CEMS Certification and Compliance Sampling Report

Silicone Facility THROX
FGTHROX
Permit # 91-07E

Dow Silicones Corporation
Michigan Operations
Midland, Michigan

Sampling Dates: November 06 & 07, 2018

**** Please note the process unit is the final copy holder and owner of this document. A temporary electronic copy will be retained by internal stack testing group for a short period of time.***

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1.0 INTRODUCTION

1.1 Summary of Test Program

Dow Silicones Corporation, a subsidiary of The Dow Chemical Company, operates a chemical manufacturing facility in Midland, Michigan. The facility uses a thermal oxidizer with a caustic scrubber and two ionizing wet scrubbers to control emissions. The treatment system includes a continuous emission monitoring system (CEMS) that continuously measures stack gas concentration of nitrogen oxides (NOx), carbon dioxide (CO_2), oxygen (O_2), total hydrocarbons (THC) and air flow rate.

An annual compliance test measuring emissions of PM_{10} and CO is required. Additionally, each of the CEMS are required to meet the analyte specific performance specification annually.

The following table summarizes the pertinent data for this compliance test:

Responsible Groups	• Dow Silicones Corporation, a subsidiary of The Dow Chemical Company • Michigan Department of Environmental Quality (MDEQ) • Environmental Protection Agency (EPA)
Applicable Regulations	• Permit-91-07E • 40 CFR Part 63 Subpart FFFF • 40 CFR 50.21 PSD • 40 CFR Part 98 • 40 CFR Part 60, Appendix B, Performance Specification 2, 3 6 and 8.
Industry / Plant	• Silicone Manufacturing THROX unit
Plant Location	• Dow Silicones Corporation, a subsidiary of The Dow Chemical Company Midland, Michigan 48667
Unit Initial Start-up	• May 2008
Date of Last Testing	• November 7th and 8th, 2017
Air Pollution Control Equipment	• Quench tower • HCl scrubber • Two ionizing wet scrubbers (IWS)
Emission Points	• SV2514-006
Pollutants/Diluent Measured	Relative Accuracy • Oxygen (O_2) RA < 20% of RM or absolute difference < 1% • Carbon Dioxide (CO_2) RA < 20% of RM or absolute difference < 1% • NOx RA <20% of RM • Total Hydrocarbon (THC) RA <20% of RM or 10% of EL (20 ppm) • Flow RA <20% of RM Compliance Test • PM_{10} 3.5 lb/hr and 13.4 tons/yr • CO 90 tons/yr • VOC 6.6 lb/hr
Test Dates	• November 6th, 2018 RA • November 6th, 2018 CO and THC Performance Test • November 7th, 2018 PM_{10} Performance Test

1.2 Key Personnel

The key personnel who coordinated the test program are:

- Matthew Miner provided support as a Process Focal Point. The Process Focal Point is responsible for coordinating the plant operation during the test and ensuring the unit is operating at the agreed upon conditions in the test plan. They also serve as the key contact for collecting any process data required and providing all technical support related to process operation.

- Laura Maiers provided support as the Environmental Focal Point for this unit. The Environmental Focal Point is responsible for ensuring that all regulatory requirements and citations are reviewed and considered for the testing. All agency communication is completed through this role. Contact information is 989-496-5327.

- Chuck Glenn served as the Test Plan Coordinator. The Test Plan Coordinator is responsible for the overall leadership of the sampling program. They also develop the overall testing plan and determine the correct sample methods.

- Spencer Hurley was the back-up for the Test Plan Coordinator. He also served as the technical review role of the test data.

- Michael Abel is a PhD chemist who serves in many roles for Environmental Analytical Chemistry (EAC). One of the roles he performs is as a technical contact for air sampling. Michael serves as a quality assurance and technical reviewer of the final test report.

- Daniel Nunez served as the Project Manager and was responsible for ensuring that the data generated meets the quality assurance objectives of the plan. Jim Edmister served as the Project Field Manager. Kyle Kennedy and Troy Baker are sampling technicians that assisted with this testing.

