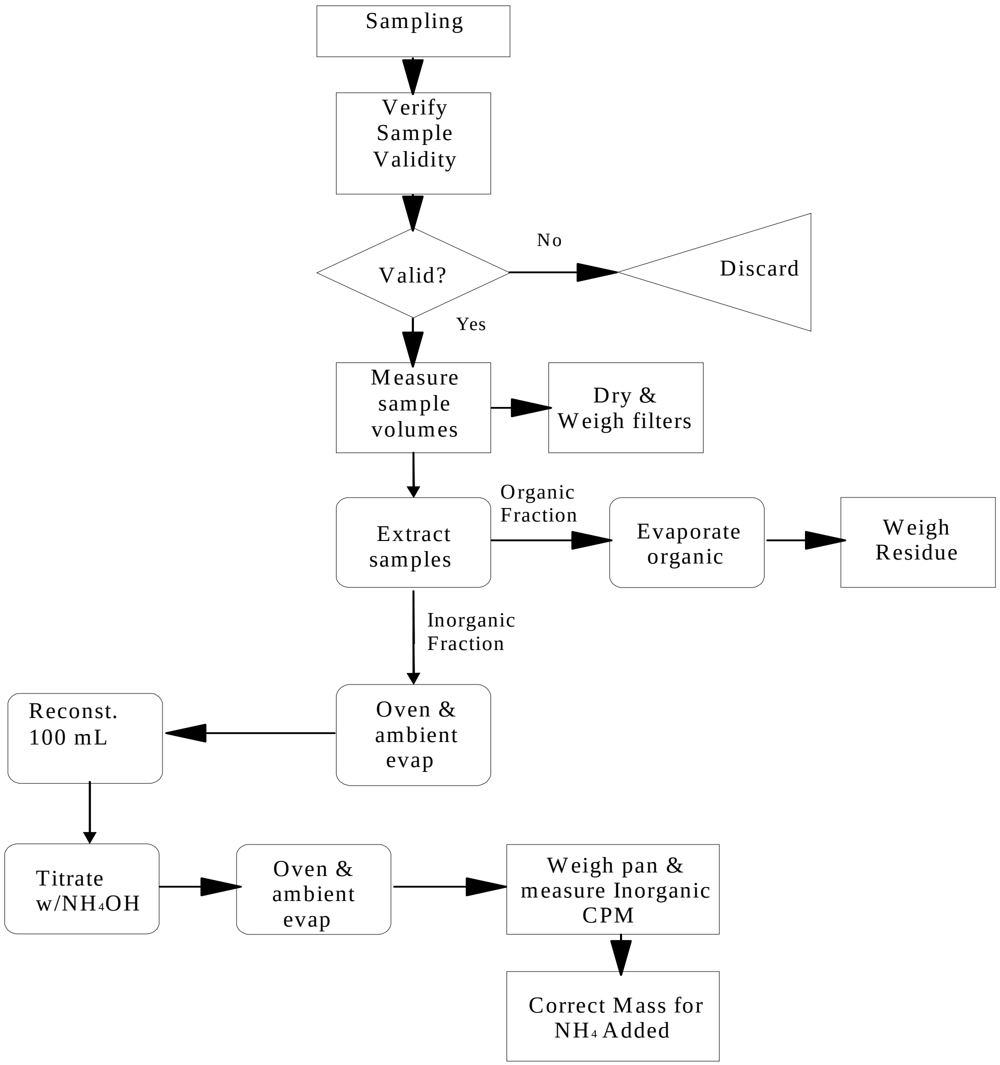
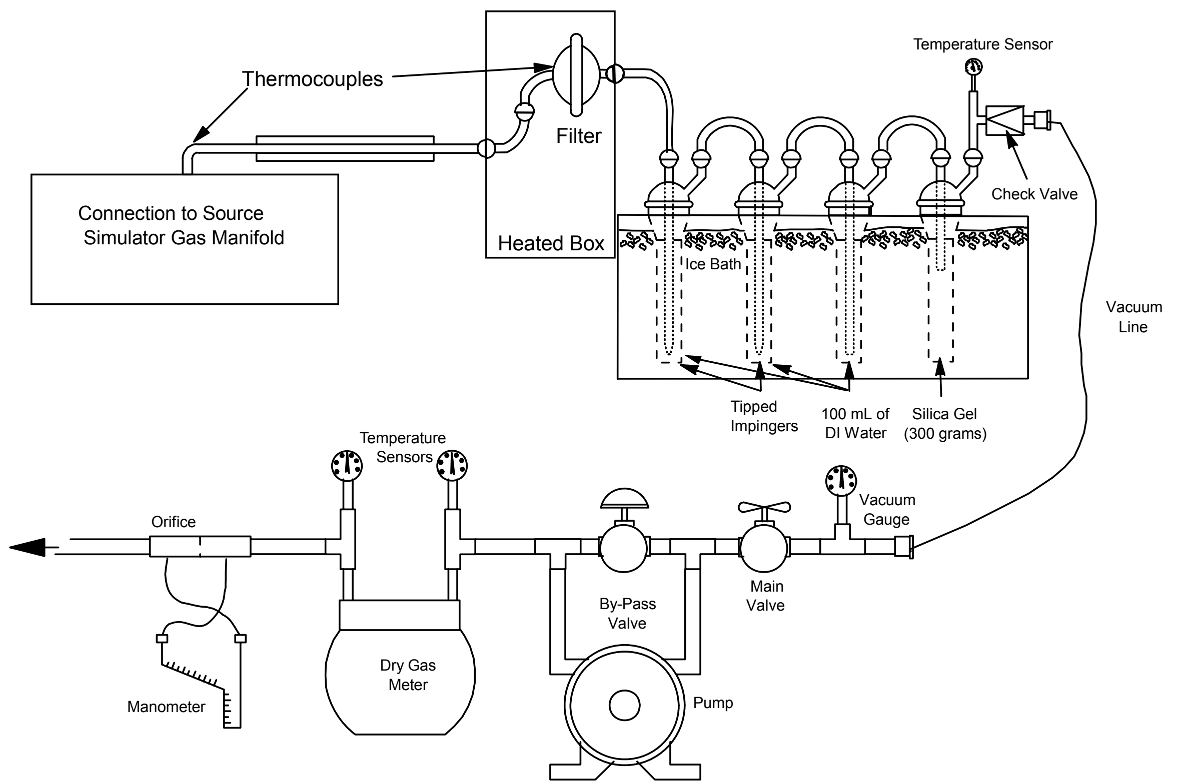
Dry Impinger Mod Sample Recovery and Analysis



