



REPORT ON COMPLIANCE TESTING

Detroit Refinery
Crude/Vacuum Heater Stack

Marathon Petroleum Company LP
1300 South Fort Street
Detroit, MI 48217
Client Reference No. 4101815470

CleanAir Project No. 13947
A2LA ISO 17025 Certificate No. 4342.01
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September 24, 2019

COMMITMENT TO QUALITY

To the best of our knowledge, the data presented in this report are accurate, complete, error free and representative of the actual emissions during the test program. Clean Air Engineering operates in conformance with the requirements of ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies.

Report Writer:



September 24, 2019

Ken Sullivan
Project Manager
ksullivan@cleanair.com
(800) 627-0033 ext. 4527

Date

I hereby certify that the information contained within the final test report has been reviewed and, to the best of my ability, verified as accurate.

Independent Report and Appendix Reviewer:



September 24, 2019

Andy Obuchowski
Midwest Engineering Group Leader
aobuchowski@cleanair.com
(800) 627-0033 ext. 4537

Date

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PROJECT PERSONNEL

Name	Affiliation	Project Responsibility
Cody Spoon	Marathon Petroleum Company LP	Client/Site Contact
Ken Sullivan	CleanAir	Project Manager / Report Writer
Doug May	CleanAir	Project Field Leader
Andy Obuchowski	CleanAir	Independent Reviewer of Report
Nadia Lazzar	CleanAir	Report Coordinator
Josh Myers	CleanAir	Field Engineer
Mo Khatib	CleanAir	Field Engineer
Michael Kavulic	CleanAir	Field Engineer

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1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to complete testing on the Crude/Vacuum Heater (EU05-CRUDEHTR-S1 & EU04-VACHTR-S-1) at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM) and sulfuric acid mist (H_2SO_4) testing to demonstrate quarterly compliance with the Michigan Department of Environmental Quality (DEQ) Permit No. MI-ROP-A9831-2012c;

A summary of the test program results is presented below. Section 2 Results provides a more detailed account of the test conditions and data analysis.

**Table 1-1:
Summary of Compliance Results**

<u>Source</u>		Average Emission	Permit Limit¹
Constituent	Sampling Method		
<u>Crude/Vacuum Heater Stack</u>			
FPM (lb/MMBtu)	USEPA 5	0.0022	N/A
H_2SO_4 (lb/MMBtu)	CTM-013 (Mod)	0.0006	N/A
PM (lb/MMBtu) ²	USEPA 5 / CTM-013 (Mod)	0.0017	0.0019
NSFPM (lb/MMBtu)	USEPA 5B	0.0010	N/A

¹ Permit limits obtained from MDEQ Renewable Operating Permit No. MI-ROP-A9831-2012c.

² PM assumed equivalent to FPM less H_2SO_4 . The letter from MDEQ referenced in the appendices further outlines the correction of PM emission for H_2SO_4 bias.

Test Program Details

Parameters

The test program included the following emissions measurements:

- filterable particulate matter (FPM)
- H_2SO_4 conducted concurrently with FPM measurements
- PM assumed equivalent to FPM minus H_2SO_4
- nonsulfuric acid filterable particulate matter (NSFPM)
- flue gas composition (e.g., O_2 , CO_2 , H_2O)
- flue gas temperature
- flue gas flow rate

Schedule

Testing was performed on August 15, 2019. The on-site schedule followed during the test program is outlined in Table 1-2.

**Table 1-2:
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Crude/Vacuum Heater	USEPA Method 5	FPM	08/15/19	09:00	10:10
2	Crude/Vacuum Heater	USEPA Method 5	FPM	08/15/19	11:03	12:17
3	Crude/Vacuum Heater	USEPA Method 5	FPM	08/15/19	13:25	14:42
4	Crude/Vacuum Heater	USEPA Method 5	FPM	08/15/19	15:31	16:54
1	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	08/15/19	09:00	10:10
2	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	08/15/19	11:03	12:17
3	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	08/15/19	13:25	14:42
4	Crude/Vacuum Heater	USEPA Method 5B	NSFPM	08/15/19	15:31	16:54
1	Crude/Vacuum Heater	CTM-013 (mod)	H ₂ SO ₄	08/15/19	09:00	10:10
2	Crude/Vacuum Heater	CTM-013 (mod)	H ₂ SO ₄	08/15/19	11:03	12:17
3	Crude/Vacuum Heater	CTM-013 (mod)	H ₂ SO ₄	08/15/19	13:25	14:42
4	Crude/Vacuum Heater	CTM-013 (mod)	H ₂ SO ₄	08/15/19	15:31	16:54

Discussion

Project Synopsis

FPM Testing

A total of four (4) 60-minute EPA Method 5 test runs were performed. FPM emission results were calculated in units of pounds per million Btu (lb/MMBtu). The final results were expressed as the average of the four (4) valid runs.