2.0 PLANT AND SAMPLING LOCATION DESCRIPTION

2.1 Facility Description

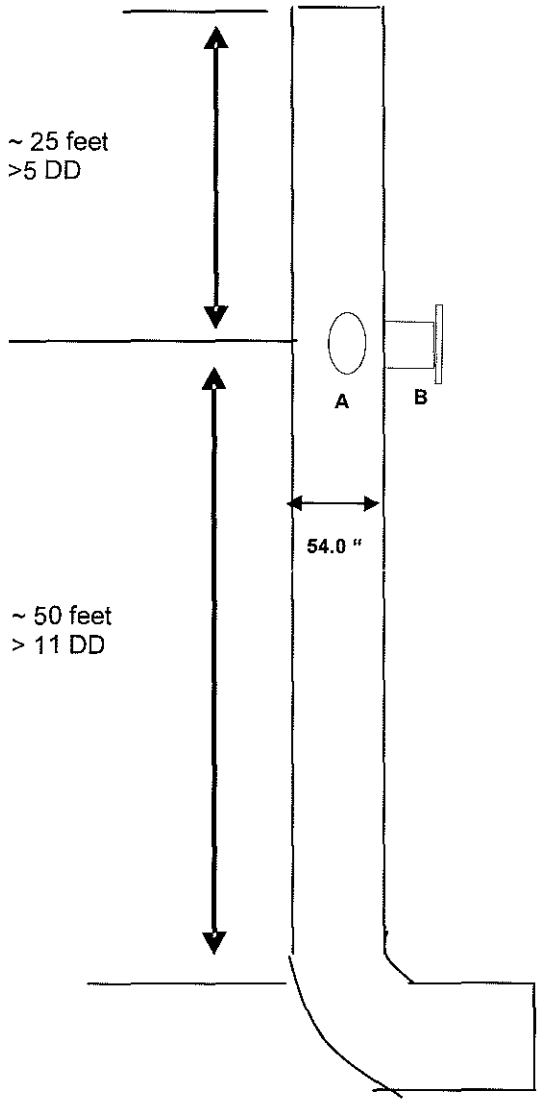
The THROX and IWS are utilized to treat emissions from various processes at the chemical facility. The typical feed rate to the THROX is approximately 28 MMBtu/hr. The permitted maximum operating rate for the THROX is 95 MMBTU/hr. The proposed production operating rate for this test is >30 MMBTU/hr.

2.2 Flue Gas Sampling Locations

Sampling was conducted on the THROX outlet stack. The CEMS sample points for the THROX stack are at least two equivalent diameters downstream from the nearest control device, the point of pollutant generation, or other point at which a change in the pollutant concentration may occur, and at least one half equivalent diameters upstream from the effluent exhaust or control device. The samples were drawn from the stack for a period of 21 minutes at the three traverse points of 17, 50, and 83% of the measurement line that passes through the centroidal area of the stack or duct cross section. A calibrated multi point averaging probe was used.

EPA M202 in conjunction with EPA M17 sampling was collected using isokinetic methodology across the stack at sample points as required by EPA M1.

Figure 2.1 Stack Description



Non-Isokinetic 16 Point Circular Traverse Layout for Outlet

Division: Dow Silicones Corporation

Facility/Block: 2514 Midland THROX

Stack ID: 54 inches

Port Ext: 6 inches

Duct Downstream Length: 50 Feet

Duct Upstream Length: 25 Feet

Duct Downstream Diameters: 11 Diameters

Duct Upstream Diameters: 5.5 Diameters

Traverse Point	Stack ID	Port Ext	Traverse Pt Distance	Traverse Pt Distance	Final Probe Mark
1	54	8	2 6/16	2 6/16	8 6/16
2	54	8	7 14/16	7 14/16	13 14/16
3	54	8	16	16	22
4	54	8	38	38	44
5	54	8	46 2/16	46 2/16	52 2/16
6	54	8	51 10/16	51 10/16	57 10/16

3.0 SUMMARY AND DISCUSSION OF TEST RESULTS

3.1 Objectives and Test Matrix

The purpose of this test was to demonstrate compliance with the regulations for the THROX at Dow Silicones Corporation, a wholly owned subsidiary of The Dow Chemical Company in Midland, Michigan. The specific objectives were:

- Determine the relative accuracy of the continuous NOx, O_2, CO_2, THC and flow monitor systems on the THROX stack.
- Determine PM_{10} (filterable and condensable), CO and VOC emissions.

