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Particulate Test Method Evaluation

Emission Test Report
Exxon Company, USA
Baton Rouge, LA

EMISSION TEST REPORT

METHOD DEVELOPMENT AND TESTING
FOR FCCU REGENERATORS
Exxon Company, U.S.A
Baton Rouge, Louisiana

EMB Report No. 82-CAT-12
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Mr. Winton Kelly, EPA Task Manager, provided overall project coordination and guidance and observed the test program. Mr. Tim Tucker represented the Exxon Company and provided assistance in scheduling and process operation. Mr. Charles Bruffey was the PEDCo Project Manager. Principal authors were Messrs. Charles Bruffey and Thomas Wagner.

QUALITY ASSURANCE ELEMENT FINDER

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SECTION 1

INTRODUCTION

On March 8, 1974, the U.S. Environmental Protection Agency (EPA) promulgated a New Source Performance Standard (NSPS) governing particulate emissions from fluid catalytic cracking unit (FCCU) regenerators. The testing procedures specified the use of Method 5 for measurement of these emissions. The data to support the NSPS were collected during 1971 and 1972 by use of the Method 5 procedures. The facilities tested were conventional regenerators equipped with electrostatic precipitators (ESP's) and carbon monoxide (CO) boilers.

Since the promulgation, EPA has received several requests to clarify the intent of the emission regulation. The EPA has stated that the materials intended to be controlled were "catalyst fines" or "mineral dust" and not condensible sulfates that were in the gas phase at the operating temperature of the control device.

In the public notice of proposed rulemaking for a revision to the FCCU new source standard,* EPA stated that because Method 5 is capable of collecting condensible matter that is not controllable by the best systems of emission reduction, a facility employing such systems could be found in noncompliance if

*44 FR 60759 Monday, October 22, 1979.

significant quantities of such condensibles were present as a result of feed changes or process variations. Consequently, EPA is evaluating sample and analytical parameters designed to minimize the collection of condensible sulfate materials from these sources.

Under contract to the Emission Measurement Branch of the EPA, PEDCo Environmental, Inc., conducted the third in a series of atmospheric emission test projects from March 2 through 9, 1983, at the Exxon Company U.S.A. refinery in Baton Rouge, Louisiana. Testing was performed at the final exit stack of the FCCU regenerator to provide data for the development of modifications to the existing test methodology to minimize the collection of condensible sulfate materials during the measurement of particulate emissions from these sources.

All samples were collected by use of four single-sample trains located at points of similar velocity and temperature in the FCCU exit stack. Nine test runs were performed during the test series. For evaluation of the effect of sample temperature on sulfate collection, the temperatures of the probe and filter box were varied for each run as follows:

Sample designation	Probe and filter box sample temperature
M5	121°C (250°F)
M5B	160°C (320°F)
M5-450	232°C (450°F)
M5W	121°C (250°F)

Paired trains were run at similar temperatures to allow within-run data comparisons as well as comparisons between methods run at different sample temperatures.

Probe rinse and filter sample fractions were subjected to a thermogravimetric analysis at predetermined temperatures to assess sample weight loss as a function of drying temperature. In addition, several samples (designated M5W) collected at 121°C (250°F) were analyzed for total water-soluble sulfate and subsequent particulate mass determination by use of modified procedures developed by the Texas Air Control Board (TACB).* This method incorporates deionized water as the sample recovery solvent and uses gravimetric analyses and an independent determination to measure water-soluble sulfates for subsequent derivation of the mass of non-water-soluble particulate (matter that does not contain any water-soluble sulfate). Ion chromatography was used to measure water-soluble sulfate. Select sample fractions also were analyzed for cation species to characterize the water-soluble sulfate as other than sulfuric acid in the samples.

Each individual sample train was followed by a modified EPA Method 8** impinger section to allow comparative analysis of sulfates as sulfuric acid (H_2SO_4) and sulfur dioxide (SO_2). Flue gas temperature, moisture content, and composition [oxygen (O_2), carbon dioxide (CO_2), and carbon monoxide (CO)] were measured in conjunction with the emission tests.

Mr. Winton Kelly, representing EPA, observed part of the test program and provided overall project coordination and guidance. Mr. Tim Tucker, representing Exxon, coordinated onsite activities and unit operation.

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*TACB - Laboratory Division - Determination of Particulate in Stack Gases Containing Sulfur Dioxide. December 1979.

**40 CFR 60, Appendix A, Reference Method 8, July 1982.

SECTION 2

PROCESS OPERATION

This methods development project was conducted on a fluid catalytic cracking unit regenerator at Exxon's Baton Rouge refinery. Exxon utilizes conventional regeneration techniques to regenerate carbon-laden catalysts. Particulate and sulfur dioxide emissions are controlled by a jet-ejector venturi scrubber. Carbon monoxide emissions are controlled by a CO boiler. A detailed description of Exxon's process operation and control equipment is not given in this report because of confidentiality considerations.

SECTION 3

SAMPLING LOCATION AND TEST AND ANALYTICAL METHODS USED

All samples were collected by means of four sampling trains, each located at single points representing average velocities in the FCCU final exit stack. The four-train sampling system was used to conduct nine test runs for a total collection of 36 individual samples. Figure 3-1 presents a schematic of the sampling site setup.

3.1 SAMPLING LOCATION

Testing was conducted at the FCCU scrubber exit stack as depicted in Figure 3-2. Four 7.0-cm (2.75-in.) i.d. sampling ports were available at 90 degrees off-center. All four sampling ports were used in this study. The sampling platform was approximately 61 meters (200 feet) above grade. The stainless steel sampling port couplings were beveled inward by 0.64 cm (0.25 in.) to produce an actual inside diameter of less than 7.0 cm (2.75 in.). Inevitably, the tight fit caused some scraping of the sampling port couplings during sampling train insertion and removal from the stack.

3.2 SAMPLING METHODS

Flue gas samples were collected simultaneously from four single points in the stack; each point represented similar

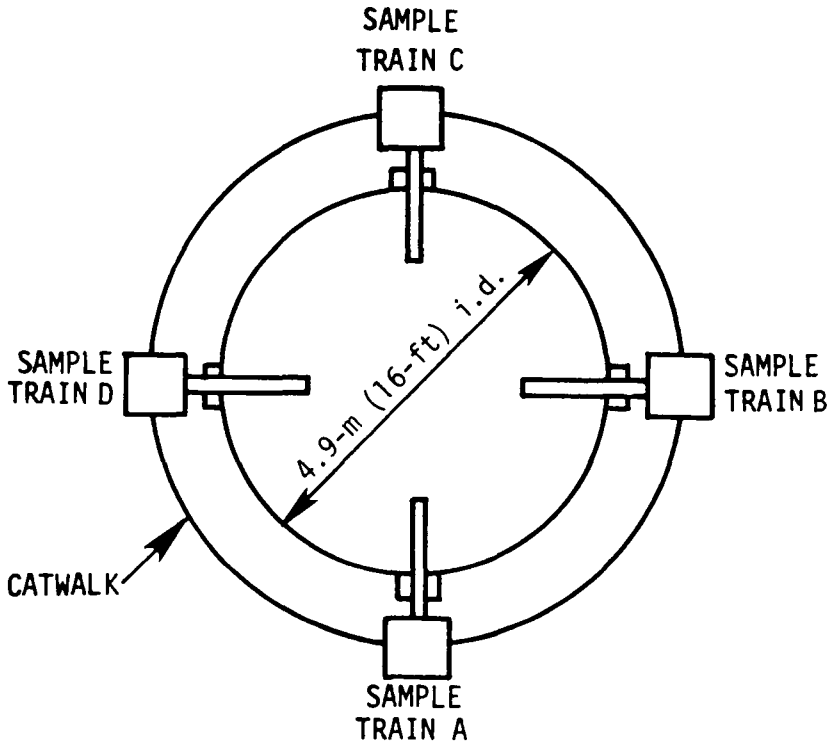

Figure 3-1. Sampling train setup - plan view.

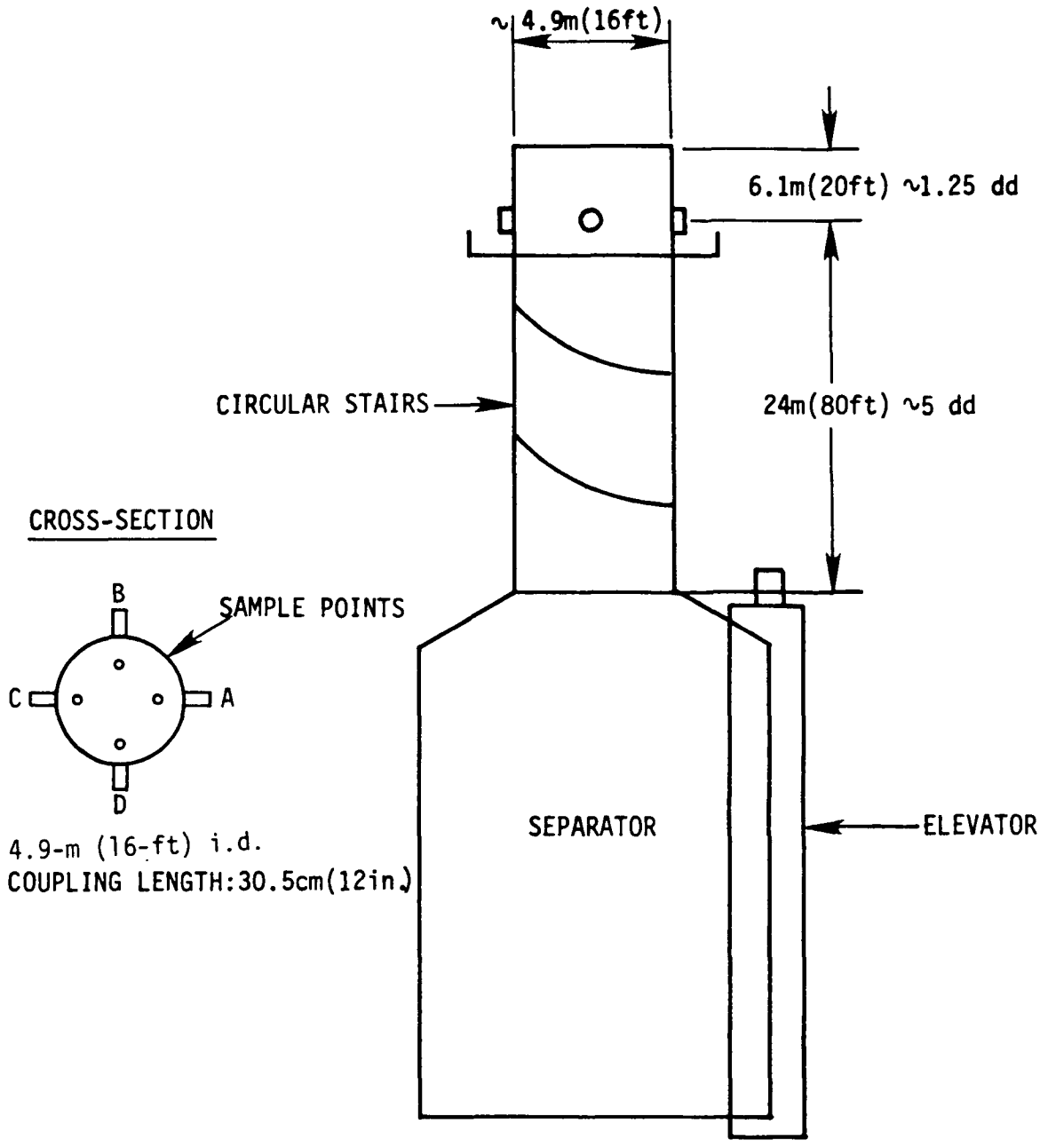

Figure 3-2. Sampling location.

velocity pressures and temperatures. The desired sampling time was 120 minutes, and readings of stack flue gas and sampling train data were recorded at 10-minute intervals for each train. In Run Nos. 4A-D, 6A-D, 7C, and 8A, the sampling time was reduced because of problems with the sampling equipment or the weather. Pitot tubes and thermocouples attached to each sampling probe were used to set isokinetic sample rates for each train. Programmable calculators were used to determine sample rates. Prior to sampling, velocity and temperature profiles were established by use of procedures described in EPA Methods 1 and 2.* These data were used to select the four sampling points.

Table 3-1 presents the sampling matrix performed during this test series. The following are a brief descriptions of the specific conditions for each train:

- Method 5 - Designation M5

  Filterable particulate was collected by use of a probe and filter assembly heated to 121°C (250°F). Acetone was used to rinse all sampling train components prior to the filter.

- Method 5B - Designation M5B

  Filterable particulate was collected by use of a probe and filter assembly heated to 160°C (320°F). Acetone was used to rinse all sampling train components prior to the filter.

- Method 5-450 - Designation M5-450

  Filterable particulate was collected by use of a probe and filter assembly heated to 232°C (450°F). Acetone was used to rinse all sampling train components prior to the filter.

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*40 CFR 60, Appendix A, Reference Methods 1 and 2, July 1983.