H₂SO₄ Testing

H₂SO₄ emissions were determined referencing Conditional Test Method 013 (CTM-013). Four (4) 60-minute CTM-013 test runs were performed concurrently with all Method 5 runs. H₂SO₄ emission results were calculated in units of lb/MMBtu. The H₂SO₄ final results were expressed as the average of four (4) valid runs.

PM Results

PM is assumed equivalent to the difference of FPM and H₂SO₄ emissions. This is recommended in a letter from the DEQ, dated December 18, 2017; "Marathon Petroleum, Crude/Vacuum Heater Stack, Request to Substitute Method 5B for Method 5, Permit: MI-ROP-A9831-2012c, SRN: A9831."

H₂SO₄ emissions were determined concurrently with FPM emissions, converted to units of lb/MMBtu and subtracted from total FPM emissions from each respective run. The PM final results were expressed as the average of the three (3) highest runs.

NSFPM Testing

A total of four (4) 60-minute EPA Method 5B test runs were performed. NSFPM emission results were calculated in units of lb/MMBtu. The final results were expressed as the average of the four (4) valid runs. Method 5B testing was conducted for supplemental purposes only.

Fuel Factor

Emission results in units of dry volume-based concentration (lb/dscf, ppm_{dv}) were converted into units of lb/MMBtu by applying an oxygen-based fuel factor (F_d) provided by MPC for each test run.

Test Conditions

The unit was operated at the maximum normal operating capacity during each of the emissions compliance test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in the test report.

End of Section

2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices, specifically Appendix C Parameters.

**Table 2-1:
Crude/Vacuum Heater – FPM Emissions**

Run No.		1	2	3	4	Average
Date (2019)		Aug 15	Aug 15	Aug 15	Aug 15	
Start Time (approx.)		09:00	11:03	13:25	15:31	
Stop Time (approx.)		10:10	12:17	14:42	16:54	
Process Conditions						
R _p	Production Rate (BPD)	150,000	150,000	150,000	150,000	150,000
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,578	8,548	8,548	8,548	
H _i	Actual heat input (MMBtu/hr)	299	299	295	295	297
Gas Conditions						
O ₂	Oxygen (dry volume %)	7.1	7.1	7.1	7.3	7.2
CO ₂	Carbon dioxide (dry volume %)	7.8	7.8	7.8	7.7	7.8
T _s	Sample temperature (°F)	300	300	301	300	300
B _w	Actual water vapor in gas (% by volume)	13.9	14.5	14.5	14.1	14.2
Gas Flow Rate						
Q _a	Volumetric flow rate, actual (acfm)	121,000	122,000	121,000	123,000	122,000
Q _s	Volumetric flow rate, standard (scfm)	82,300	83,300	82,200	84,000	82,900
Q _{std}	Volumetric flow rate, dry standard (dscfm)	70,900	71,300	70,300	72,200	71,100
Sampling Data						
V _{mstd}	Volume metered, standard (dscf)	36.92	36.79	36.22	37.35	36.82
%I	Isokinetic sampling (%)	103.3	102.4	102.2	102.6	102.6
Laboratory Data						
m _{filter}	Matter collected on filter(s) (g)	0.00246	0.00252	0.00224	0.00276	
m _s	Matter collected in solvent rinse(s) (g)	0.00037	0.00013	0.00042	0.00056	
m _n	Total FPM (g)	0.00283	0.00265	0.00266	0.00332	
FPM Results						
C _{sd}	Particulate Concentration (lb/dscf)	1.69E-07	1.59E-07	1.62E-07	1.96E-07	1.71E-07
E _{lb/hr}	Particulate Rate (lb/hr)	0.718	0.680	0.682	0.850	0.732
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00219	0.00206	0.00209	0.00258	0.00223