3.2 Facility Operations

During the CEMS and Performance test, the plant was operated at greater than 50% of normal operating rates. The operating rate for this unit was determined based on mmBtu/Hr rate.

3.3 Comments / Exceptions

- As allowed by 40 CFR Part 60, PS 2, 3 and 4, this Performance Specification Test consisted of a minimum of 9 RM tests used for RA calculations. More than nine sets of RM tests may have been performed. If this option was selected, a maximum of three sets of the test results were rejected so long as the total number of test results used to determine the RA was greater than or equal to nine. All data was reported, including the rejected data.
- Jeremy Howe and Gina McCann of the Michigan Department of Environmental Quality were present during the Performance Test sampling.

Summary of Results
Continuous Emission/Emission Rate Monitor Certification

Table 3.1 Performance Results for Emission Reporting Tags

Monitor	Results	Allowable	Pass/Fail Semi/Annual
NOx Mass Emissions (lb/hr)	5 %	No greater than 20% RA using RM	Pass
			Pass
Nox Emissions During RATA	3.9 lb/hr 17.1 tpy	36 TPY	**Pass**

Please note that the relative accuracy performance results for NOx emission reporting tag reflect the relative accuracy based on a comparison with the reference method and emission reporting tag. The flow meter used to calculate mass NOx emissions was the "Vol Flow".

Table 3.2 Performance Results for CEMS System

Monitor	Results	Allowable	Pass/Fail Semi/Annual
CO2 Conc. (%)	5.3 %	No greater than 20.0 % of mean value of RM or the absolute difference between RM and CEMS <= 1.0%	Pass
	0.2 %		Pass
			Pass
O2 Conc. (%)	2.9 %	No greater than 20.0 % of mean value of RM or the absolute difference between RM and CEMS <= 1.0%	Pass
	0.2 %		Pass
			Pass
THC Conc. (ppmv @ 3% O2)	92 %	No greater than 20.0 % RA using RM or No greater than 10 % RA using EL	Use Alternative
	6 %		Pass
			Pass
Vol Flow (scfm)	16 %	No greater than 20% RA using RM	Pass
SIC Flow (scfm)	12 %	No greater than 20% RA using RM	Pass

Operational Rates during RATA

Run	Run Time	Gas Flow Dry Vent (lb/hr)	Gas Flow Wet Vent (lb/hr)	Gas Flow MeCl (lb/hr)	Gas Flow THROX Out Stack (scfm)	Silicon Loading (lb/hr)	Heat Input (mmBtu/hr)
Run 1	1040/1100	840	364	124.8	13714	0.9	32.0
Run 2	1101/1121	863	345	121.0	13609	0.9	32.1
Run 3	1122/1142	894	342	122.0	13613	0.9	32.1
Run 4	1210/1230	947	431	141.1	13607	1.0	32.7
Run 5	1231/1251	929	416	139.7	13563	1.0	32.1
Run 6	1252/1312	965	432	140.7	13550	1.1	32.2
Run 7	1335/1355	1083	340	128.7	13693	5.6	32.3
Run 8	1356/1416	1127	336	191.5	13869	8.7	33.1
Run 9	1417/1437	1126	375	143.0	14355	12.4	32.7
Run 10	1517/1537	1040	394	121.8	14095	2.9	32.4
Run 11	1538/1558	1019	386	117.2	14162	2.9	32.3
Run 12	1559/1619	985	382	1135.5	14479	3.0	32.3
Average	**N/A**	**987**	**379**	**133.8**	**13859**	**3.4**	**32.4**

Emission Results CO/THC

Sample Type	Test Method	Sampling Time (Min/Run)	Allowable Emission Rate	Actual Emission Rate*
PM_{10} as Total Particulate Matter	EPA Method 5/202	60	3.5 lb/hr 13.4 ton/yr	1.4 lb/hr 6.3 ton/yr
Carbon Monoxide	EPA Method 10	60	90 ton/yr	< 1 ton/yr
THC as Propane (lb/hr)	EPA Method 25A	60	6.6 lb/hr	< 0.1 lb/hr

* Emissions based on average of three one-hour runs.