TABLE 3-1. SAMPLING MATRIX

Run No.	Sampling Train No.	Sampling method[a]			
		M5 121°C (250°F)	M5B 160°C (320°F)	M5-450 232°C (450°F)	M5W 121°C (250°F)
1	1A	X			
	1B	X			
	1C				X
	1D				X
2	2A				X
	2B				X
	2C		X		
	2D		X		
3	3A				X
	3B				X
	3C	X			
	3D	X			
4	4A				X
	4B				X
	4C		X		
	4D		X		
5	5A	X			
	5B	X			
	5C				X
	5D				X
6	6A				X
	6B		X		
	6C		X		
	6D				X

(continued)

TABLE 3-1 (continued)

Run No.	Sampling Train No.	Sampling method[a]			
		M5 121°C (250°F)	M5B 160°C (320°F)	M5-450 232°C (450°F)	M5W 121°C (250°F)
7	7A		X		
	7B		X		
	7C			X	
	7D			X	
8	8A	X			
	8B	X			
	8C		X		
	8D		X		
9	9A		X		
	9B			X	
	9C		X		
	9D			X	

[a]M5 (Method 5) - Probe and filter heated to 121°C (250°F).
M5B (Method 5B) - Probe and filter heated to 160°C (320°F).
M5 (Method 5) - Probe and filter heated to 232°C (450°F).
M5W (Method 5) - Probe and filter heated to 121°C (250°F); water rinse of nozzle, probe, and front filter holder glassware.

- Method 5W - Designation M5W

  Filterable particulate was collected by use of a probe and filter assembly heated to 121°C (250°F). Deionized, distilled water was used to rinse all sampling train components prior to the filter.

In each train, the probe and filter temperatures were set at a predetermined level and monitored during each test by means of multiterminal digital indicators with thermocouple leads located in each probe and immediately behind the Method 5 filter frits.

The back half of each sampling train consisted of a Modified Method 8 assembly with either five or six impingers. An empty impinger(s) was used to prevent back-half carryover resulting from water condensation. An unheated Method 5 filter assembly was inserted between the IPA and H_2O_2 impingers to preclude any sulfuric acid mist carryover. The contents of each impinger were as follows:

Impinger	Contents - Five Impinger Runs	Impinger	Contents - Six Impinger Runs
1	Empty	1	Empty
2	150 ml 80% IPA	2	Empty
3	100 ml 10% H_2O_2	3	150 ml 80% IPA
4	100 ml 10% H_2O_2	4	100 ml 10% H_2O_2
5	300 grams silica gel	5	100 ml 10% H_2O_2
		6	300 grams silica gel

All filters (Whatman Reeve Angel 934 AH) used in the Method 5 position were heated to 300°C prior to identification and tare weighing.

Because the gas stream appeared saturated and, at times, contained water droplets, two moisture determinations were made.

The first determination involved calculations based on the water collected in the sampling trains, and the second involved psychrometric calculations. In each case, the lower value (saturation at stack temperature) was used as the correct moisture content in all calculations, as prescribed by EPA Method 4.*

Also, approximate measurements were made to determine the degree of turbulent flow at the test location, as detailed in Method 2 of the Federal Register.* Select traverse points were checked by aligning the face openings of the pitot tube perpendicular to the stack cross-sectional plane, designated "0 degree reference." A null (zero) pitot reading obtained at 0 degree reference indicates an acceptable flow condition at a given point. A pitot tube angular notation of ±10 degrees is considered acceptable for achieving a null reading. At the scrubber outlet test location, the degree of angular rotation was highly variable and often greater than 10 degrees. Plume observation also indicated cyclonic flow conditions in the stack. The rotational, swirling flow would tend to cause larger particles and particles entrained in water droplets to move toward the walls of the stack. Since the four sampling trains were located approximately 1.2 m (4 ft) from the 4.9-m (16-ft) round stack wall at each port, the spatial and temporal variations in velocity and particulate concentration could have affected the within-run precision and increased the variability in the reported results.

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*40 CFR 60, Appendix A, Reference Methods 2 and 4, July 1983.

A flue gas grab sample collected during each of the first five tests was also analyzed for O_2, CO_2, and CO by means of an Orsat analyzer. In the last four tests, a Fyrite analyzer was used to measure the O_2 and CO_2 content of the flue gas. The flue gas composition was used to calculate stack gas molecular weight.

3.3 SAMPLE ANALYSIS

Table 3-2 lists all the samples collected during this test program and their respective analyses.

3.3.1 Particulate Analysis

The filter particulate catch was placed in a tared glass weighing dish, desiccated for 24 hours, and weighed until a constant weight was achieved.* The probe rinse fraction was transferred to a tared beaker, evaporated to dryness at ambient temperature and pressure, desiccated for 24 hours, and weighed to a constant weight.**

After this initial analysis, probe rinse and filter fractions were heat-conditioned in an oven for 6 hours (except where noted), according to the treatment sequence presented in Table 3-2. Each sample fraction was cooled and desiccated for 24 hours after removal from the oven and weighed to a constant weight.** Filter and acetone blanks were treated much that same as the actual samples.

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*Previous data show that samples collected at 120°C will not come to a constant weight. At least three separate weighings were obtained, and the lowest weight achieved was reported as the ambient weight.

**Criteria as specified in 40 CFR 60, Appendix A, EPA Reference Method 5, July 1983.

TABLE 3-2. ANALYTICAL PLAN

Run No.	Sampling Train No.	Sampling method	Thermogravimetric analysis[a]			Water-soluble sulfate determination[b]	Cations by ICP[c]
			Ambient → 160° → 232° → 316°C	Ambient → 232° → 316°C	Ambient → 316°C		
1	1A	M5	X (24)				
	1B	M5	X (24)				
	1C	M5W				X	
	1D	M5W				X	
2	2A	M5W				X	
	2B	M5W				X	
	2C	M5B	X				
	2D	M5B	X (24)				
3	3A	M5W				X	
	3B	M5W				X	
	3C	M5		X (24)			
	3D	M5		X (24)			
4	4A	M5W				X	
	4B	M5W				X	
	4C	M5B		X			
	4D	M5B		X			
5	5A	M5			X		X
	5B	M5			X (24)		X
	5C	M5W				X	X
	5D	M5W				X	X
6	6A	M5W				X	X
	6B	M5B			X (24)		X
	6C	M5B			X		X
	6D	M5W				X	X

(continued)

TABLE 3-2 (continued)

Run No.	Sampling Train No.	Sampling method	Thermogravimetric analysis[a]			Water-soluble sulfate determination[b]	Cations by ICP[c]
			Ambient → 160° → 232° → 316°C	Ambient → 232° → 316°C	Ambient → 316°C		
7	7A	M5B	X				
	7B	M5B	X				
	7C	M5-450	X (24)				
	7D	M5-450	X				
8	8A	M5	X				
	8B	M5	X (24)				
	8C	M5B	X				
	8D	M5B	X (24)				
9	9A	M5-450			X (24)		
	9B	M5B			X		
	9C	M5B			X (24)		
	9D	M5-450			X		

[a]Thermogravimetric conditioning of probe rinse and filter fractions at indicated temperatures after initial desiccation and ambient weights were obtained. All other samples were heat-conditioned for 6 hours, except where noted with (24). These samples were conditioned for 24 hours.

[b]In this procedure, the mass of total water-soluble sulfates in the sample was determined and subtracted from the total sample mass.

[c]These samples were analyzed for cations by ICP analytical techniques.

Note: All back halves represent a modified Method 8, with analysis for sulfates as sulfuric acid and sulfur dioxide.

3.3.2 Water-Soluble Sulfate Determination

This method is designed to determine the particulate catch corrected for any water-soluble sulfate retained in the Method 5 sample fractions. As documented in previous studies, the condensible sulfate problem can be attributed to sulfuric acid. This makes a direct gravimetric analysis difficult for two reasons. First, sulfuric acid is a powerful desiccating agent itself; therefore, if a significant amount of sulfuric acid is present, the Method 5 criteria for constant weight of the particulate cannot be met. Second, the number of water molecules associated with each sulfuric acid molecule is not consistent. The water-soluble sulfate method developed by the Texas Air Board was designed to overcome these problems. This method converts any sulfuric acid present to a suitable form for accurate gravimetric analysis. Ammonium hydroxide is added to form ammonium sulfate in the aqueous solutions. Ammonium hydroxide is used because any excess reagent will evaporate. This procedure allows the determination of the gross particulate (sulfate as ammonium sulfate plus other particulate), the determination of sulfate as ammonium sulfate from the Method 6 titration or ion chromatography, and subsequently, the determination of non-water-soluble sulfate particulate by subtraction of the sulfate (as ammonium sulfate) from the gross particulate.

Each sample fraction plus blanks were handled and analyzed as follows:

- Filter - The filter was cut into small pieces and placed in a 125-ml Erlenmeyer flask with a standard type joint equipped with an air condenser. The contents of the shipping container were rinsed into the flask. About 50 ml of distilled water was added and the contents gently refluxed for 6 to 8 hours. The solution was then cooled and diluted with water to exactly 250 ml in a volumetric flask. This solution was reserved for total soluble sulfate analysis, which is described below.

- Probe Rinse - The probe wash was poured into a 250-ml volumetric flask. The sample bottle was rinsed with distilled water and the rinsings were added to the flask. The solution was then diluted to the mark with distilled water (or, if greater than 250 ml, the volume was measured). This solution was reserved for total soluble sulfate analysis, which is described below.

Total Soluble Sulfate--

A 15-ml aliquot* was drawn from the settled samples (filter and rinse) into separate sample containers with a clean, dry pipet (only solution was transferred--no solid; if necessary, a portion of the sample was centrifuged). The sulfate ion ($SO_4^=$) concentration in each aliquot was determined by ion chromatography (IC). A syringe was used to inject 1 ml of the aliquot into the 100-μl sample loop of the IC. The conductivity response of the sample was compared with the calibration curve to obtain $SO_4^=$ concentration in ml/liter. Dilutions were prepared and reanalyzed if the initial response was out of the linear calibration range (0.1 to 15 mg/liter). Blank filter and water samples were prepared and analyzed in the same manner as the actual samples.

*The pipet is not rinsed. This deviation from normal procedures is necessary because the volume removed from the volumetric flask is required in the calculations.

Mass Determination--

Filter and Rinse Solution Preparation - The remaining contents of each volumetric flask (235 ml) were poured into separate tared 250-ml beakers, and the flask was rinsed with distilled water to transfer all particulate matter. The filter solution in Beaker A and the rinse solution in Beaker B were evaporated to approximately 100 ml at 105°C and allowed to cool before the next analysis was made.

Filter and Rinse Solution Analysis - Five drops of phenolphthalein indicator were added to all the tared beakers. Concentrated NH_4OH was then added drop by drop until the solution turned pink. The samples were returned to the oven and evaporated to dryness at 105°C, then cooled in a desiccator and weighed to a constant weight. Results were reported to the nearest 0.1 mg. For this method, "constant weight" means a difference of no more than 0.5 mg or 1 percent of the total weight less beaker and/or filter tare, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Calculations--

Nomenclature--

FP = weight of particulate* on the filter in Beaker A, mg

PRP = weight of probe rinse particulate* in Beaker B, mg

NWSSP = weight of non-water-soluble sulfate particulate**, mg

AS_f = weight of ammonium sulfate in filter sample, mg

AS_{pr} = weight of AS in probe rinse sample, mg

V_{evap} = volume of solution evaporated in Beaker A (filter) or Beaker B (probe rinse), ml

C_{SO_4} = concentration of sulfate in filter or probe rinse solution aliquots, mg/liter

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*Particulate with H_2SO_4 converted to $(NH_4)_2SO_4$.

**Particulate excluding water-soluble sulfates.

Equations--

$$FP(mg) = \text{gross weight Beaker A} - \text{tare weight Beaker A} - \text{filter tare weight} \quad \text{(Eq. 1)}$$

$$PRP(mg) = \text{gross weight Beaker B} - \text{tare weight Beaker B} \quad \text{(Eq. 2)}$$

$$AS(mg) = C_{SO_4}\ (mg/liter) \times V_{evap}\ (ml) \times \frac{liter}{1000\ ml} \times 1.376\ \left(\frac{mg\ AS}{mg\ SO_4}\right) \quad \text{(Eq. 3)}$$

Mass of Non-Water-Soluble Sulfate Particulate

The sum of the particulate* collected on the filter (FP) and the particulate* collected in the probe rinse (PRP) is equal to the sum of non-water-soluble sulfate particulate (NWSSP) and ammonium sulfate (AS) in both samples:

$$FP + PRP = NWSSP + AS_f + AS_{pr} \quad \text{(Eq. 4)}$$

The NWSSP can be found by rearranging the equation and substituting appropriate values determined by Equations 1, 2, and 3.

$$NWSSP = FP + PRP - AS_f - AS_{pr} \quad \text{(Eq. 5)}$$

3.3.3 Sulfuric Acid Mist Analysis

The amount of sulfuric acid that passed through the particulate filter was initially determined through analysis of the IPA solution recovered in the first impinger(s) and the backup filter. The volume of the sample solution was recorded. A 20-ml aliquot of this solution was pipetted into a 250-ml Erlenmeyer

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*Particulate with H_2SO_4 converted to $(NH_4)_2SO_2$.

flask with 2 to 3 drops of thorin indicator and titrated to a pink end point by use of 0.0100 N barium perchlorate. Results from the titrametric analysis were highly variable because the amount of condensed water in the sample made it difficult to distinguish the titrametric end point. Therefore, 10- to 20-ml aliquots of each sample were diluted with 100 ml of deionized, distilled water, and ion chromatography was used in the analyses for sulfates ($SO_4^{=}$). A blank was titrated for each sample in the same manner.

3.3.4 Sulfur Dioxide Analysis

A 20-ml aliquot of the hydrogen peroxide solution was pipetted into a 250-ml Erlenmeyer flask with 80 ml of 100 percent IPA and 2 to 3 drops of thorin indicator. The solution was then titrated to a pink end point by use of 0.0100 N barium perchlorate. Blanks were titrated in a similar manner. Several peroxide impingers were checked by IC for comparative purposes. The IC and titrametric analysis compared favorably.

3.3.5 Sulfate Analysis by Ion Chromatography

Samples were analyzed for total sulfates as SO_4 by use of standard ion chromatography (IC) analytical techniques. The IC procedures were used to determine sulfate values obtained as part of the water-soluble sulfate method. In addition, within-run samples, heat-conditioned to 315°C, were extracted with distilled water, as described in Method M5, and aliquots were analyzed for total sulfates by IC for comparative purposes.