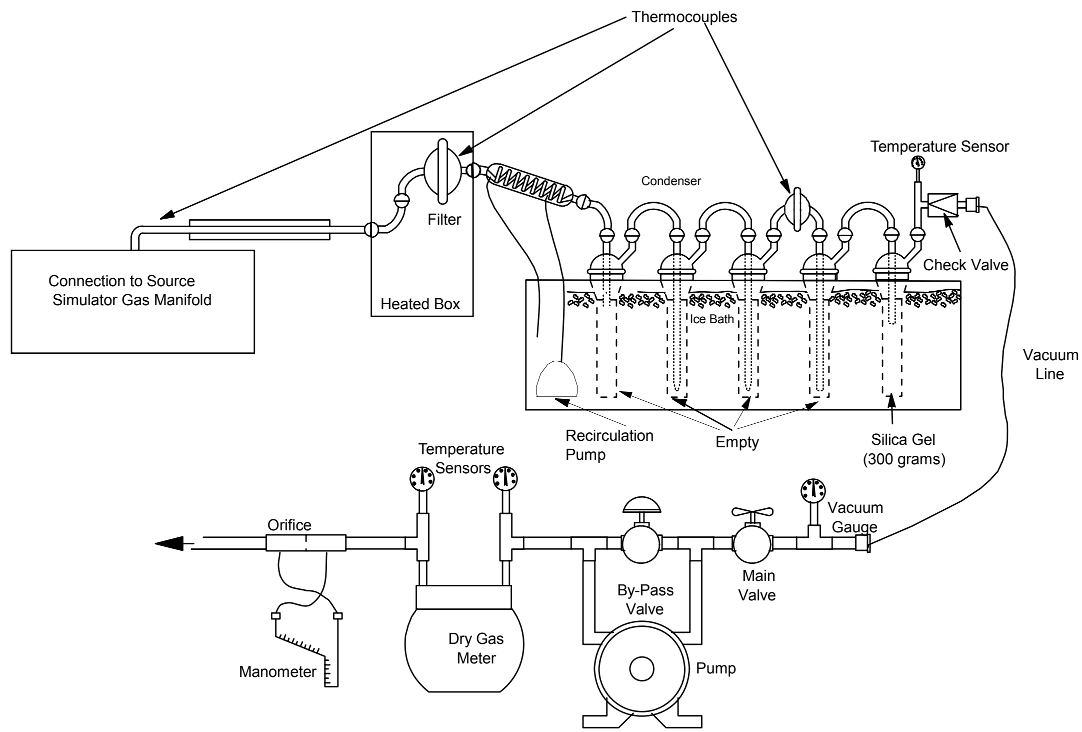
M-202 Dry Impinger Modification Equipment