Testing Run Data CO/THC

PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
Run Date	11/06/2018	11/06/2018	11/06/2018	N/A
Run Times	1040/1139	1210/1309	1335/1434	N/A
Stack Gas Wet Flow Std Cond (scfh)	7.15E+05	7.09E+05	6.99E+05	7.08E+05
Stack Gas Dry Flow (dscfh)	6.21E+05	6.15E+05	6.07E+05	6.14E+05
Conc. THC as Propane (ppmv)	< 0.6	< 0.6	< 0.6	< 0.6
THC as Propane Emissions (Lb/Hr)	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Conc. CO in Outlet (ppmv)	< 0.6	< 0.6	< 0.6	< 0.6
Reported CO Emissions (ton/yr)	**< 1**	**< 1**	**< 1**	**< 1**

Please note flow used for emissions are the average of the 3 RATA runs during sample time (for example Run 1 = average of Runs 1-3 during RATA)

Operational Rates during CO/THC

PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
Run Date	11/06/2018	11/06/2018	11/06/2018	N/A
Run Times	1040/1139	1210/1309	1335/1434	N/A
Gas Flow Dry Vent (lb/hr)	866	947	1122	978
Gas Flow Wet Vent (lb/hr)	350	426	350	376
Gas Flow MeCl (lb/hr)	122.6	140.5	154.4	139.2
Gas Flow THROX Out Stack (scfm)	13645	13573	13972	13730
Silicon Loading (lb/hr)	0.9	1.0	8.9	3.6
Heat Input (mmBtu/hr)	32.1	32.4	32.7	32.4

Emission Results

Sample Type	Test Method	Sampling Time (Min/Run)	Allowable Emission Rate	Actual Emission Rate*
PM_{10} as Total Particulate Matter	EPA Method 5/202	60	3.5 lb/hr 13.5 ton/yr	1.4 lb/hr 6.3 ton/yr

* Emissions based on average of three one-hour runs.

Testing Run Data PM

PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
Run Date	11/07/2018	11/07/2018	11/07/2018	N/A
Run Times	0940/1010 1015/1045	1115/1145 1150/1220	1512/1542 1547/1617	N/A
Stack Gas Wet Flow (cf/hr)	9.40E+05	9.66E+05	9.96E+05	7.22E+05
Stack Gas Wet Flow Std Cond (scf/hr)	8.13E+05	8.39E+05	8.62E+05	6.52E+05
Stack Gas Dry Flow (dscf/hr)	7.02E+05	7.32E+05	7.61E+05	5.75E+05
Volume gas collected (dscf/hr)	37.902	39.039	40.429	40.96
Nozzle Volume @ Stack Cond (cf/hr)	51.567	52.303	53.706	50.77
Total Particulate Weight M17 (g)	0.0328	0.0139	0.0417	0.0215
Total Particulate Weight M202 (g)	0.0030	0.0040	0.0090	0.0050
Total Weight (g)	0.0358	0.0179	0.0507	0.0265
Emissions Total PM (lb/hr)	**1.5**	**0.7**	**2.1**	**1.4**
Emissions Total PM (ton/yr)	**6.4**	**3.2**	**9.2**	**6.3**

Operational Rates during PM

PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
Run Date	11/07/2018	11/07/2018	11/07/2018	N/A
Run Times	0940/1045	1115/1220	1512/1617	N/A
Gas Flow Dry Vent (lb/hr)	622	638	813	691
Gas Flow Wet Vent (lb/hr)	356	375	431	387
Gas Flow MeCl (lb/hr)	148.0	124.4	114.8	129.1
Gas Flow THROX Out Stack (scfm)	14499	14393	14601	14498
Silicon Loading (lb/hr)	3.3	1.4	1.4	2.0
Heat Input (mmBtu/hr)	32.8	33.2	33.8	33.3

4.0 SAMPLING AND ANALYTICAL PROCEDURES

4.1 Relative Accuracy Test Methods

The relative accuracies of the CEMS is determined by comparison to EPA methods for measurement of each component gas. The performance specifications (PS) require the use of the following methods:

- PS 2 - Method 7E for NO_x;
- PS 3 - Method 3A for O_2;
- PS 3 - Method 3A for CO_2;
- PS 6 - Methods 1, 2, 3 and 4 for flow; and
- PS 8 - Method 25A for THC