3.3.6 Cation Analysis by Inductively Coupled Plasma (ICP)

The extracts of selected filter and rinse particulate (see Table 3-2) were analyzed for cations. Metallic ions and a cross-check on sulfur were determined by ICP.

SECTION 4

SUMMARY AND DISCUSSION OF TEST RESULTS

This section summarizes the results of the field sampling program. The results are presented to allow both within-run and between-run data comparisons with emphasis on the thermogravimetric and water-soluble sulfate test results. Appendix A contains computer printouts and example calculations. Appendices B and C contain the raw field and laboratory data sheets, respectively. Appendix D details the sample and analytical procedures used, and Appendix E addresses equipment calibration guidelines and results.

4.1 SAMPLE DATA

Table 4-1 summarizes pertinent sample data. The actual probe and filter temperatures, stack temperature, and moisture content represent average values from each individual sampling train. Isokinetic criteria defined in Reference Method 5* were met in each case, with the exception of Sample Runs 2B, 3A, and 8A. Run No. 3A had a post-test leak rate three times greater than the allowable limit because of a cracked piece of glassware in the back half of the sampling train. During Run No. 8A, the

*40 CFR 60, Appendix A, Reference Method 5, July 1983.

TABLE 4-1. SUMMARY OF SAMPLE CONDITIONS

Test No.	Date (1983) and time (24-h)	Train ID	Sample[a] type	Sample temperature, °C (°F)				Meter volume,[b] dNm³ (dscf)	Average stack temperature, °C (°F)	Average moisture content,[c] %
				Probe		Filter				
				Desired	Actual	Desired	Actual			
1	3/2 1056-1257	1A	M5	121 (250)	131 (267)	121 (250)	134 (273)	1.46 (51.66)	73 (163)	25.3
		1B	M5	121 (250)	138 (281)	121 (250)	134 (273)	1.45 (51.28)		
		1C	M5W	121 (250)	120 (249)	121 (250)	129 (264)	1.44 (50.71)		
		1D	M5W	121 (250)	128 (263)	121 (250)	128 (263)	1.48 (52.14)		
2	3/3 0936-1137	2A	M5W	121 (250)	124 (256)	121 (250)	129 (265)	1.36 (48.06)	74 (166)	25.6
		2B	M5W	121 (250)	129 (265)	121 (250)	130 (266)	1.31 (46.24)		
		2C	M5B	160 (320)	161 (323)	160 (320)	167 (332)	1.24 (43.93)		
		2D	M5B	160 (320)	163 (326)	160 (320)	162 (324)	1.23 (43.33)		
3	3/3 1414-1615	3A	M5W	121 (250)	127 (261)	121 (250)	128 (263)	2.38 (83.87)	73 (163)	25.6
		3B	M5W	121 (250)	125 (257)	121 (250)	126 (260)	2.64 (93.35)		
		3C	M5	121 (250)	126 (260)	121 (250)	125 (258)	2.45 (86.67)		
		3D	M5	121 (250)	122 (253)	121 (250)	127 (262)	2.31 (81.43)		
4	3/4 1058-1209	4A	M5W	121 (250)	126 (260)	121 (250)	126 (260)	1.60 (56.46)	71 (160)	26.6
		4B	M5W	121 (250)	125 (258)	121 (250)	127 (258)	1.59 (56.00)		
		4C	M5B	160 (320)	164 (327)	160 (320)	170 (338)	1.56 (55.21)		
		4D	M5B	160 (320)	165 (330)	160 (320)	165 (328)	1.55 (54.65)		
5	3/7 1024-1225	5A	M5	121 (250)	124 (256)	121 (250)	131 (268)	2.74 (96.86)	77 (170)	24.3
		5B	M5	121 (250)	129 (265)	121 (250)	133 (271)	2.78 (98.21)		
		5C	M5W	121 (250)	130 (267)	121 (250)	129 (264)	2.72 (96.14)		
		5D	M5W	121 (250)	128 (263)	121 (250)	128 (263)	2.65 (93.73)		
6	3/7 1540-1701	6A	M5W	121 (250)	125 (258)	121 (250)	122 (253)	2.01 (71.13)	71 (160)	27.5
		6B	M5B	160 (320)	168 (333)	160 (320)	157 (316)	2.00 (70.90)		
		6C	M5B	160 (320)	168 (334)	160 (320)	156 (313)	1.99 (70.20)		
		6D	M5W	121 (250)	124 (256)	121 (250)	122 (253)	1.98 (70.02)		

(continued)

TABLE 4-1 (continued)

Test No.	Date (1983) and time (24-h)	Train ID	Sample[a] type	Sample temperature, °C (°F)				Meter volume,[b] dNm³ (dscf)	Average stack temperature, °C (°F)	Average moisture content,[c] %
				Probe		Filter				
				Desired	Actual	Desired	Actual			
7	3/8 0934-1135	7A	M5B	160 (320)	163 (325)	160 (320)	167 (333)	2.84 (100.26)	78 (172)	23.3
		7B	M5B	160 (320)	159 (319)	160 (320)	166 (331)	2.87 (101.42)		
		7C	M5-450	232 (450)	223 (434)	232 (450)	205 (403)	2.18 (76.79)		
		7D	M5-450	232 (450)	158 (317)	232 (450)	234 (453)	2.83 (100.00)		
8	3/8 1300-1501	8A	M5	121 (250)	131 (268)	121 (250)	134 (273)	2.38 (84.19)	77 (170)	22.9
		8B	M5	121 (250)	125 (258)	121 (250)	127 (261)	2.74 (96.61)		
		8C	M5B	160 (320)	165 (329)	160 (320)	163 (325)	2.60 (91.71)		
		8D	M5B	160 (320)	166 (330)	160 (320)	166 (330)	2.71 (95.74)		
9	3/9 0945-1146	9A	M5B	160 (320)	163 (325)	160 (320)	160 (320)	2.86 (101.02)	77.2 (171)	24.8
		9B	M5-450	232 (450)	234 (455)	232 (450)	200 (393)	2.85 (100.87)		
		9C	M5B	160 (320)	164 (326)	160 (320)	162 (324)	2.71 (95.84)		
		9D	M5-450	232 (450)	149 (300)	232 (450)	213 (416)	2.88 (101.58)		

[a]Designation:

M5 = Reference Method 5 - desired probe and filter temperature, 121°C (250°F).
M5B = Reference Method 5B - desired probe and filter temperature, 160°C (320°F).
M5-450 = Modified Method 5 - desired probe and filter temperature, 232°C (450°F).
M5W = Modified Method 5 - desired probe and filter temperature, 121°C (250°F) with a water rinse of the probe and analysis for total water soluble sulfate and corresponding mass determination.

[b]Meter volume measured in dry normal cubic meters (dry standard cubic feet).

[c]Average of four sampling trains.

vacuum suddenly dropped. Sampling was immediately discontinued. An examination of the sampling train, revealed a broken glass connector between the back-half filter holder and H_2O_2 impinger. Sample volumes for these runs were corrected for leakage, which caused the nonisokinetic test condition for these runs. As noted in Section 3, the desired sampling time was 120 minutes. Test 4A-D was run for 70 minutes, Test 6A-D for 80 minutes, Test 7C for 90 minutes, and Test 8A for 103 minutes.

4.2 THERMOGRAVIMETRIC ANALYTICAL RESULTS

Table 4-2 presents the thermogravimetric analytical results. The filterable particulate reported in Table 4-2 represents material collected in the sampling probe and on the filter for each sample type (M5, M5B, M5-450). Also reported are the ambient filter weights for samples designated M5W. All weights are reported in milligrams (mg) and sample concentrations in milligrams per dry normal cubic meters (mg/dNm^3).

As previously noted, samples were heat-conditioned at each designated interval for 6 hours, except for select samples that were heated for 24 hours for comparative purposes. Table 4-3 provides within-run comparisons on a total weight basis, and Table 4-4 presents a comparison of weight loss in milligrams above 160°C (320°F). Because of the variability of reported results, an absolute assessment of sample conditioning time (6 hours versus 24 hours) is not possible. Data from Runs 2, 7, and 8 (Table 4-3) indicate no significant difference in weight loss

TABLE 4-2. SUMMARY OF THERMOGRAVIMETRIC ANALYTICAL RESULTS

Test No.	Train ID	Sample type	Filterable particulate following conditioning at indicated temperatures, mg							
			Ambient		160°C (320°F)		232°C (450°F)		316°C (600°F)	
			Probe	Filter	Probe	Filter	Probe	Filter	Probe	Filter
1	1A[a]	M5	73.7	136.3	61.6	134.6	55.3	129.2	51.1	126.6
	1B[a]	M5	18.6	147.3	11.2	146.3	8.2	137.6	7.2	136.8
	1C	M5W	-	113.0	-	-	-	-	-	-
	1D	M5W	-	142.2	-	-	-	-	-	-
2	2A	M5W	-	142.7	-	-	-	-	-	-
	2B	M5W	-	140.1	-	-	-	-	-	-
	2C	M5B	29.0	108.1	16.5	106.2	14.4	106.5	12.6	103.0
	2D[a]	M5B	26.7	136.0	17.4	133.4	14.3	130.6	14.4	129.1
3	3A	M5W	-	253.8	-	-	-	-	-	-
	3B	M5W	-	261.4	-	-	-	-	-	-
	3C[a]	M5	83.9	192.0	-	-	61.8	182.8	61.5	174.6
	3D[a]	M5	40.1	245.8	-	-	20.8	228.1	20.1	227.0
4	4A	M5W	-	152.9	-	-	-	-	-	-
	4B	M5W	-	162.6	-	-	-	-	-	-
	4C[a]	M5B	36.1	126.6	-	-	22.7	114.0	22.3	114.0
	4D	M5B	30.2	148.2	-	-	16.9	143.0	15.3	138.3
5	5A	M5	57.7	235.0	-	-	-	-	38.8	200.3
	5B[a]	M5	24.5	248.6	-	-	-	-	13.5	206.7
	5C	M5W	-	204.7	-	-	-	-	-	-
	5D	M5W	-	244.2	-	-	-	-	-	-
6	6A	M5W	-	171.7	-	-	-	-	-	-
	6B[a]	M5B	24.4	181.8	-	-	-	-	12.3	168.1
	6C	M5B	34.7	150.2	-	-	-	-	18.4	136.3
	6D	M5W	-	172.7	-	-	-	-	-	-
7	7A	M5B	46.5	247.7	37.5	244.5	35.5	237.7	33.3	221.2
	7B	M5B	27.6	250.8	22.1	246.8	20.9	239.7	19.9	218.8
	7C[a]	M5-450	20.9	143.3	13.8	142.4	10.6	128.2	10.4	126.7
	7D	M5-450	24.9	226.6	13.1	224.6	13.2	215.1	12.4	213.1

(continued)

TABLE 4-2 (continued)

Test No.	Train ID	Sample type	Filterable particulate following conditioning at indicated temperatures, mg							
			Ambient		160°C (320°F)		232°C (450°F)		316°C (600°F)	
			Probe	Filter	Probe	Filter	Probe	Filter	Probe	Filter
8	8A[a,b]	M5	53.5	173.4	42.9	170.3	37.6	149.6	36.4	147.2
	8B[b]	M5	339.1	249.2	325.5	245.2	319.5	215.7	318.1	212.5
	8C	M5B	38.5	167.0	25.5	164.4	22.4	162.2	20.8	144.6
	8D[a]	M5B	38.9	209.7	28.7	205.0	25.7	183.4	22.1	180.0
9	9A[a]	M5B	90.1	305.2	-	-	-	-	66.3	286.9
	9B	M5-450	44.2	280.2	-	-	-	-	21.3	269.2
	9C[a]	M5B	35.6	244.5	-	-	-	-	14.1	226.2
	9D	M5-450	43.1	293.6	-	-	-	-	26.9	275.6

[a]Heated for 24 hours; all others heated for 6 hours.

[b]Probe rinse contamination not included in averages.

TABLE 4-3. DIRECT COMPARISON OF PARTICULATE WEIGHTS AT 6- AND 24-HOUR HEAT-CONDITIONING PERIODS

Run No.	Heat time, h	Sample type	Ambient weight,[a] mg	Weight after heating at indicated temperature,[b] mg		
				160°C	232°C	316°C
2C	6	M5B	137.1	122.7 (11)	120.9 (12)	115.6 (16)
2D	24	M5B	162.7	150.8 (7)	144.9 (11)	143.5 (12)
4C	24	M5B	162.7	NA	136.7 (16)	136.3 (16)
4D	6	M5B	178.4	NA	159.9 (10)	153.6 (14)
5A	6	M5	292.7	NA	NA	239.1 (18)
5B	24	M5	273.1	NA	NA	220.2 (19)
6B	24	M5B	206.2	NA	NA	180.4 (13)
6C	6	M5B	184.9	NA	NA	154.7 (16)
7C	24	M5-450	164.2	156.2 (5)	138.8 (15)	137.1 (17)
7D	6	M5-450	251.5	237.7 (5)	228.3 (9)	225.5 (10)
8C	6	M5B	205.5	189.9 (8)	184.6 (10)	165.4 (20)
8D	24	M5B	248.6	233.7 (6)	209.1 (16)	202.1 (19)

[a]Ambient weight (rinse and filter fractions) in milligrams.

[b]Weight after heat treatment at indicated temperature. The numbers in parentheses represent the relative percent weight loss for each heat interval compared with the ambient weights.

NA = Not applicable (see Analytical Plan, Section 3, Page 3-10).