Table 2-2:
Crude/Vacuum Heater – H₂SO₄ Emissions

Run No.		1	2	3	4	Average
Date (2019)		Aug 15	Aug 15	Aug 15	Aug 15	
Start Time (approx.)		09:00	11:03	13:25	15:31	
Stop Time (approx.)		10:10	12:17	14:42	16:54	
Process Conditions						
P ₁	Charge rate (BPD)	150,000	150,000	150,000	150,000	150,000
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,578	8,548	8,548	8,548	
H _i	Actual heat input (MMBtu/hr)	299	299	295	295	295
Gas Conditions						
O ₂	Oxygen (dry volume %)	7.1	7.6	7.0	7.0	7.2
CO ₂	Carbon dioxide (dry volume %)	7.8	7.5	7.9	7.9	7.8
T _s	Sample temperature (°F)	302	301	303	301	302
B _w	Actual water vapor in gas (% by volume)	14.5	13.8	14.2	13.8	14.1
Sampling Data						
V _{mstd}	Volume metered, standard (dscf)	26.40	26.41	26.20	26.26	26.32
Laboratory Data (Ion Chromatography)						
m _n	Total H ₂ SO ₄ collected (mg)	0.6110	0.6198	0.5129	0.4411	
Sulfuric Acid Vapor (H₂SO₄) Results						
C _{sd}	H ₂ SO ₄ Concentration (lb/dscf)	5.10E-08	5.17E-08	4.32E-08	3.70E-08	4.57E-08
C _{sd}	H ₂ SO ₄ Concentration (ppmdv)	0.201	0.203	0.170	0.146	0.180
E _{Fd}	H ₂ SO ₄ Rate - Fd-based (lb/MMBtu)	0.000663	0.000695	0.000555	0.000476	0.000597

**Table 2-3:
Crude/Vacuum Heater – PM Emissions**

Run No.		1	2	3	4	Average
Date (2019)		Aug 15	Aug 15	Aug 15	Aug 15	
Start Time (approx.)		09:00	11:03	13:25	15:31	
Stop Time (approx.)		10:10	12:17	14:42	16:54	
Process Conditions						
R _p	Production Rate (BPD)	150,000	150,000	150,000	150,000	150,000
F _d	Oxygen-based F-factor (dsct/MMBtu)	8,578	8,548	8,548	8,548	
H _i	Actual heat input (MMBtu/hr)	299	299	295	295	297
Gas Conditions						
O ₂	Oxygen (dry volume %)	7.1	7.1	7.1	7.3	7.2
CO ₂	Carbon dioxide (dry volume %)	7.8	7.8	7.8	7.7	7.8
T _s	Sample temperature (°F)	300	300	301	300	300
B _w	Actual water vapor in gas (% by volume)	13.9	14.5	14.5	14.1	14.2
FPM Results						
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00219	0.00206	0.00209	0.00258	0.00223
Sulfuric Acid Vapor (H₂SO₄) Results						
E _{Fd}	H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	0.000663	0.000695	0.000555	0.000476	0.000597
Particulate Matter (as PM₁₀) Results¹						
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00153	0.00136	0.00154	0.00210	0.00172

¹ Final PM result is the average of three (3) highest valid runs (Runs 1, 3, & 4).

**Table 2-4:
Crude/Vacuum Heater – NSFPM Emissions**

Run No.		1	2	3	4	Average
Date (2019)		Aug 15	Aug 15	Aug 15	Aug 15	
Start Time (approx.)		09:00	11:03	13:25	15:31	
Stop Time (approx.)		10:10	12:17	14:42	16:54	
Process Conditions						
P ₁	Charge Rate (BPD)	150,000	150,000	150,000	150,000	150,000
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,578	8,548	8,548	8,548	
H _i	Actual heat input (MMBtu/hr)	299	299	295	295	297
Gas Conditions						
O ₂	Oxygen (dry volume %)	7.3	7.0	7.1	7.0	7.1
CO ₂	Carbon dioxide (dry volume %)	7.7	7.9	7.8	7.9	7.8
T _s	Sample temperature (°F)	300	300	300	299	300
B _w	Actual water vapor in gas (% by volume)	14.8	14.5	14.6	14.8	14.7
Gas Flow Rate						
Q _a	Volumetric flow rate, actual (acfm)	114,000	117,000	119,000	119,000	117,000
Q _s	Volumetric flow rate, standard (scfm)	77,700	80,100	81,200	81,500	80,100
Q _{std}	Volumetric flow rate, dry standard (dscfm)	66,200	68,500	69,300	69,500	68,400
Sampling Data						
V _{mstd}	Volume metered, standard (dscf)	34.36	35.37	35.66	36.02	35.35
%I	Isokinetic sampling (%)	102.9	102.3	102.0	102.8	102.5
Laboratory Data						
m _{filter}	Matter collected on filter(s) (g)	0.00180	0.00066	0.00089	0.00103	
m _s	Matter collected in solvent rinse(s) (g)	0.00014	0.00007	0.00017	0.00033	
m _n	Total NSFPM (g)	0.00194	0.00073	0.00106	0.00136	
NSFPM Results						
C _{sd}	Particulate Concentration (lb/dscf)	1.24E-07	4.54E-08	6.56E-08	8.35E-08	7.97E-08
E _{lb/hr}	Particulate Rate (lb/hr)	0.494	0.187	0.273	0.348	0.325
E _{Fd}	Particulate Rate - F _d -based (lb/MMBtu)	0.00164	0.000584	0.000849	0.00107	0.00104