4.2 Performance Test

The PM_{10} and CO emissions is determined using the following methods:

- Methods 1-4 for volumetric flow rate;
- Methods 5 and 202 for PM_{10} (filterable and condensable);
- Method 10 for CO; and
- Method 25A for THC as Propane

4.3 Procedures

Relative Accuracy

The above methods is performed using mobile continuous emission monitors provided by The Dow Chemical Company internal testing team. Gas is withdrawn from the stack and transported to monitors located at ground level. A stainless-steel probe is inserted into the stack and used to collect sample gas. A Teflon sample line heated to 250°F transported sample gas from the probe to the analyzers. The analyzers is kept at a constant temperature inside the mobile laboratory.

Sample gas is collected continuously from the stack for a period of 21 minutes per run at the three traverse points of 16.7%, 50% and 83.3% of the measurement line that passes through the centroidal area of the stack or duct cross section. At the mobile laboratory, the stack gas is routed to a condenser and then transported to the analyzers for analysis.

The Relative Accuracy Tests is conducted by comparison of the CEMS response to a value measured by a Performance Test Method (PTM) which, in this case, is Method 7E for NOx, EPA Method 25A for THC, EPA Methods 1-4 for Flowrate and 3A for O_2.

EPA Method 1 (Sample Point Determination)
The number and location of traverse points in the stack is determined according to the procedures outlined in EPA Method 1.

EPA Method 2 (Flue Gas Velocity and Volumetric Flow Rate)
The flue gas velocity and volumetric flow rate is determined according to the procedures outline in 40 CFR 60, Appendix A, EPA Method 2. Velocity measurements is made using S-type pitot tubes conforming to the geometric specifications outlined in EPA Method 2. Differential pressures is measured with fluid manometer. Flue gas temperature, velocity, and volumetric flow rate data is recorded.

EPA Method 3A (Flue Gas Composition and Molecular Weight)
EPA Method 3A (Instrumental Method) is utilized to determine the diluent during each run on the outlet.

An analyzer measured O_2 content on the basis of the strong paramagnetic properties of O_2 relative to other compounds present in combustion gases. In the presence of a magnetic field, O_2 molecules become temporary magnets. The analyzer determines the sample gas O_2 concentration by detecting the displacement torque of the sample test body in the presence of a magnetic field.

An analyzer measured CO_2 based on its absorption of infrared radiation. The infrared unit uses a single beam, single wavelength technique, with wavelength selection being achieved by a carefully specified narrow band optical filter making it highly selective for CO_2 measurement in the presence of other infrared-absorbing gases.

EPA Method 4 (Moisture)
A calibrated Method 5 console will pull stack gas samples through a Method 5 probe equipped with a glass liner to determine percent moisture of the stack gas. Stack gas is bubbled through two impingers containing water, one empty impinger, and one impinger containing silica gel. All of the impingers is weighed prior to sampling. The impinger train is kept iced in order to knock out all moisture in the stack gas. After the final leak check following each run, the exterior of the impingers is dried off and the impingers were weighed to determine percent moisture. ***Dow requested to complete up to 4-63 minute moisture runs. A sample is collected to coincide with the runs. For each moisture sample, no more than 3 runs is represented.***

EPA Method 7E (NO_X Sampling and Analysis)

EPA Method 7E is utilized to determine nitrogen oxide concentrations during each run on the outlet.

An analyzer measured NOx using chemiluminescence technology. Ozone is combined with nitric oxide to form nitrogen dioxide in an activated state. The activated NO_2 luminesces broadband visible to infrared light as it reverts to a lower energy state. A photomultiplier and associated electronics counts the photons that are proportional to the amount of NO present. Since the stream contains both NO and NO_2, the amount of nitrogen oxide (NO_2) must first be converted to nitric oxide, NO, by passing the sample through a converter before the above ozone activation reaction is applied. The above reaction yields the amount of NO and NO_2 combined in the air sample.

Please note The Dow Chemical Company has elected to complete a post-run bias and drift assessment after each set of three 21-minute runs for all analytes as allowed in EPA Method 7E 8.5 for all gas phase analyzer methods. EPA Method 7E section 8.5 reads as follows:

Post-Run System Bias Check and Drift Assessment. How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

EPA Method 25A (Total VOC Sampling and Analysis)

EPA Method 25A is utilized to determine total THC as propane concentrations during each run on the outlet.