TABLE 4-4. COMPARISON OF WEIGHT LOSSES ABOVE 160°C

Run No.	Sample type	Heating time, h	Ambient weight, mg	Total weight loss to 315°C (600°F), mg	Weight loss above 160°C (320°F), mg
2C	M5B	6	137.1	21.5	7.1
2D	M5B	24	162.7	19.2	7.3
7C	M5-450	24	164.2	27.1	19.1
7D	M5-450	6	251.5	26.0	12.2
8C	M5B	6	205.5	40.1	24.5
8D	M5B	24	248.6	46.5	31.6

at 160°C between the 6- and 24-hour samples. As presented in Table 4-4, however, the samples heated for 24 hours showed higher weight loss above 160°C than those heated for 6 hours regardless of the initial ambient weight. Also, the total weight loss to 315°C (600°F) is comparable (Table 4-4) for each conditioning time. Based on these results, a thermogravimetric conditioning period of at least 6 hours seems appropriate.

Table 4-5 presents a comparison of particulate concentrations after heat conditioning at the indicated temperatures. The average concentrations and standard deviations are given in milligrams per dry normal cubic meter for all samples of a similar type and temperature. The number of data points at each temperature is also shown. Table 4-6 summarizes the relative percent weight loss by sample fraction at the indicated temperatures, and Figure 4-1 graphically depicts these data for Run 7. Table 4-7 summarizes the EPA Method 8* analytical results for sulfuric acid (H_2SO_4) and sulfur dioxide (SO_2).

Data presented in Tables 4-5 and 4-6 for each sample type exhibit the same basic characteristics as samples collected at other FCCU sources and analyzed in a similar manner. The data suggest, however, that biases in particulate measurements caused by sulfuric acid (H_2SO_4) are less significant than observed for samples collected at other FCCU sources evaluated under this task assignment. The ambient concentration of the M5 samples averaged

*40 CFR 60, Appendix A, Reference Method 8, July 1982.

TABLE 4-5. COMPARISON OF FILTERABLE PARTICULATE CONCENTRATION AFTER CONDITIONING AT TEMPERATURES OF 160°, 232°, AND 315°C

Run No.	Sample ID	Ambient		160°C		232°C		315°C	
		Total weight[a], mg	Concentration, mg/dNm³	Total weight, mg	Concentration mg/dNm³	Total weight, mg	Concentration, mg/dNm³	Total weight, mg	Concentration, mg/dNm³
1A	M5	210.0	143.6	196.1	134.1	184.5	126.1	177.7	121.5
1B	M5	165.9	114.3	157.5	108.5	145.8	100.4	144.0	99.2
3C	M5	275.9	112.4	-	-	244.6	99.7	236.1	96.2
3D	M5	285.9	124.0	-	-	248.9	108.0	247.1	107.2
5A	M5	292.7	106.7	-	-	-	-	239.1	87.2
5B	M5	273.1	98.2	-	-	-	-	220.2	79.2
8A	M5	226.9	95.2	213.2	89.4	187.2	78.5	183.6	77.0
8B[b]	M5	588.3	215.1	570.7	208.6	535.2	195.7	530.6	194.0
		Average = 113.5 σ[c] = 16.5 N[d] = 7		Average = 110.7 σ = 22.4 N = 3		Average = 102.5 σ = 17.1 N = 5		Average = 95.4 σ = 15.8 N = 7	
2C	M5B	137.1	110.2	122.7	98.7	120.9	97.2	115.6	92.9
2D	M5B	162.7	132.6	150.8	122.9	144.9	118.1	143.5	117.0
4C	M5B	162.7	104.1	-	-	136.7	87.4	136.3	87.2
4D	M5B	178.4	115.3	-	-	159.9	103.3	153.6	99.3
6B	M5B	206.2	102.7	-	-	-	-	180.4	89.9
6C	M5B	184.9	93.0	-	-	-	-	154.7	77.8
7A	M5B	294.2	103.6	282.0	99.3	273.2	96.2	254.5	89.6
7B	M5B	278.4	97.0	268.9	93.6	260.6	90.8	238.7	83.1
8C	M5B	205.5	79.1	189.9	73.1	184.6	71.1	165.4	63.7
8D	M5B	248.6	91.7	233.7	86.2	209.1	77.1	202.1	74.6
9A	M5B	395.3	138.2	-	-	-	-	354.7	124.0
9C	M5B	280.1	103.2	-	-	-	-	240.7	88.7
		Average = 105.9 σ[c] = 16.7 N[d] = 12		Average = 95.6 σ = 16.5 N = 6		Average = 92.7 σ = 14.8 N = 8		Average = 90.7 σ = 16.8 N = 12	
7C	M5-450	164.2	75.5	156.2	71.8	138.8	63.8	137.1	63.1
7D	M5-450	251.5	88.8	237.7	84.0	228.3	80.6	225.5	79.6
9B	M5-450	324.4	113.6	-	-	-	-	290.5	101.7
9D	M5-450	336.7	117.1	-	-	-	-	302.5	105.2
		Average = 98.8 σ[c] = 20.0 N[d] = 4		Average = 77.9 σ = 8.6 N = 2		Average = 72.2 σ = 11.9 N = 2		Average = 87.4 σ = 19.8 N = 4	

[a]Total filterable catch (probe and filter).

[b]Probe rinse contamination; value not included in group averages.

[c]Standard deviation with N-1 weighting of data.

[d]Number of data points.

TABLE 4-6. FILTERABLE PARTICULATE RELATIVE PERCENT WEIGHT LOSS AFTER CONDITIONING AT TEMPERATURES 160°, 232°, AND 315°C

Run No.	Sample ID	Ambient temperature Conc., mg		160°C (320°F) Conc., mg		160°C (320°F) Wt. loss, %		232°C (450°F) Conc., mg		232°C (450°F) Wt. loss, %		315°C (600°F) Conc., mg		315°C (600°F) Wt. loss, %	
		Rinse	Filter	Rinse	Filter	Rinse	Filter	Rinse	Filter	Rinse	Filter	Rinse	Filter	Rinse	Filter
1A	M5	73.7	136.3	61.5	134.6	17	1	55.3	129.2	25	5	51.1	126.6	31	7
1B	M5	18.6	147.3	11.2	146.3	40	1	8.2	137.6	56	7	7.2	136.8	61	7
3C	M5	83.9	192.0	-	-	-	-	61.8	182.8	26	5	61.5	174.6	27	9
3D	M5	40.1	245.8	-	-	-	-	20.8	228.1	48	7	20.1	227.0	50	8
5A	M5	57.7	235.0	-	-	-	-	-	-	-	-	38.8	200.3	33	15
5B	M5	24.5	248.6	-	-	-	-	-	-	-	-	13.5	206.7	45	17
8A	M5	53.5	173.4	42.9	170.3	20	2	37.6	149.6	30	14	36.4	147.2	32	15
8B[a]	M5	339.1	249.2	325.5	245.2	-	2	319.5	215.7	-	13	318.1	212.5	-	15
2C	M5B	29.0	108.1	16.5	106.2	43	2	14.4	106.5	50	2	12.6	103.0	57	5
2D[a]	M5B	26.7	136.0	17.4	133.4	35	2	14.3	130.6	46	4	14.4	129.1	46	5
4C	M5B	36.1	126.6	-	-	-	-	22.7	114.0	37	10	22.3	114.0	38	10
4D	M5B	30.2	148.2	-	-	-	-	16.9	143.0	44	4	15.3	138.3	49	7
6B	M5B	24.4	181.8	-	-	-	-	-	-	-	-	12.3	168.1	49	8
6C	M5B	34.7	150.2	-	-	-	-	-	-	-	-	18.4	136.3	47	9
7A	M5B	46.5	247.7	37.5	244.5	19	1	35.5	237.7	24	4	33.3	221.2	28	11
7B	M5B	27.6	250.8	22.1	246.8	20	2	20.9	239.7	24	4	19.9	218.8	28	13
8C	M5B	38.5	167.0	25.5	164.4	34	2	22.4	162.2	42	3	20.8	144.6	46	13
8D	M5B	38.9	209.7	28.7	205.0	26	2	25.7	183.4	34	13	22.1	180.0	43	14
9A	M5B	90.1	305.2	-	-	-	-	-	-	-	-	67.8	286.9	25	6
9B	M5B	35.6	244.2	-	-	-	-	-	-	-	-	14.1	226.6	60	7
7C	M5-450	20.9	143.3	13.8	142.4	34	1	10.6	128.2	49	11	10.4	126.7	50	12
7D	M5-450	24.9	226.6	13.1	224.6	47	1	13.2	215.1	47	5	12.4	213.1	50	6
9B	M5-450	44.2	280.2	-	-	-	-	-	-	-	-	21.3	269.2	52	4
9D	M5-450	43.1	293.6	-	-	-	-	-	-	-	-	26.9	275.6	38	6

$$\text{Weight loss} = \frac{\text{Ambient weight} - 160°, 232°, 315°\text{C weight}}{\text{Ambient weight}} \times 100$$

[a]Probe rinse contaminated.

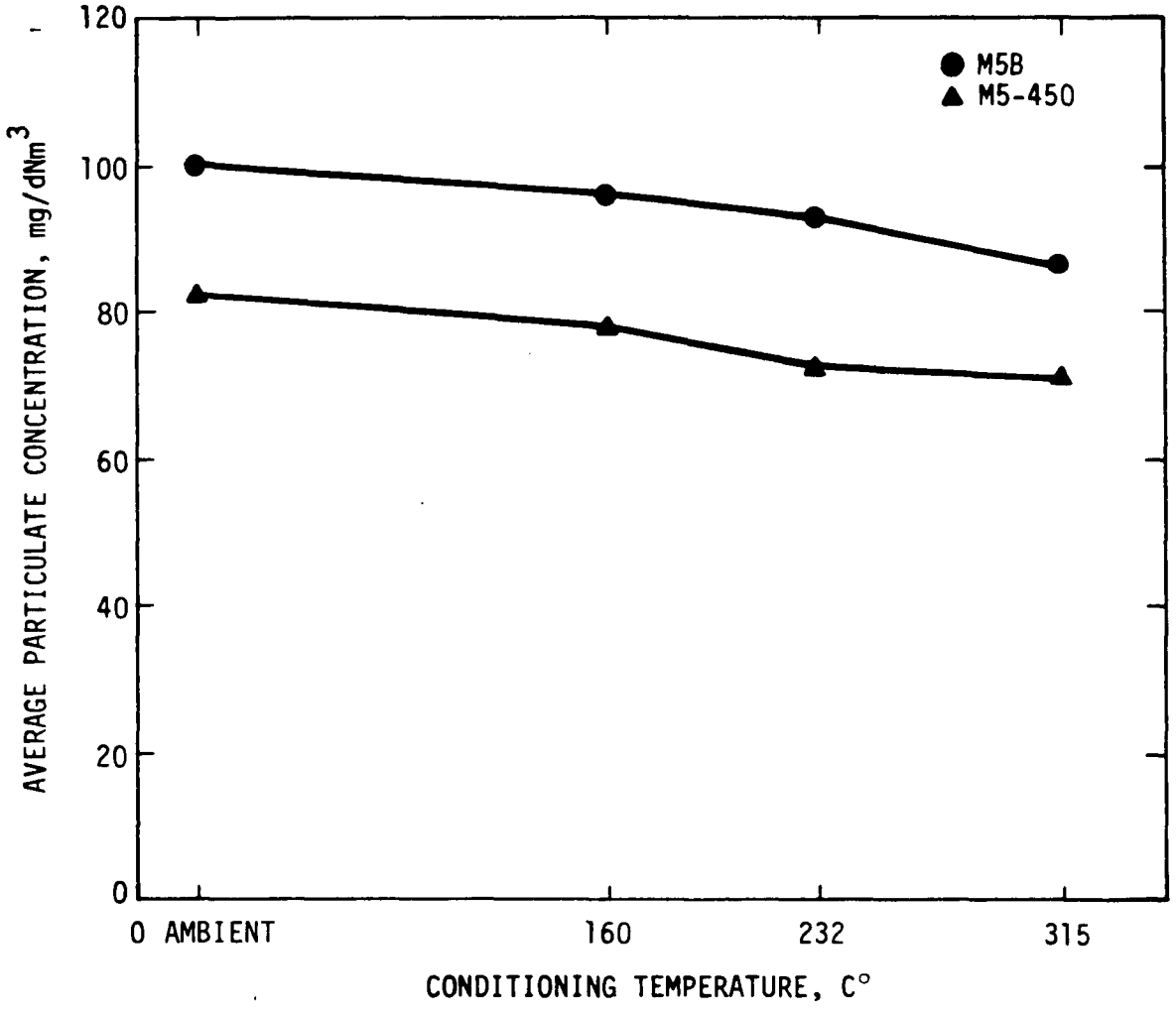

Figure 4-1. Average particulate concentration for Run 7 at indicated sample conditioning temperature.