End of Section

3. DESCRIPTION OF INSTALLATION

Process Description

MPC's facility in Detroit, Michigan, produces refined petroleum products from crude oil. MPC must continue to demonstrate that select process units are in compliance with permitted emission limits.

The Crude Unit (EU05-CRUDE) separates crude oil into various fractions through the use of distillation processes. These fractions are sent to other units in the refinery for further processing. The Crude Unit consists of process vessels (including heat exchangers and fractionation columns), the Alcorn Heater (EU05-CRUDEHTR-S1), tanks, containers, compressors, pumps, piping, drains, and various components (pump and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Vacuum Unit (EU04-VACUUM) separates the reduced crude from the Crude Unit through the use of a vacuum column. The reduced crude is separated into light vacuum gas oil, medium vacuum gas oil, heavy vacuum gas oil, and a bottoms product called flux. The various fractions are sent to other units in the refinery for further processing. The vacuum unit consists of process vessels (including heat exchangers and vacuum column), two process heaters, tanks, containers, two cooling towers, flare, compressors, pumps, piping, drains, and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

Both the Crude Heater (EU05-CRUDEHTR-S1) and the Vacuum Heater (EU04-VACHTR-S1) are fired by refinery fuel gas. Emissions are vented to the atmosphere via a common stack known as the Crude/Vacuum Heater Stack (SV04-H1-05-H1), where testing was performed.

Test Location

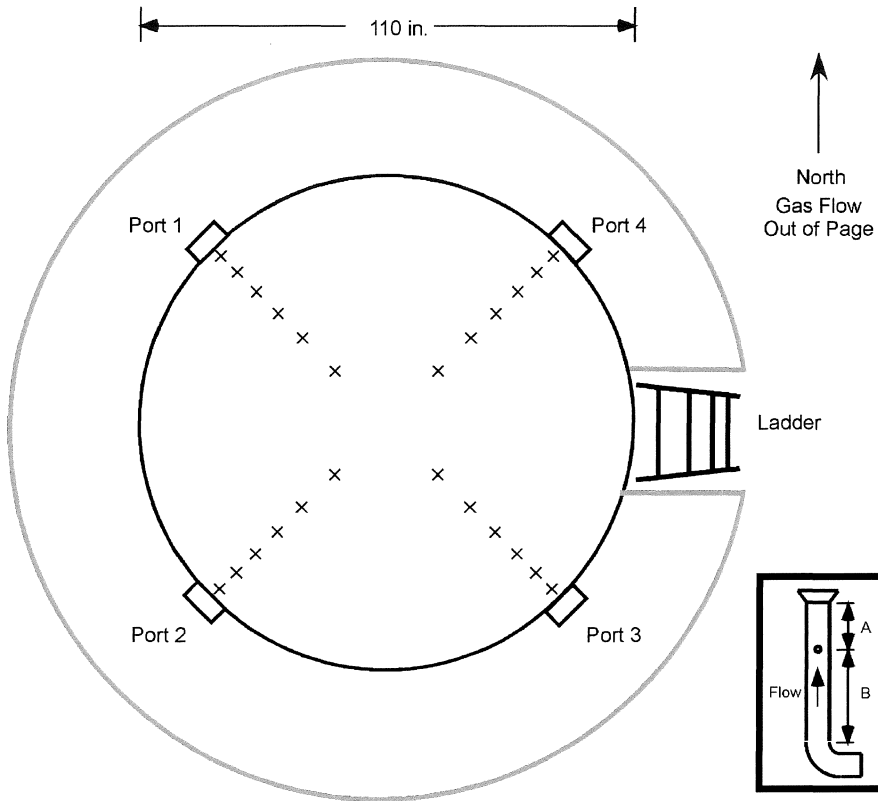
The sample point locations were determined by EPA Method 1. Table 3-1 presents the sampling information for the test location described in this report. The figure shown on page 9 represents the layout of the test location.