A gas sample is extracted from the source through a heated line to a flame ionization analyzer (FIA). Results is reported as volume concentration equivalent to propane.

4.3 List of Sampling Equipment

REFERENCE METHOD	EQUIPMENT	ID #	RANGE	SPAN
Method 3A (O_2)	Teledyne Paramagnetic Analyzer	(S/N:376)	0-25 %	19.9 %
Method 3A (CO_2)	Teledyne Infrared Analyzer	(S/N: 344)	0-25 %	19.8 %
Method 7E (NO_x)	Thermo Chemiluminescent Analyzer	(S/N: 1434963661)	0-3000 ppmv	146.6 ppmv
Method 25A (THC)	CAA FID Analyzer	(S/N: CO1021)	0-20000 ppmv	30.4 ppmv

4.4 List of CEMS Equipment

Monitor System	EQUIPMENT	ID #
Oxygen FGTHROX	Brad Gaus Model 4705	S/N: 10687
Carbon Dioxide FGTHROX	California Analytical Instruments Model ZRE	S/N: N4K1905
Total Hydrocarbon FGTHROX	California Analytical Instruments Model 600 HFID	S/N: C01027
Nitrogen Oxides FGTRHOX	Thermo Scientific Model 42I	S/N: 0733125534
Air Flow FGTHROX	Monitoring Solutions Model CEM Flow	S/N: 012808-000-1017
Air Flow FGTHROX	SIC Model FLSE100-PK17835HSHS	S/N: 13488341

Performance Test

EPA Method 1 (Sample Point Determination)
EPA Method 2 (Flue Gas Velocity and Volumetric Flow Rate)
EPA Method 3A (Flue Gas Composition and Molecular Weight)
EPA Method 4 (Moisture)
EPA Method 25A (Total VOC Sampling and Analysis)

Same description as mentioned above. However, all readings are completed over a one-hour period for three test runs.

EPA Method 10 (CO Sampling and Analysis)
EPA Method 10 will be utilized to determine carbon monoxide concentrations during each run on the outlet.

An analyzer measured CO based on its absorption of infrared radiation. The infrared unit uses a single beam, single wavelength technique, with wavelength selection being achieved by a carefully specified narrow band optical filter making it highly selective for CO measurement in the presence of other infrared-absorbing gases.

EPA M202 in Conjunction with EPA M5 (Filterable and Condensable Particulate Matter Sampling and Analysis)
EPA Method 202 is utilized in conjunction with EPA Method 17 to determine both filterable (FPM) and condensable particulate matter (CPM) concentrations during each run on the outlet.

Using EPA Method 5 methodology, filterable particulate matter (FPM) is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The FPM mass is determined gravimetrically after the removal of uncombined water.

EPA Method 202 methodology is used to collect condensable particulate matter (CPM) in dry impingers after filterable PM has been collected on a filter maintained as specified in Method 5 of appendix A-6 to part 60. The organic and aqueous fractions of the impingers and an out-of-stack CPM filter are then taken to dryness and weighed. The total of the impinger fractions and the CPM filter represents the CPM. Analysis for FPM and CPM is completed by Enthalpy Analytical.

FIGURE 4.1: SAMPLING TRAIN USED FOR NOx, CO, CO2, O_2 - Glass Wool Filter not used