TABLE 4-7. SUMMARY OF H_2SO_4 AND SO_2 ANALYTICAL DATA

Test No.	Train ID	Sample type	Total H_2SO_4[a]		Total SO_2[b]		Total sulfur	
			mg	mg/dNm³	mg	mg/dNm³	mg	mg/dNm³
1	1A	M5	210	143.8	23.0	15.8	80.2	54.8
	1B	M5	39.7	27.4	37.1	25.6	31.6	21.7
	1C	M5W	74.8	51.9	11.9	8.3	30.4	21.2
	1D	M5W	57.8	39.1	13.5	9.1	25.7	17.4
2	2A	M5W	45.7	33.6	32.0	23.5	31.0	22.7
	2B	M5W	63.0	48.1	8.3	6.3	24.8	18.9
	2C	M5B	63.4	51.1	9.7	7.8	25.6	20.6
	2D	M5B	72.7	59.1	23.2	18.9	35.4	28.8
3	3A	M5W	252	105.9	0.5	<1.0	82.6	34.8
	3B	M5W	253	95.8	2.6	<1.0	84.0	31.8
	3C	M5	137	55.9	1.8	<1.0	45.7	18.6
	3D	M5	179	77.5	1.8	<1.0	59.4	25.8
4	4A	M5W	80.5	50.3	10.5	6.6	31.6	19.8
	4B	M5W	40.2	25.3	15.4	9.7	20.9	13.1
	4C	M5B	59.8	38.3	6.4	4.1	22.8	14.6
	4D	M5B	68.0	43.9	10.4	6.7	27.4	17.7
5	5A	M5	23.2	8.5	414.8	151.4	215	78.4
	5B	M5	12.1	4.4	493.0	177.3	251	90.1
	5C	M5W	-	-	392.8	144.4	197[c]	72.2[c]
	5D	M5W	32.4	12.2	443.0	167.2	232	87.5
6	6A	M5W	22.4	11.1	320.0	159.2	167	83.1
	6B	M5B	25.2	12.5	320.0	159.2	168	83.9
	6C	M5B	17.3	8.7	289.3	145.4	150	75.7
	6D	M5W	27.6	13.9	317.7	160.5	168	84.7
7	7A	M5B	17.3	6.1	525.5	185.0	269	94.6
	7B	M5B	31.1	10.8	525.2	183.0	273	95.1
	7C	M5-450	34.5	15.8	324.2	148.7	174	79.8
	7D	M5-450	45.5	16.1	501.9	177.3	266	94.0
8	8A	M5	23.2	9.8	272.2	114.4	144	60.3
	8B	M5	24.3	8.9	349.3	127.5	183	66.8
	8C	M5B	37.4	14.4	271.4	104.4	148	57.0
	8D	M5B	29.6	10.9	304.1	112.2	162	59.7
9	9A	M5B	320	111.9	358.6	125.4	284	99.3
	9B	M5-450	53.6	18.7	540.9	189.1	288	100.9
	9C	M5B	26.7	9.9	504.6	186.2	261	96.3
	9D	M5-450	24.2	8.4	561.5	195.0	289	100.4

[a]Total H_2SO_4 (SO_3/H_2SO_4 mist) analyzed by ion chromatography. Runs 1 through 4 are considered void because of contamination of sample solutions (see Page 4-15).

[b]Total SO_2 analyzed per Method 8 (40 CFR 60, Appendix A, Reference Method 8, July 1982).

[c]Based on SO_2 values only.

113.5 mg/dNm³ with a standard deviation of 16.5 mg/dNm³, compared with 105.9 mg/dNm³ and 16.7 mg/dNm³ for the M5B runs and 98.8 mg/dNm³ and 20.0 mg/dNm³ for the M5-450 runs. The average ambient M5 concentration was approximately 7 percent higher than the M5B and 15 percent higher than the M5-450 sample concentrations at ambient conditions. Considering the variability in results for each sample type as exhibited by the group standard deviations, the ambient weight results are reasonably comparable for each sample type.

Correspondingly, the M5 concentration after heating to 315°C averaged 95.4 mg/dNm³ with a standard deviation of 15.8 mg/dNm³, compared with 90.7 mg/dNm³ and 16.8 mg/dNm³ for the M5B runs and 87.4 mg/dNm³ and 19.8 mg/dNm³ for the M5-450 runs. On a concentration basis, the M5 runs exhibited a total weight loss averaging 16 percent when heated to 315°C, compared with 14 percent for M5B and 11 percent for M5-450.

In the M5 runs for which gravimetric data are available after heating to 160°C, the maximum relative percent weight loss of the filter fraction was 2 percent, which is comparable to the available M5B and M5-450 filter data (Table 4-6). The percent weight loss of the filter fraction heated to 315°C ranged from 7 to 17 percent for the M5 runs, from 5 to 14 percent for M5B, and from 4 to 12 percent for M5-450. In general, the greater filter weight loss occurred at a conditioning temperature of 232°C. Since the thermogravimetric procedure would be expected to eliminate the H_2SO_4 and associated water at 160°C, the data suggest

that residual H_2SO_4 or other sulfate species not volatilized at 160°C are being eliminated at the higher conditioning temperatures. The probe rinse fraction for each sample type consistently showed higher percent weight losses than the filter fractions, but the total catch in the probe was significantly less than the filter fraction and resulted in a distortion of the rinse weight loss data when compared with the filter data. With few exceptions, the largest percent weight loss from the rinse fractions for each sample type occurred at 160°C and additional losses were consistently observed at the higher conditioning temperatures. Figure 4-1 shows a comparison of the Method 5B data and Method 5-450 data for Run 7. These data show a relatively consistent difference (18 mg/dNm³) at each conditioning temperature. The data also indicate little bias due to sulfuric acid (<5 percent) and little bias due to other condensible matter (<14 percent total weight loss). The average difference of 18 mg/dNm³ between these two methods for this run could be attributable to particulate stratification in the stack (see Section 3).

The Method 8 analytical results for sulfates as H_2SO_4 and SO_2 were shown in Table 4-7. The results of Tests 1 through 4 and 9A are considered void because traces of hydrogen peroxide (H_2O_2) found in the isopropanol sample fractions caused an anomaly in reported results. The IPA fractions were initially titrated per Method 8, but the titrametric end points were difficult to distinguish and results were highly variable. These sample fractions were then reanalyzed by ion chromatography (IC)

and the IC results are reported. The reported SO_2 titrametric results were also checked by IC and these results compared favorably. Although the H_2SO_4 and SO_2 data for Tests 1 through 4 are considered void, the total sulfur measured in the back half of the sampling train should not be affected by the presence of H_2O_2 in the IPA. Note that the total sulfur reported for Tests 1 through 4 is less than that reported for Tests 5 through 9; thus, the increase in total sulfur is probably due to process variation or minor upset condition. This increase in total sulfur for Runs 5 through 9 corresponds to an overall increase in the filterable particulate catch for each sample type in these tests. No significant difference was noted in the weight loss for these samples, however, compared with data from Runs 1 through 4. The total amount of H_2SO_4 measured during Runs 5 through 9 is significantly less than the H_2SO_4 measured at similar sources evaluated under this task assignment. Also, no consistent correlation exists between increased sample temperature and a corresponding increase in back-half H_2SO_4 content for these sample runs. The H_2SO_4 catch averaged 23.5 mg during the M5 and M5W runs compared with 26.3 mg during the M5B runs. During the M5-450 runs, H_2SO_4 averaged 39.5 mg in the back half, but the variability in reported results (7C and D and 9B and D) and the limited amount of data preclude making an accurate assessment of sample temperature and back-half H_2SO_4 content.

Tables 4-8 and 4-9 present precision estimates for the heat treatments evaluated. In Table 4-8, each group represents two

TABLE 4-8. STATISTICAL DATA FOR GROUPED RUNS AFTER CONDITIONING AT INDICATED TEMPERATURES

Run No.	Sample type	$\bar{X}$,[a] mg/dNm³	Ambient σ,[b] mg/dNm³	CV,[c] %	160°C (320°F)			232°C (450°F)			316°C (600°F)		
					$\bar{X}$, mg/dNm³	σ, mg/dNm³	CV, %	$\bar{X}$, mg/dNm³	σ, mg/dNm³	CV, %	$\bar{X}$, mg/dNm³	σ, mg/dNM³	CV, %
1A-B	M5	129.0	20.7	16.1	121.3	18.1	14.9	113.3	18.2	16.1	110.4	15.8	14.3
3C-D	M5	118.2	8.2	6.9	-	-	-	103.9	5.9	5.7	101.7	7.8	7.7
5A-B	M5	102.5	6.0	5.9	-	-	-	-	-	-	83.2	5.7	6.9
8A-B[d]	M5	-	-	-	-	-	-	-	-	-	-	-	-
2C-D	M5B	121.4	15.8	13.0	110.8	17.1	15.4	107.7	14.8	13.7	105.0	17.0	16.2
4C-D	M5B	109.7	7.9	7.2	-	-	-	95.4	11.2	11.7	93.3	8.6	9.2
6B-C	M5B	97.9	6.9	7.0	-	-	-	-	-	-	83.9	8.6	10.3
7A-B	M5B	100.3	4.7	4.7	96.5	4.0	4.2	93.5	3.8	4.1	86.4	4.6	5.3
8C-D	M5B	85.4	8.9	10.4	79.7	9.3	11.7	74.1	4.2	5.7	69.2	7.7	11.1
9A-C	M5B	120.7	24.7	20.5	-	-	-	-	-	-	106.4	25.0	23.5
7C-D	M5-450	82.2	9.4	11.4	77.9	8.6	11.1	72.2	11.9	16.5	71.4	11.7	16.4
9B-D	M5-450	115.4	2.5	2.2	-	-	-	-	-	-	103.5	2.5	2.4

[a]Mean filterable concentration.

[b]Within-run standard deviation with N-1 weighting for sample data.

[c]Coefficient variance is the standard deviation expressed as a percent of the mean concentration.

[d]Run 8B considered void due to probe rinse contamination. Runs 8A and B excluded from statistical analysis.

TABLE 4-9. SUMMARY OF PRECISION ESTIMATES AFTER CONDITIONING AT INDICATED TEMPERATURES

Run No.	Sample type	Ambient			160°C (320°F)			232°C (450°F)			316°C (600°F)		
		$\overline{X}$,[a] mg/dNm³	σ,[b] mg/dNm³	$\overline{CV}$,[c] %	$\overline{X}$, mg/dNm³	σ, mg/dNm³	$\overline{CV}$, %	$\overline{X}$, mg/dNm³	σ, mg/dNm³	$\overline{CV}$, %	$\overline{X}$, mg/dNm³	σ, mg/dNM³	$\overline{CV}$, %
1,3,5	M5	116.5	11.6 N[d] = 6	10.0	121.3	18.1 N = 2	14.9	108.6	12.1 N = 4	11.1	98.4	9.8 N = 6	9.9
2,4,6, 7,8,9	M5B	105.9	11.5 N = 12	10.8	95.6	10.1 N = 6	10.6	92.7	8.5 N = 8	9.2	90.7	11.9 N = 12	13.1
7,9	M5-450	98.8	6.0 N = 4	6.0	77.9	8.6 N = 2	11.0	72.2	11.9 N = 2	16.5	87.4	7.1 N = 4	8.1

[a]Mean filterable concentration based on grouped run values. Test No. 8 not included in calculations.

[b]Mean standard deviation of grouped runs ($\frac{\Sigma\sigma i}{N}$).

[c]Mean coefficient variation (percent) calculated using the mean standard deviation and the filterable concentration of grouped runs.

[d]N = Number of data points.

simultaneous runs of the same sample. Presented for each run group and temperature are the mean filterable concentration, the standard deviation with N-1 weighting for sample data, and the percent coefficient of variation (CV), which expresses the standard deviation as a percent of the mean concentration. Table 4-9 summarizes precision estimates for M5, M5B, and M5-450 test data at each conditioning temperature. The mean filterable concentrations were calculated by averaging the individual run data to minimize roundoff errors. The mean standard deviations were calculated by averaging standard deviation values for each set of grouped runs (Table 4-8) to minimize the effect of temporal variation in emissions. In this way, the mean standard deviation of the grouped runs ($\bar{\sigma}$ in Table 4-9) more accurately reflects method precision than does the standard deviation of individual run concentrations ($\bar{\sigma}$ in Table 4-5). The number of data points included in each calculation is shown to assist in evaluating the precision estimates.

The mean standard deviation for three M5 run groups (Runs 8A and B excluded) was 11.6 mg/dNm^3 at ambient conditions, which corresponds to a mean coefficient of variation (CV) of 10.0 percent. The six M5B run groups had a mean standard deviation of 11.5 mg/dNm^3 and a corresponding mean CV of 10.8 percent at ambient conditions. The two M5-450 run groups had a mean standard deviation of 6.0 mg/dNm^3 and a corresponding mean CV of 6.0 percent at ambient conditions.

The mean standard deviation for one M5 run group heated to 160°C (320°F) was 18.1 mg/dNm³, and the corresponding CV was 14.9 percent. For the three M5B run groups heated to 160°C, the mean standard deviation and CV were 10.1 mg/dNm³ and 10.6 percent, respectively. The one M5-450 run group heated to 160°C showed a mean standard deviation of 8.6 mg/dNm³ and a CV of 11.0 percent.

Precision data for the two M5 run groups heated to 232°C (450°F) included a mean standard deviation of 12.1 mg/dNm³ and a CV of 11.1 percent. For the four M5B run groups, the average standard deviation and CV were 8.5 mg/dNm³ and 9.2 percent. The one M5-450 run showed a mean standard deviation of 11.9 mg/dNm³ and a CV of 16.5 percent.

Precision data for the three M5 groups heated to 316°C (600°F) included a mean standard deviation of 9.8 mg/dNm³ and a CV of 9.9 percent. Two of the three run groups had a mean standard deviation of less than 8.0 mg/dNm³ and a corresponding CV of less than 8 percent. For the M5B samples, the mean standard deviation and CV were 11.9 mg/dNm³ and 13.1 percent, respectively. Four of the six M5B runs, however, had a mean standard deviation of less than 9 mg/dNm³ and a corresponding CV of less than 10 percent. For the M5-450 runs, the mean standard deviation and CV were 7.1 mg/dNm³ and 8.1 percent.

All of these statistical results indicate a variable degree of precision for the majority of samples. Generally, the within-run agreement was expected to improve after each stage of heat treatment due to elimination of sulfate biases. The precision

estimates for each sample type remained relatively consistent, however, and actually decreased in some cases, particularly at the conditioning temperatures of 160° and 232°C. At 315°C, the precision estimates were comparable to those obtained at ambient conditions for each sample type. As noted in Section 3, the scrubber outlet gas stream contained waste droplets and exhibited cyclonic flow conditions as determined by plume observation and turbulent flow data obtained by means of procedures described in EPA Reference Method 2.* As a result of these flow conditions, spatial and temporal variations in gas velocity and particulate concentration could have affected the within-run precision and thus increased the degree of variability in reported results.