- Equipment Meeting Summary

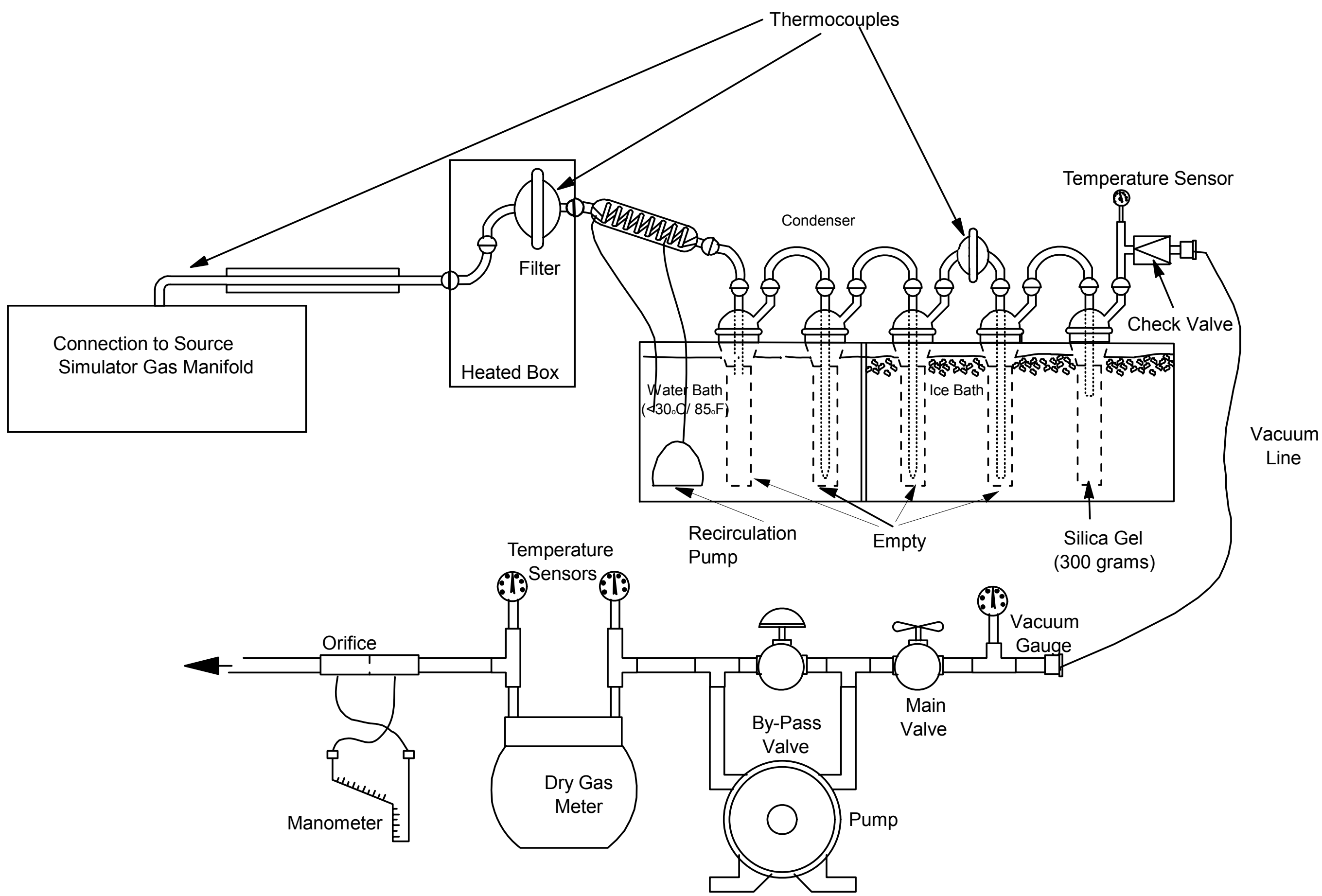
Round 1 Method 202 Train



Round 1 Dry Impinger Train



Round 2 Dry Impinger Train



Round 2 Equipment

- From Common Manual Method Sampling Equipment
- Method 23 Condenser
- Separate or divided impinger boxes
  - Ambient Temperature Ambient Temperature (80-85°F)
    - Water Drop out
    - First Impinger
    - Cold Filter
  - Ice Bath Ice water temperature
    - Final Impinger and Silica Trap

Phase 2 Observations

- Two impinger boxes or one divided box are required
  - Two boxes make changing ports difficult?
  - Ambient Temperature filter bridges two boxes subject to breakage?
  - Heating or cooling ambient filter dependent of weather conditions
  - Water deposit on filter mixed with organic CPM may blind filter

ERG