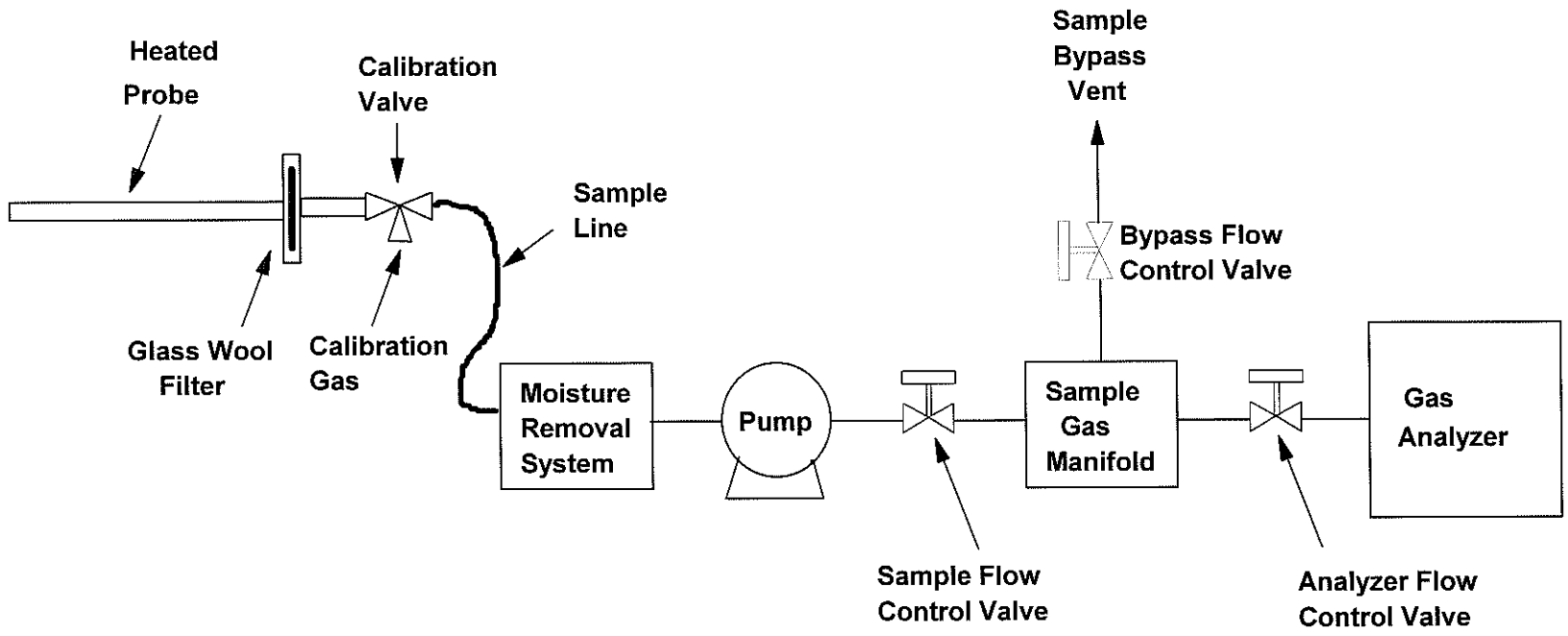


FIGURE 4.2: SAMPLING TRAIN FOR VOC (M25A) - Glass Wool Filter not used