4.3 WATER-SOLUBLE SULFATE ANALYTICAL DATA

Table 4-10 summarizes results from the water-soluble sulfate analysis performed on the indicated samples. Because particulate cannot be determined gravimetrically in the presence of sulfuric acid due to the inexact amount of water retained by the acid, the method is designed to convert the acid to a nonhydroscopic, nonvolatile product--in this case ammonium sulfate. The acid is converted to ammonium sulfate, and the weight of ammonium sulfate formed is subtracted from the total weight. The reported values represent the particulate concentration corrected for total water-soluble sulfates determined by ion chromatography. The TACB method also allows the use of a barium perchlorate titration, as described in EPA Method 6.* Previous studies have shown

*40 CFR 60, Appendix A, Reference Methods 2 and 6, July 1983.

TABLE 4-10. SUMMARY OF WATER-SOLUBLE SULFATE ANALYTICAL RESULTS

Test No.	Sample ID	Total NWSSP,[a] mg	Concentration, mg/dNm³	Statistical data for grouped runs		
				$\overline{X}$,[b] mg/dNm³	$\overline{\sigma}$,[c] mg/dNm³	$\overline{CV}$,[d] %
1C	M5W	105.2	73.3	79.6	8.8	11.1
1D	M5W	126.7	85.8			
2A	M5W	131.5	96.6	98.3	2.3	2.4
2B	M5W	130.8	99.9			
3A	M5W	239.6	100.9	94.1	9.6	10.2
3B	M5W	230.7	87.3			
4A	M5W	147.5	92.3	91.0	1.9	2.1
4B	M5W	142.0	89.6			
5C	M5W	162.3	59.6	69.8	14.4	20.7
5D	M5W	212.2	80.0			
6A	M5W	152.2	75.6	76.8	1.7	2.2
6D	M5W	154.6	78.0			
	Average = 84.9 σ = 12.2 N = 12					

[a]Total non-water-soluble sulfate particulate matter (probe and filter fractions) determined by the modified Texas Air Board analytical method.

[b]Mean filterable concentration.

[c]Standard deviation with N-1 weighting of data.

[d]Coefficient of variance is the standard deviation expressed as a percentage of the mean concentration.

that titrametric and IC analyses yield comparable results.[6,7] Section 3 and Appendix D of this report detail the sample preparation and analytical techniques as well as equipment and reagents used to perform this analysis. Appendix C contains analytical data for this method.

The M5W sample runs showed an average concentration of 84.9 mg/dNm³ and a standard deviation of 12.2 mg/dNm³. Statistical data for grouped runs exhibited an acceptable degree of precision, as characterized by a mean standard deviation of 6.5 mg/dNm³ and a corresponding mean coefficient of variation (CV) of 7.6 percent. A comparison of the M5W results with the thermogravimetric results for M5 and M5B at 315°C (concentration basis) shows that the M5W results averaged 81.2 mg/dNm³ during Runs 1, 3, and 5, whereas the M5 results averaged 98.4 mg/dNm³ during the same runs. In Runs 2, 4, and 6, the average values were 88.7 mg/dNm³ for M5W and 94.0 mg/dNm³ for M5B. No direct comparison with M5-450 is possible; however, the overall average M5-450 concentration at 315°C of 87.4 mg/dNm³ compares favorably with the average M5W concentration of 84.9 mg/dNm³.

These data are consistent with the basic principle of the thermogravimetric procedure in that only H_2SO_4 and associated water are removed by heating at 160°C, whereas additional sulfate species (metal sulfates, ammonium sulfate, and possibly some residual H_2SO_4) could not be removed. If these other sulfate species were water-soluble, the expected M5W results would be

lower because the method is designed to correct for total water-soluble sulfate, which includes H_2SO_4.

In an effort to characterize this difference, the within-run heat-conditioned samples were extracted with water, and aliquots were analyzed by ion chromatography (IC) for residual water-soluble sulfates as $SO_4^{=}$. Table 4-11 presents the results of the within-run residual sulfate analysis. As shown, both the rinse and filter fractions contained residual sulfate ranging from 2.0 to 15.3 mg in the probe fraction and from 5.2 to 28.2 mg in the filter fraction. All samples exhibited the same basic characteristics; i.e, residual water-soluble sulfate was found in each sample fraction.

The particulate concentrations of samples conditioned to 315°C were corrected for residual sulfate and compared against the M5W results. Table 4-12 summarizes the comparative data. The M5 samples in Runs 1, 3, and 5, averaged 90.2 mg/dNm³, compared with 81.2 mg/dNm³ for M5W. The M5B samples in Runs 2, 4, and 6 averaged 83.2 mg/dNm³ compared with 88.7 mg/dNm³ for M5W. Considering the variability in reported results because of source conditions, the overall complexity of the M5W sample analysis, and the number of analytical steps involved in the thermogravimetric and IC procedures, the data presented in Table 4-12 show that the M5W results are comparable to the M5 and M5B results heated to 315°C and corrected for residual sulfate. These data substantiate the general conclusion that the primary difference in particulate concentrations between samples heat-conditioned to

TABLE 4-11. SUMMARY OF RESULTS FOR RESIDUAL SULFATE ($SO_4^=$) IN WITHIN-RUN SAMPLES CONDITIONED AT 315°C

Sample ID	Sample type[a]	Residual sulfate as $SO_4^=$[b]		
		Probe, mg	Filter, mg	Total, mg
1A	M5	15.3	9.6	24.9
1B	M5	2.0	6.1	8.1
2C	M5B	2.4	5.4	7.8
2D	M5B	3.5	11.4	14.9
3C	M5	4.0	9.4	13.4
3D	M5	5.3	11.5	16.8
4C	M5B	4.1	5.2	9.3
4D	M5B	3.2	13.7	16.9
5A	M5	14.0	11.7	25.7
5B	M5	3.0	8.9	11.9
6B	M5B	3.0	28.2	31.2
6C	M5B	2.1	25.5	27.6

[a]These samples, previously heat conditioned to ≧315°C, were extracted with water and analyzed for total sulfate ($SO_4^=$) with ion chromatography (IC).

[b]Total sulfate ($SO_4^=$) determined by IC from aliquots of probe rinse and filter fractions.

TABLE 4-12. COMPARISON OF WITHIN-RUN PARTICULATE CONCENTRATION AFTER CORRECTION FOR RESIDUAL SULFATE TO THE M5W TEST RESULTS

Sample ID	Uncorrected particulate concentration,[a] mg/dNm³	Corrected particulate concentration,[b] mg/dNm³
1A M5	121.5	104.4
1B M5	99.2	93.6
1C M5W	NA[c]	73.3
1D M5W	NA	85.8
2A M5W	NA	96.6
2B M5W	NA	99.9
2C M5B	92.9	86.6
2D M5B	117.0	104.8
3A M5W	NA	100.9
3B M5W	NA	87.3
3C M5	96.2	90.7
3D M5	107.2	99.9
4A M5W	NA	92.3
4B M5W	NA	89.6
4C M5B	87.2	81.2
4D M5B	99.3	88.3
5A M5	87.2	77.8
5B M5	79.2	74.9
5C M5W	NA	59.6
5D M5W	NA	80.0
6A M5W	NA	75.6
6B M5B	89.9	74.3
6C M5B	77.8	63.9
6D M5W	NA	78.0

[a]The uncorrected concentrations for M5 and M5B samples are calculated concentrations after conditioning at 315°C.

[b]The corrected particulate concentrations for the M5 and M5B samples were calculated by subtracting the weight of residual sulfate as $SO_4^=$ (Table 4-11) from the total catch at 315°C and dividing by the sample volume.

[c]Not applicable.

315°C and the calculated M5W results represents water-soluble sulfate species not removed by thermal treatment. As a further check, the remaining M5, M5B, and M5-450 sample fractions were extracted with water and analyzed by IC for residual sulfate. These data, which are summarized in Table 4-13, exhibit similar characteristics to the data presented in Tables 4-10, 4-11, and 4-12. Residual sulfate as $SO_4^=$ was found in each sample and ranged from 1.7 to 23.2 mg in the rinse fraction and 9.6 to 32.8 mg in the filter fraction.

In the characterization of sulfate species other than H_2SO_4, extracts of samples from each sample type were analyzed by ICP for cations; the results of this analysis are presented in Table 4-14.

A 40-element ICP scan was determined. Four nonmetals were included in this list: boron, phosphorous, silicon, and sulfur. Sulfur was converted to the equivalent amount of sulfate. The results are presented in Table 4-15. Twenty elements were below 0.01 mg/liter or not detected, and nine others were less than 0.1 mg/liter. These nine elements were cadmium, cobalt, copper, lithium, molybdenum, nickel, strontium, titanium, and vanadium. At 0.1 mg/liter, the contribution of these elements is insignificant compared with that of sodium at 5 mg/liter. The agreement of the sulfate values obtained on the IC and by ICP is good when one considers the ability of ICP to detect sulfur.

Table 4-16 presents the charge balance for the 16 samples analyzed by ICP. Calculations of this charge balance are based

TABLE 4-13. SUMMARY OF RESULTS FOR RESIDUAL SULFATE ($SO_4^=$) ON SAMPLES CONDITIONED AT 315°C

Run No.	Sample[a] ID	Total sulfates as $SO_4^=$, mg Rinse	Filter	Total[b] residual sulfate ($SO_4^=$), mg	Particulate[c] concentration, mg/dNm³ Uncorrected	Corrected
7A	M5B	13.8	19.0	32.8	89.6	78.1
7B	M5B	5.1	14.2	19.3	83.1	76.4
7C	M5-450	1.7	9.6	11.3	63.1	57.8
7D	M5-450	3.0	11.1	14.1	79.6	74.6
8A	M5	14.7	10.7	25.4	77.0	66.4
8B[d]	M5	2.4	18.4	20.8	194.0[d]	186.3[d]
8C	M5B	2.7	9.6	12.3	63.7	58.9
8D	M5B	8.1	13.4	21.5	74.6	66.6
9A	M5B	23.2	32.8	56.0	124.0	104.4
9B	M5-450	5.0	25.8	30.8	101.7	90.9
9C	M5B	2.1	28.4	30.5	88.7	77.4
9D	M5-450	9.7	30.2	39.9	105.2	91.3

[a]These samples, previously heat-treated at 315°C, were extracted with water and analyzed for total sulfate ($SO_4^=$) by IC.

[b]Total residual sulfate is the summation of the rinse and filter fraction in mg.

[c]The uncorrected concentrations represent rinse and filter catch after heat conditioning at 315°C. The corrected values represent particulate concentration after adjusting the sample fractions for the $SO_4^=$ values obtained by IC analysis.

[d]Probe rinse contaminated.

TABLE 4-14. CATIONS FOUND IN WATER EXTRACTION BY ICP

Sample ID	Sample type	Metal, mg						
		Al^{+3}	Ca^{+2}	Fe^{+3}	K^{+}	Mg^{+2}	Na^{+}	Zn^{+2}
5A Probe rinse	M5	<0.01	0.14	<0.01	0.05	<0.01	7.20	0.06
5A Filter	M5	0.28	0.65	0.07	<0.01	0.32	2.75	0.03
5B Probe rinse	M5	<0.01	0.08	<0.01	0.02	0.01	1.42	0.06
5B Filter	M5	0.22	0.85	0.03	0.09	0.04	1.78	0.02
5C Probe rinse	M5W	<0.03	0.14	<0.01	0.12	<0.02	1.70	0.13
5C Filter	M5W	0.03	0.58	0.01	0.58	0.22	8.50	<0.01
5D Probe rinse	M5W	0.05	0.24	0.13	0.76	0.10	5.06	0.11
5D Filter	M5W	0.04	0.42	0.01	0.52	0.15	9.50	<0.01
6A Probe rinse	M5W	0.06	0.29	0.04	1.12	0.13	8.94	0.15
6A Filter	M5W	0.78	0.48	0.10	0.04	0.02	1.58	0.01
6B Probe rinse	M5B	0.01	0.11	0.01	0.28	0.05	1.32	0.05
6B Filter	M5B	0.04	0.30	0.04	0.14	0.06	10.75	0.01
6C Probe rinse	M5B	0.01	0.06	0.02	0.01	0.01	0.86	0.05
6C Filter	M5B	<0.01	0.30	<0.01	0.02	0.18	10.25	<0.01
6D Probe rinse	M5W	<0.03	0.17	0.17	0.18	<0.02	3.44	0.10
6D Filter	M5W	1.08	0.45	0.12	0.25	0.09	1.35	0.01

TABLE 4-15. SOLUBLE SULFATE PRESENT IN SAMPLE ANALYZED BY ICP

Sample ID	IC sulfate, mg		ICP sulfate, mg	
	Probe rinse	Filter	Probe rinse	Filter
5A M5	14.0	11.1	13.2	10.5
5B M5	3.0	8.9	2.8	6.7
5C M5W	3.9	38.2	4.4	27.7
5D M5W	14.3	39.1	11.6	29.2
6A M5W	17.2	24.8	14.6	21.0
6B M5B	3.0	28.2	2.8	24.7
6C M5B	2.1	25.5	2.2	23.2
6D M5W	13.1	27.2	11.9	25.5

TABLE 4-16. CHARGE BALANCE RESULTS FOR SAMPLES ANALYZED BY ICP

Sample ID	Charge balance[a]	
	Probe rinse	Filter
5A M5	1.11	0.93
5B M5	1.10	0.82
5C M5W	1.09	0.55
5D M5W	0.93	0.57
6A M5W	1.28	0.36
6B M5B	1.25	0.85
6C M5B	1.03	0.90
6D M5W	0.63	0.39

[a]Milliequivalents cations/milliequivalents sulfate.

on each cation having the charge listed in Table 4-14 and all sulfate presented as SO_4^{-2}. The values for the M5W filter samples averaged 0.47 and 0.98 for the probe rinse samples. These values indicate that possibly 53 percent of the sulfate on the filter is present as sulfuric acid and less than 2 percent of the probe rinse sulfate is sulfuric acid. This is in direct contrast to the M5 and M5B sample after heat-conditioning at 315°C, in which the average charge balance for the probe rinse was 1.12; this value is close enough to 1.00 at these low levels to lead to the conclusion that the remaining sulfate is present as metal salts. The average charge balance for the M5 and M5B filters is 0.88, which means either that 88 percent of the sulfate is present as metal sulfates or that some of the metal salts are present as bisulfates, which would account for the charge balance being less than 1.00.