**Table 3-1:
Sampling Point Information**

Source		Run	Points	Minutes	Total		
Constituent	Method (USEPA)	No.	Ports	per Point	per Point	Minutes	Figure
<u>Crude/Vacuum Heater Stack</u>							
FPM	5	1-4	4	6	2.5	60	3-1
NSFPM	5B	1-4	4	6	2.5	60	3-1
H ₂ SO ₄	CTM-013 (Mod)	1-4	1	1	60	60	N/A ¹

¹ CTM-013 (Mod) sampling were conducted from a single point near the center of the duct.

**Figure 3-1:
 FPM and NSFPM Sample Point Layout**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	39.2
2	25.0	27.5
3	17.7	19.5
4	11.8	13.0
5	6.7	7.4
6	2.1	2.3

Duct diameters upstream from flow disturbance (A): 5.3 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 2.4 Limit: 2.0

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (USEPA) and the Michigan DEQ. These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>.

Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery, and analytical procedures. Any modifications to standard test methods are explicitly indicated in this appendix.

In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications, along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's A2LA accreditation.

CleanAir follows specific QA/QC procedures outlined in the individual methods and in USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source-Specific Methods," EPA/600/R-94/038C. Appendix D contains additional QA/QC measures, as outlined in CleanAir's internal Quality Manual.

Title 40 CFR Part 60, Appendix A

- Method 1 "Sample and Velocity Traverses for Stationary Sources"
- Method 2 "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)"
- Method 3 "Gas Analysis for the Determination of Dry Molecular Weight"
- Method 4 "Determination of Moisture Content in Stack Gases"
- Method 5 "Determination of Particulate Matter Emissions from Stationary Sources"
- Method 5B "Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources"

CTM-013 (Modified)

"Determination of Sulfur Oxides Including Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Vapor and Mist from Stationary Sources Using a Controlled Condensation Sampling Apparatus"

Methodology Discussion

FPM – USEPA Method 5

FPM emissions were determined using EPA Method 5.

The front-half of the sampling train consisted of a glass nozzle, glass liner, and filter holder heated to $248^{\circ}\text{F} \pm 25^{\circ}\text{F}$ and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

After exiting the front-half filter, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars were collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe, and heated filter) was recovered per Method 5 requirements, using acetone as the recovery solvent.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Upon receipt, the filters desiccated for 24 hours at ambient temperature. The front-half rinses were evaporated at ambient temperature and pressure. The masses from each fraction were then summed for a total FPM mass.

H₂SO₄ – CTM-013 (Modified)

H₂SO₄ emissions were determined referencing modified CTM-013.

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at a temperature of $650^{\circ}\text{F} \pm 25^{\circ}\text{F}$ and a quartz fiber filter (to remove PM) maintained at the same temperature as the probe.

The sample then passed through a glass coil condenser for collection of sulfuric acid vapor and/or mist. A glass frit/filter was located at the condenser outlet for the collection of residual sulfuric acid mist (SAM) not collected by the condenser. The condenser temperature is regulated by a water jacket and the SAM filter is regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at $140^{\circ}\text{F} \pm 9^{\circ}\text{F}$ plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point which eliminates the possibility of oxidation of dissolved SO₂ into the H₂SO₄-collecting fraction of the sample train).

After exiting the SAM filter, the sample gas then continued through a series of four (4) glass knock-out jars: two (2) containing water, one (1) empty and one (1) containing silica gel for residual moisture removal. The exit temperature from the knock-out jar set is maintained below 68°F . The sample gas then flowed into a dry gas meter where the collected sample gas volume is determined by means of a calibrated, dry gas meter.

The H₂SO₄-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H₂O as the recovery/extraction solvent; any H₂SO₄ disassociates into sulfate ion (SO₄²⁻) and was stabilized in the H₂O matrix until analysis. Following the initial sample recovery, a second DI H₂O rinse was completed.

Samples, back-up rinses, and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for ion chromatography analysis.

NSFPM – USEPA Method 5B

NSFPM emissions were determined using EPA Method 5B.

The front-half of the sampling train consisted of a glass nozzle, glass liner, and filter holder heated to 320°F ± 25°F and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5B requirements.

After exiting the front-half filter, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars were collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe, and heated filter) was recovered per Method 5B requirements, using acetone as the recovery solvent.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Upon receipt, the filters dessicated for 24 hours at ambient temperature. The front-half rinses were evaporated at ambient temperature and pressure. The masses from each fraction were then summed for a total FPM mass.

End of Section