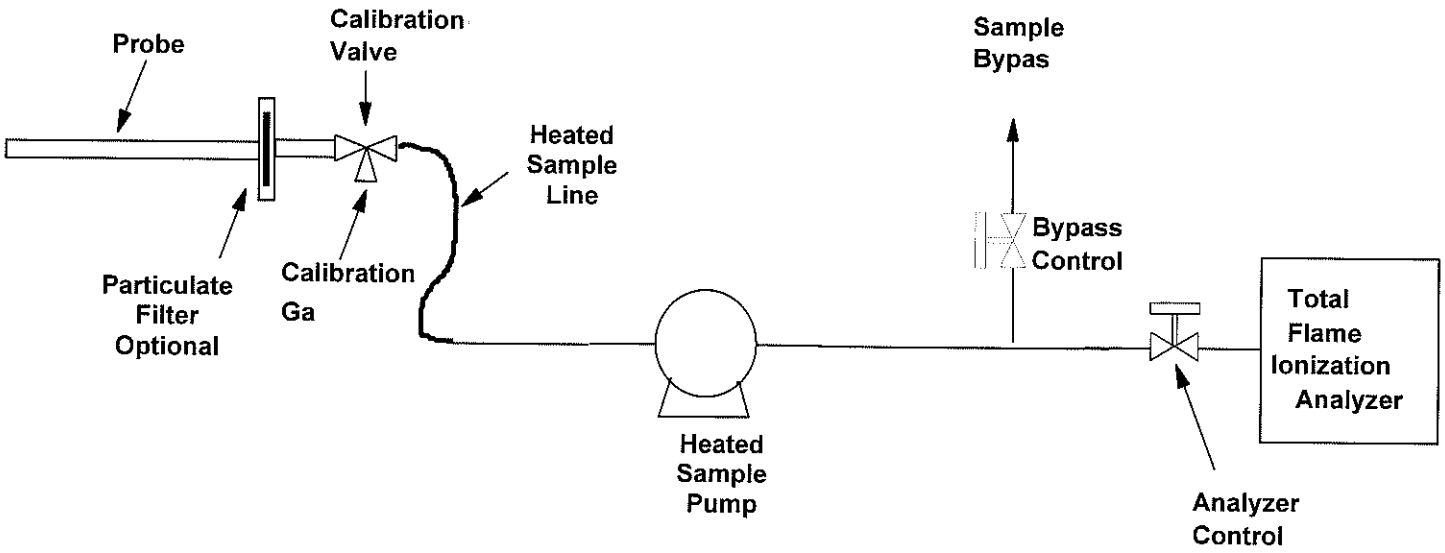
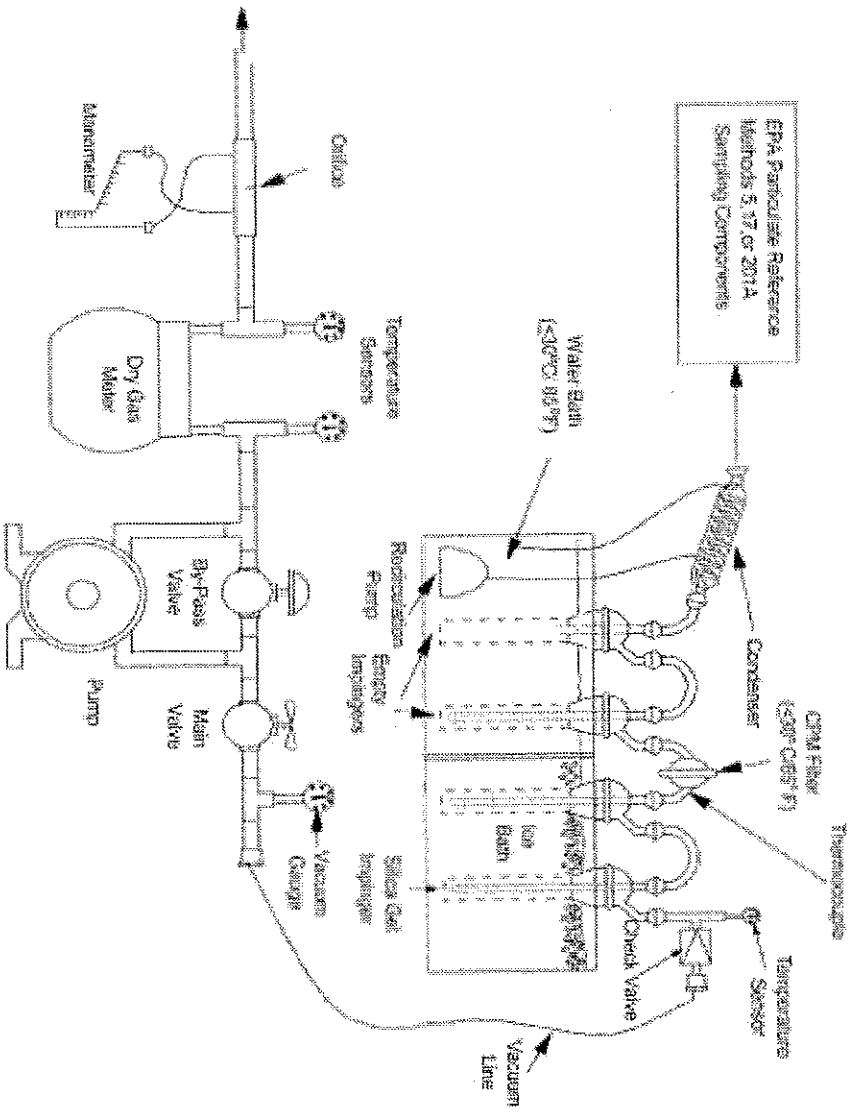


FIGURE 4.3: SAMPLING TRAIN FOR CPM (M202 with M17)



5.0 CALCULATIONS