The results of the charge balances for the samples collected at this site, although similar for the filters, differ considerably for the probe rinse samples from those collected at previous sites[6,7] that did not have a scrubber as part of the emission control system. The charge balance for the filter samples averaged 0.44 and 0.54 for the previous sites[6,7] compared with 0.47 for this site. The probe rinse samples averaged 0.11 and 0.09 for the previous sites[6,7] compared with 0.98 for this scrubbed source. The charge balance for the probe rinse portions of these runs shows that the sulfates are present as metal salts rather

than sulfuric acid. This is consistent with the thermogravimetric results, which showed a smaller percent weight loss upon heat conditioning than in previous studies. The residual sulfate remaining after heat conditioning of these samples was also significantly higher than in previous studies.

4.4 RECOMMENDATIONS FOR SAMPLING AND ANALYTICAL METHODOLOGY

Data in this study show that emissions from this scrubber-controlled FCCU unit are considerably different from emissions from ESP-controlled FCCU units. Compared with the two previous sites,[6,7] which were ESP-controlled FCC units, the scrubber-controlled unit showed the following variations:

1) Less condensible H_2SO_4 collection; i.e., lower percentage weight loss upon heating.

2) The percent weight losses of M5, M5B, and M5-450 are comparable rather than widely different as in previous studies.

3) Considerably lower H_2SO_4 and SO_2 concentrations were determined in the back half of the sampling train.

4) Considerably more residual sulfate remained in the heat-conditioned particulate samples.

5) The M5W results are considerably lower than the thermogravimetric results before correction for residual sulfate.

6) The cation concentration, especially sodium, found in the extracts of the heat-conditioned samples is significantly higher for this site.

After allowances were made for the sampling difficulties cited in Section 3 of this report, these data indicate that although the scrubber reduces concentrations of sulfuric acid and SO_2, it also increases the relative amount of metal sulfates that contributes to the particulate catch and is not removed by

thermal conditioning. The EPA has stated that the intent of the NSPS for particulate emissions from FCC units is to control "catalyst fines" or "mineral dust" and not the condensible sulfates that are present in the gas phase at the control device operating temperature. Emissions from fluid catalytic cracking and thermoform catalytic cracking units are known to contain sulfur oxides; therefore, sulfuric acid (H_2SO_4) and/or its metal and ammonium salts are the most probable forms of water-soluble sulfates. Water-soluble sulfate exists in many complex chemical forms, the most common being sulfuric acid. The results of this study show that H_2SO_4 is a significant sulfate species in the FCCU emission stream, and metal sulfates (primarily sodium) constitute another significant water-soluble sulfate species. Therefore, a particulate sampling method designed to minimize the collection of residual H_2SO_4 immediately prior to gravimetric analysis is not sufficient to minimize potentially high biases in particulate measurements from this type of source.

It is evident that sample temperature affects the retention of condensible sulfate (H_2SO_4 in this case) material in the front half of the standard Method 5 sampling train, but sulfuric acid is not necessarily the predominant sulfate species in a scrubber-controlled source.

From an analytical standpoint, the thermogravimetric procedure is the easiest and least expensive technique for reducing H_2SO_4 bias on rinse and filter samples collected at this source. The analytical data indicate that H_2SO_4 and its associated water

are significantly reduced by heating sample fractions to at least 160°C (320°F) prior to gravimetric analysis. Observed weight losses at higher treatment temperatures (which are significant for these samples) are primarily attributable to the volatilization of residual H_2SO_4 and other water-soluble sulfates not removed by heating at 160°C. The results of the water-soluble sulfate analysis of selected samples support this conclusion. The average particulate concentrations in M5, M5B, and M5-450 samples conditioned to 315°C and corrected for residual water-soluble sulfate (as determined by ion chromatography) compared within 10 percent of the M5W results.

Based on the results of this and similar studies,[2-7] PEDCo offers the following recommendations relative to the sampling and analytical methodology for particulate measurement at FCCU sources.

4.4.1 Texas Air Control Board Method

The results of this study show that the Texas Air Control Board (TACB) method entitled "Determination of Particulate in Stack Gases Containing Sulfur Dioxide" is applicable to these sources. Modifications to procedures detailed in the TACB method are presented in Section 3 and Appendix D of this report. A copy of the method as received from the TACB is presented in Appendix D.

Prior to analyzing field samples, PEDCo conducted an extensive laboratory evaluation of the method. The experimental design and the results of this study are described in a separate

method evaluation report issued under this task assignment. This method entails the use of the sampling procedures and temperature [121°C (250°F)] described in EPA Reference Method 5, except that deionized, distilled water is used instead of acetone as the rinse reagent. The method converts any sulfuric acid present to a suitable form for accurate gravimetric analysis. Ammonium hydroxide is added to form ammonium sulfate in the aqueous solutions. The procedure allows for the determination of gross particulate (sulfate as ammonium sulfate and other particulate), the determination of sulfate as ammonium sulfate from a Method 6 titration or ion chromatography, and subsequently, the determination of non-water-soluble sulfate particulate by the subtraction of sulfate (as ammonium sulfate) from the gross particulate. No direct comparison between this method and the thermogravimetric procedures is possible because the method corrects for total water-soluble sulfate (including H_2SO_4), whereas the thermogravimetric procedure corrects primarily for H_2SO_4 and associated water. The fact that the average heat-treated sample concentrations corrected for residual water-soluble sulfate compare within 10 percent of the calculated M5W concentration explains the consistently lower values obtained by M5W compared with the heat-treated samples. Obviously, because this method corrects for total water-soluble sulfate, the particulate results obtained are expected to be equal to or lower than those in samples collected at the same or higher temperature and analyzed thermogravimetrically, regardless of treatment temperature. Considering the

overall complexity of the analytical procedure, the precision and accuracy of the method are exceptionally good, as characterized by a standard deviation of 6.5 mg/dNm³ and a relative standard deviation of 7.6 percent for this set of data.

4.4.2 Modified Method 5

Because of the complexity of the TACB analytical procedure, an alternative methodology incorporating higher sampling temperatures in conjunction with the thermogravimetric analysis seems appropriate if not totally sufficient to remove the sulfate bias. Sampling and analytical procedures contained in EPA Reference Method 5 are recommended, with the following modifications, to determine particulate emissions from sources of this type:

1. Sample collection temperatures should be maintained at no less than 160°C (320°F), and the probe and filter temperature should be monitored directly by thermocouple leads located at the exit of the sample probe and immediately behind the filter frit. Most commercially available stack sampling equipment is capable of maintaining front-half temperatures of 160°C (320°F); however, sampling at temperatures above 205°C (400°F) will probably require equipment modifications to ensure maintenance of the temperature required and the integrity of sampling train components.

2. Prior to the gravimetric analysis, probe rinse and filter fractions should be heated in an oven at not less than 160°C (320°F) (higher temperatures would be preferable) for 6 hours or more. Prior to weighing, sample fractions should be allowed to cool in a desiccator for approximately 2 hours and weighed according to the constant weight criteria detailed in Reference Method 5.

3. These results also indicate that the combination train (Reference Methods 5 and 8) may not yield accurate results for particulate and H_2SO_4 unless the probe and filter temperatures are considerably higher than 160°C (320°F). The data indicate that the combination Reference Methods 5 and 8 train can be used to sample for

particulate and SO_2 simultaneously, provided the train is air-purged for at least 15 minutes after testing is completed to remove the SO_2 adsorbed in the IPA.

SECTION 5

QUALITY ASSURANCE

Because the goal of testing is to produce representative emission results, quality assurance is one of the main facets of stack sampling. Quality assurance guidelines provide the detailed procedures and actions necessary for defining and producing acceptable data. Four such documents were used in this test program to ensure the collection of acceptable data and to provide a definition of unacceptable data. The following documents comprise this source-specific test plan prepared by PEDCo and reviewed by the Emission Measurement Branch: the EPA Quality Assurance Handbook Volume III, EPA-600/4-77-027; the PEDCo Environmental Emission Test Quality Assurance Plan; and the PEDCo Environmental Laboratory Quality Assurance Plan. The last two, which are PEDCo's general guideline manuals, define the company's standard operating procedures that are routinely followed by the emission testing and laboratory groups. In addition, data obtained from similar test programs conducted under this task assignment were utilized to assess the between-source analytical trends of the methods employed.

Appendix F provides more detail on the quality assurance procedures, such as QA objective; data reduction; quality control

checks; performance and system audits; preventive maintenance; precision, accuracy, and completeness; corrective action; and quality assurance reports to management.

The following steps were taken in this specific test program to ensure that the testing and analytical procedures produced quality data.

- Calibration of all field sampling equipment. (Appendix E describes calibration guidelines in more detail.)
- Checks of train configuration and calculations.
- Onsite quality assurance checks such as leak checks on the sampling train, pitot tube, and Orsat line and quality assurance checks of all test equipment prior to use.
- Use of designated analytical equipment and sampling reagents.

Table 5-1 lists the sampling equipment used and the calibration guidelines and limits. In addition to the pre- and post-test calibrations, a field audit was performed on the meter consoles used for sampling. PEDCo constructed critical orifices for use in this audit. Figures 5-1 through 5-4 show example audit runs for each dry gas meter used for testing. Onsite calculations were performed for each test run to ensure isokinetic sampling sites. Pertinent test data were compared with expected values as an additional validation check.

As a check on the reliability of the thermogravimetric analytical procedure, sets of blank filters and acetone were resubmitted to the laboratory for blank analysis. Table 5-2 presents example results of the thermogravimetric blank analysis.

TABLE 5-1. FIELD EQUIPMENT CALIBRATION

Equipment	Train	ID No.	Calibrated against	Allowable deviation	Actual deviation	Within allowable limits	Comments
Meter box	A	FB-2	Wet test meter	Y ±0.05 Y pre-test	+0.001	X	
				ΔH @ ±0.15	-0.02	X	
				(Y ±0.05 Y post-test)	-0.001	X	
	B	FB-3			+0.005	X	
					-0.04	X	
					+0.013	X	
	C	FB-5			+0.006	X	
					-0.07	X	
					+0.002	X	
	D	FB-6			+0.002	X	
					-0.03	X	
					+0.02	X	
Pitot tube	A&B	402	Geometric specifications	See Appendix E	0.0	X	CP = 0.84
	C&D	401			0.034	X	
		250			0.034	X	
Digital indicator	A&B	124	Millivolt signals	0.5%	0.37%	X	
	C&D	125			0.23%	X	
Thermocouple	A&B	178	ASTM-2F	±1.5% (±2% saturated)	-0.4	X	
	C&D	121			1.2	X	
		206			1.2	X	
Orsat analyzer	All	145	Standard gas	±0.5%	-0.25%	X	CO_2
					0.0%	X	O_2

(continued)

TABLE 5-1 (continued)

Equipment	Train	ID No.	Calibrated against	Allowable deviation	Actual deviation	Within allowable limits	Comments
Impinger thermometer	A	391	ASTM-2F	±2°F	0°F	X	
	B	452			-1°F	X	
	C	390			2°F	X	
	D	451			-2°F	X	
Balance	All	196	Type S weights	±0.5 g	+0.25 g	X	
Barometer	All	229	NBS traceable barometer	±0.10 in.Hg (0.20 post-test)	0.0 in.Hg	X	
Dry gas thermometer	A	FB-6 inlet	ASTM-2F	±5°F	-1°F	X	
		FB-6 outlet			+1°F	X	
	B	FB-3 inlet			-3°F	X	
		FB-3 outlet			-3°F	X	
	C	FB-5 inlet			+4°F	X	
		FB-5 outlet			-3°F	X	
	D	FB-2 inlet			-2°F	X	
		FB-2 outlet			-2°F	X	
Probe nozzle	A	1A	Caliper	Dn ±0.004 in.	0.001	X	
		2A			0.000	X	
		3A-9A			0.001	X	
	B	1B			0.001	X	
		2B			0.002	X	
		3B-9B			0.001	X	
	C	1C			0.001	X	
		2C			0.001	X	
		3C-9C			0.000	X	
	D	1D			0.002	X	
		2D			0.000	X	
		3D-9D			0.002	X	

DATE: 2/28/83 CLIENT: USEPA

BAROMETRIC PRESSURE (P_{bar}): 29.77 in. Hg METER BOX NO. 2

ORIFICE NO. 5 PRETEST γ: 0.977

ORIFICE K FACTOR: 5.412×10^{-4} AUDITOR: M. Phillips

Orifice manometer reading ΔH in H_2O	Dry gas meter reading V_i/V_f ft^3	Temperatures: Ambient T_{ai}/T_{af} °F	Dry gas meter: Inlet T_{ii}/T_{if} °F	Dry gas meter: Outlet T_{oi}/T_{of} °F	Duration of run Ø min
2.25	801.400	56	50	53	15.0
	814.085	57	53	54	

Dry gas meter volume V_m ft^3	Average temperatures: Ambient T_a °F	Average temperatures: Dry gas meter T_m °F	$V_{m_{std}}$ ft^3	$V_{m_{act}}$ ft^3	Audit γ	γ deviation %
12.685	57	53	13.063	12.786	0.979	0.2%

$V_{m_{std}}$	$V_{m_{act}}$
$\frac{(17.647)(V_m)(P_{bar} + \Delta H/13.6)}{(T_m + 460)}$	$\frac{(1203)(\text{Ø})(K)(P_{bar})}{(T_a + 460)^{1/2}}$

Audit γ	γ deviation, %
$\frac{V_{m_{act}}}{V_{m_{std}}}$	$\frac{(\gamma \text{ audit} - \gamma \text{ pre-test})(100\%)}{(\gamma \text{ audit})}$

Audit γ must be in the range, pre-test $\gamma \pm 0.05\ \gamma$

Figure 5-1. Audit report dry gas meter (Meter Box FB-2).

DATE: 2/28/83 CLIENT: USEPA

BAROMETRIC PRESSURE (P_{bar}): 30.04 in. Hg METER BOX NO. FB 3

ORIFICE NO. 5 PRETEST γ: 0.999

ORIFICE K FACTOR: 5.412×10^{-4} AUDITOR: M. Phillips

Orifice manometer reading ΔH in H_2O	Dry gas meter reading V_i/V_f ft^3	Temperatures: Ambient T_{ai}/T_{af} °F	Dry gas meter: Inlet T_{ii}/T_{if} °F	Dry gas meter: Outlet T_{oi}/T_{of} °F	Duration of run Ø min
2.50	843.063	74	80	71	15.0
	855.760	76	80	71	

Dry gas meter volume V_m ft^3	Average temperatures: Ambient T_a °F	Average temperatures: Dry gas meter T_m °F	$V_{m_{std}}$ ft^3	$V_{m_{act}}$ ft^3	Audit γ	γ deviation %
12.697	75	76	12.634	12.683	1.004	0.5%

$V_{m_{std}}$	$V_{m_{act}}$
$\frac{(17.647)(V_m)(P_{bar} + \Delta H/13.6)}{(T_m + 460)}$	$\frac{(1203)(\text{Ø})(K)}{(T_a + 460)^{1/2}}(P_{bar})$

Audit γ	γ deviation, %
$\frac{V_{m_{act}}}{V_{m_{std}}}$	$\frac{(\gamma \text{ audit} - \gamma \text{ pre-test})(100\%)}{(\gamma \text{ audit})}$

Audit γ must be in the range, pre-test $\gamma \pm 0.05\ \gamma$

Figure 5-2. Audit report dry gas meter (Meter Box FB-3).

DATE: 2/28/83 CLIENT: USEPA

BAROMETRIC PRESSURE (P_{bar}): 29.77 in. Hg METER BOX NO. FB5

ORIEICE NO. 7 PRETEST γ: 0.983

ORIFICE K FACTOR: 5.036×10^{-4} AUDITOR: M. Phillips

Orifice manometer reading ΔH in H_2O	Dry gas meter reading V_i/V_f ft^3	Temperatures: Ambient T_{ai}/T_{af} °F	Dry gas meter: Inlet T_{ii}/T_{if} °F	Dry gas meter: Outlet T_{oi}/T_{of} °F	Duration of run Ø min
2.0	693.098	58	62	59	15.0
	704.970	56	63	59	

Dry gas meter volume V_m ft^3	Average temperatures: Ambient T_a °F	Average temperatures: Dry gas meter T_m °F	$V_{m_{std}}$ ft^3	$V_{m_{act}}$ ft^3	Audit γ	γ deviation %
11.872	57	61	12.030	11.898	0.989	0.6%

$V_{m_{std}}$	$V_{m_{act}}$
$\frac{(17.647)(V_m)(P_{bar} + \Delta H/13.6)}{(T_m + 460)}$	$\frac{(1203)(\text{Ø})(K)(P_{bar})}{(T_a + 460)^{1/2}}$

Audit γ	γ deviation, %
$\frac{V_{m_{act}}}{V_{m_{std}}}$	$\frac{(\gamma \text{ audit} - \gamma \text{ pre-test})(100\%)}{(\gamma \text{ audit})}$

Audit γ must be in the range, pre-test $\gamma \pm 0.05\ \gamma$

Figure 5-3. Audit report dry gas meter (Meter Box FB-5).

DATE: 2/28/83 CLIENT: USEPA

BAROMETRIC PRESSURE (P_{bar}): 30.04 in. Hg METER BOX NO. FB6

ORIEICE NO. 7 PRETEST γ: 0.960

ORIFICE K FACTOR: 5.036×10^{-4} AUDITOR: M. Phillips

Orifice manometer reading ΔH in H_2O	Dry gas meter reading V_i/V_f ft^3	Temperatures: Ambient T_{ai}/T_{af} °F	Dry gas meter: Inlet T_{ii}/T_{if} °F	Dry gas meter: Outlet T_{oi}/T_{of} °F	Duration of run Ø min
1.70	610.719	74	76	74	15.0
	623.085	76	79	75	

Dry gas meter volume V_m ft^3	Average temperatures: Ambient T_a °F	Average temperatures: Dry gas meter T_m °F	$V_{m_{std}}$ ft^3	$V_{m_{act}}$ ft^3	Audit γ	γ deviation %
12.366	75	76	12.281	11.802	0.961	0.1%

$V_{m_{std}}$	$V_{m_{act}}$
$\frac{(17.647)(V_m)(P_{bar} + \Delta H/13.6)}{(T_m + 460)}$	$\frac{(1203)(\text{Ø})(K)}{(T_a + 460)^{1/2}} \frac{(P_{bar})}{}$

Audit γ	γ deviation, %
$\frac{V_{m_{act}}}{V_{m_{std}}}$	$\frac{(\gamma \text{ audit} - \gamma \text{ pre-test})(100\%)}{(\gamma \text{ audit})}$

Audit γ must be in the range, pre-test $\gamma \pm 0.05\ \gamma$

Figure 5-4. Audit report dry gas meter (Meter Box FB-6).

TABLE 5-2. EXAMPLE OF A THERMOGRAVIMETRIC ANALYSIS OF FILTER AND ACETONE BLANKS (milligrams)

Sample	Lab ID	Tare weight	Ambient temp.		Weight after conditioning at indicated temperature					
					160°C		232°C		316°C	
			Weight	Net	Weight	Net	Weight	Net	Weight	Net
Filter	CW507	324.9	324.9	0.0	325.0	+0.1	324.6	-0.3	324.5	-0.4
Acetone[a]	CW504[a]	106,912.7	106,917.8	+5.1	106,913.0	+0.3	106,911.9	-0.8	106,911.8	-0.9
	CW506[b]	106,546.6	106,548.6	+2.0	106,546.3	-0.3	106,545.5	-1.1	106,545.4	-1.2

[a]Initial volume, 457 ml.

[b]Initial volume, 292 ml.

The reported net weights are reasonable (considering the number of times each sample fraction was handled) and show good analytical techniques. In addition, several particulate samples were reanalyzed to preclude weighing error as a source of variability in reported results.

Audit solutions prepared by EPA were used to check the analytical procedures and reagents for SO_2 sampling analysis. Figure 5-5 presents the results of this analytical audit. Table 5-3 summarizes the reagent blank analysis performed on the isopropyl alcohol (IPA) and hydrogen peroxide used for sampling. The audit test shows that the analytical techniques were good.

Table 5-4 presents the results of the H_2SO_4 analysis by both titration and ion chromatography. As discussed in Section 4, traces of peroxide found in IPA sample solutions caused some SO_2 to be absorbed in the IPA and thus increased the reported values for $SO_4^=$ as H_2SO_4/SO_3 and decreased the reported SO_2 values. Ion chromatography was used to validate titrametric data because the end points were difficult to distinguish, especially for the IPA solutions. The data show good correlation between titrametric and IC SO_2 analysis. The IC analytical results for $SO_4^=$ and H_2SO_4/SO_3 compared favorably.

As an assessment of the reliability of the procedures used in determining the non-water-soluble sulfate particulate concentration, blank filter and deionized, distilled water samples were analyzed along with each set of field samples. Table 5-5 presents example blank results for this method.

Plant USEPA - EMB Exxon **PN Number** 3530-14

Date samples received 3-14-83 **Date analyzed** 3-21-83 & 3-22-83

Samples analyzed by C. Stull

Reviewed by I. Bennett **Date of Review** 3-29-83

Sample Number	mg SO_2/dscm Determined	Source of Sample	Accepted Value	% Difference
LCC SC282 # 2572 CW591	1419.9	T. Wagner	1410.8	+ 0.65
LCC SC282 # 8419 CW592	2297.8	T. Wagner	2325.9	- 1.21
LCC SC282 # 8419 CW592	2300.1	T. Wagner	2325.9	- 0.98

Figure 5-5. Audit report SO_2 analysis.

Plant USEPA Emp Exxon **PN Number** 3530-14

Date samples received 3-14-83 **Date analyzed** 3-22-83

Samples analyzed by C. Stoll

Reviewed by I. Bennett **Date of Review** 3-29-83

Sample Number	mg SO_2/dscm Determined	Source of Sample	Accepted Value	% Difference
[illegible]	1436.1	T. [illegible]	1410.8	+ 1.79

Figure 5-5. Audit report SO_2 analysis (continued).

TABLE 5-3. REAGENT BLANK ANALYSIS FOR IPA AND H_2O_2

Sample type	Sample ID	mg of $SO_4^=$	
		as SO_2	as H_2SO_4
10% H_2O_2	CW588	<0.1	-
	CW589	<0.1	-
	CW590	<0.2	-
80% IPA	CW549	-	<0.3
	CW550	-	<0.2
	CW551	-	<0.3

TABLE 5-4. ION CHROMATOGRAPHY CHECKS

H_2O_2 Impinger Solutions:

Run No.	Lab No.	SO_2, total mg	
		Titration	IC
1BM5	CW553	37.1	39.3
4AM5W	CW564	10.5	11.7
6AM5W	CW572	320	334
7DM5450	CW579	502	510

IPA Impinger Solutions:

Run No.	Lab No.	H_2SO_4, total mg	
		Titration	IC
1AM5	CW514	135	210
1BM5	CW515	62.8	39.7
1CM5W	CW516	76.3	74.8
1DM5W	CW517	80.1	57.8
2AM5W	CW518	60.8	45.7
2BM5W	CW519	79.1	63.0
2CM5B	CW520	78.2	63.4
2DM5B	CW521	78.0	72.7
3AM5W	CW522	264	252
3BM5W	CW523	278	253
3CM5	CW524	178	137
3DM5	CW525	212	179
4AM5W	CW526	107	80.5
4BM5W	CW527	75.3	40.2
4CM5B	CW528	89.5	59.8
4DM5B	CW529	99.1	68.0
5AM5	CW530	31.9	23.2
5BM5	CW531	21.9	12.1
5CM5W	No Sample		
5DM5W	CW532	31.8	32.4
6AM5W	CW533	32.6	22.4
6BM5B	CW534	31.0	25.2
6CM5B	CW535	24.4	17.3
6DM5W	CW536	27.7	27.6

(continued)

TABLE 5-4 (continued)

IPA Impinger Solutions (continued):

Run No.	Lab No.	H_2SO_4, total mg	
		Titration	IC
7AM5B	CW537	29.5	17.3
7BM5B	CW538	47.3	31.1
7CM5450	CW539	40.1	34.5
7DM5450	CW540	58.9	45.5
8AM5	CW541	33.6	23.2
8BM5B	CW542	26.5	24.3
8CM5B	CW543	31.0	37.4
8DM5B	CW544	37.3	29.6
9AM5B	CW545	327	320
9BM5450	CW546	66.6	53.6
9CM5B	CW547	27.0	26.7
9DM5450	CW548	24.1	24.2
IPA Blank No. 1&2	CW549	<0.3	a
IPA Blank No. 3-6	CW550	<0.2	a
IPA Blank No. 7-9	CW551	<0.3	a
H_2O Blank	CW513	-	<0.60

[a]IPA concentration caused erratic results.

TABLE 5-5. NON-WATER-SOLUBLE SULFATE BLANK ANALYTICAL DATA

Sample type	Lab ID	Net particulate weight including ammonium sulfate, mg	C_{SO_4}, mg/liter	Volume evaporated,[a] ml	NWSSP, mg
Filter	CW508	0.0	2.22	235	-0.7
Probe rinse	CW511	2.7	<1.00	593	2.7
Filter	CW510	5.7	2.19	235	5.0
Probe rinse	CW512	1.7	<1.00	622	1.7
Filter	CW509	1.2	2.11	235	0.5
Probe rinse	CW513	1.8	1.61	572	0.5

[a]15 ml were removed for IC analysis.

Table 5-6 summarizes blank analytical data for the ion chromatography analyses performed on rinse and filter samples.

The IC was calibrated daily with standard solutions of 1.0, 2.5, 5.0, 10.0, and 15.0 mg/liter. A standard reference solution (SRS) at 8.0 ppm was analyzed at the beginning, the end, and after every 10 samples during an analysis day. The measured SRS value had to be within ±5 percent of the theoretical value as the previous 10 samples were reanalyzed after the instrument was recalibrated. Ten percent of the samples were analyzed in duplicate. These samples agreed within ±5 percent.

TABLE 5-6. ION CHROMATOGRAPHY BLANK ANALYTICAL DATA

Sample type	Lab ID	C_{SO_4}, mg/liter	Volume, ml	$SO_4^{=}$, mg
Filter	CW509	3.55	250	0.9
Rinse (acetone)	CW503	<1.0	250	<0.2
Rinse (acetone)	CW505	<1.0	250	<0.2

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