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Industrial Boilers SO_2 Continuous Monitoring

Emission Test Report

Argonne National Laboratories Argonne, Illinois

Volume 1: Summary

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Industrial Boiler Continuous Emission Monitoring at the Argonne National Laboratories Argonne, Illinois

Revised Draft Final Report
Volume 1

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SECTION 1

INTRODUCTION

The United States Environmental Protection Agency (EPA) is currently engaged in developing an industrial boiler, sulfur reduction standard. In order to support the New Source Performance Standard for industrial boilers, sufficient performance and financial background data must first be developed at a representative facility currently using best available control technology (BACT) for sulfur dioxide control. To help develop the necessary support data, Radian Corporation was contracted by the Emission Measurement Branch (EMB) of EPA to conduct a 90-day SO_2 and CO_2 monitoring program around the flue gas desulfurization (FGD) system located at the Argonne National Laboratory (ANL) near Chicago, Illinois.

The ANL-FGD system was selected for use during this program for two reasons. First, ANL utilizes a spray dryer/fabric filter system. This control technology is presently considered among the best available for SO_2 control. Second, under an existing EPA-funded program (EPA Contract No. 89-F2-A041), ANL was contracted to thoroughly characterize the FGD system using high sulfur coal ($\sim$3.5%). The objective of the EPA/ANL program was to evaluate the system's effectiveness under different operating conditions. Data obtained during both the EPA/ANL program and EPA/Radian program could be used to complement each other.

The original scope of work for this test program called for using the existing Contraves-Goerz continuous gas monitors at ANL, if possible, for collecting the desired FGD inlet and outlet SO_2 and CO_2 emission data. During initial phases of the program, an evaluation was performed by Radian to determine if the existing Contraves-Goerz monitors could be used to collect these data. Based on the results of the evaluation, a decision was

made to not rely upon the Contraves-Goerz monitors. Instead, the EPA Method 6B sampling and analysis procedure (described in Section 4) was used throughout the program to collect the necessary SO_2 emission rate data.

SO_2 emission monitoring tests and process data collection were initiated by Radian on August 1, 1983 at the ANL Unit 5 boiler spray dryer/baghouse FGD system. Duplicate EPA Method 6B samples were simultaneously collected each day at the FGD inlet and outlet. Pertinent boiler and FGD operational data were also collected daily using a Radian DART data acquisition system and operator process log data sheets. The test program was halted on August 29, 1983 because the FGD system was not operating at its maximum performance level of SO_2 removal.

The primary purpose of this report is to present the results of the monitoring program conducted at ANL, by Radian, from August 1 through August 29, 1983. Section 2 includes a summary and discussion of the SO_2 emission rate data and process data collected during this program. The quality assurance/quality control (QA/QC) results are presented in Section 3. An evaluation of the EPA Method 6B precision and reliability, as it pertains to this program, is included with the QA/QC results. A brief description of the process configuration and location of the sampling points is presented in Section 4. A description of the sampling and analysis procedures are presented in Section 5. Section 6 includes a description of the process monitoring procedures and Section 7 includes example calculations.

A copy of the actual EPA Method 6B sampling data sheets, the operator logsheets, and DART process data sheets are included as appendices in a separate data volume (Volume II). A copy of the EPA Method 6, 6A, 6B, and Subpart D of the Federal Register are included in the appendices.

Section 2

PRESENTATION AND DISCUSSION OF RESULTS

This section presents a summary of the EPA Method 6B test results, the 24-hour average process data, and the coal ultimate analysis and proximate analysis results. A discussion of the EPA Method 6B, SO_2 emission rate data and 24-hour average process data collected during this program is also presented in this section.

2.1 PRESENTATION OF RESULTS

Table 2-1 contains a summary of results of the EPA Method 6B tests. For convenience, the SO_2 concentration was reported in parts per million (ppm) and the average SO_2 emission rate was reported in both nanograms per Joule (ng/J) and pounds per million Btu (lbs/10^6 Btu). Table 2-1 includes a comment section to help explain certain discrepancies in the data and identify process upsets. EPA Method 6B, SO_2 emission rate tests were not conducted on August 26, 27, 28, and 29 because the FGD system was not operating because of an electrical short, and the sampling system was undergoing a quality assurance audit. All of the supporting EPA Method 6B data sheets are included in Appendix A of Volume II.

Table 2-2 contains a summary of Unit 5 boiler and FGD system 24-hour average process data. The 24-hour average process data presented in Table 2-2 originated from one of three sources. These include the Radian DART data sheets and the "Dry Panel" and "Wet Panel" operator log process data sheets. The "Dry Panel" refers to the main instrument panel located near the boiler control panel. The "Wet Panel" refers to the instrument panel located in the slaking house. All three sources were used because the DART was not in operation during the entire reporting period and because certain

process data from both instrument panels could not be monitored by the DART. The ANL Unit 5 boiler and FGD Operator Logsheets and the DART 60-minute and 24-hour average process data printouts are included in Appendices B and C, respectively, of Volume II.

To help identify where the process data in Table 2-2 originated, numbers in parentheses are used to denote "Dry Panel" observations and numbers in brackets are used to denote "Wet Panel" observations. The remaining process data were collected using the DART. Blank spaces in Table 6-2 indicate that the instrument monitoring the parameter of interest was not operable or that a portion of the boiler or FGD system was not operating.

Table 2-3 contains a summary of the ultimate and proximate coal analyses performed on the two coals used by the ANL Unit 5 boiler from August 1 through August 26, 1983. The results are reported on both a wet and dry basis. The F_c-factor (dry basis) calculated from the analysis of each coal is also included in Table 2-3.

TABLE 2-1. SUMMARY OF EPA METHOD 6B DATA COLLECTED AT ANL UNIT 5 FGD SYSTEM FROM AUGUST 1 THROUGH AUGUST 29, 1983

Date[a] (MMDD)	Sampling Location	Sample Train A Results			Sample Train B Results			Average SO_2 Removal Efficiency
		SO_2 (ppm)	CO_2 (%)	Emission Rate (ng/J)	SO_2 (ppm)	CO_2 (%)	Emission Rate (ng/J)	
0801	Inlet	724	6.0	1530	1310	9.4	1770	---
0801	---	---	---	---	---	---	---	
0802	Inlet	1550	9.7	2030	1550	11.4	1720	86.9
0802	Outlet	135	8.9	192	224	9.5	299	
0803	Inlet	1610	9.1	2240	1660	9.0	2250	86.5
0803	Outlet	208	8.7	303	---*	---*	---*	
0804	Inlet	593*	6.5*	1160*	1540	10.3	1900	92.1
0804	Outlet	116	9.8	150	---	10.1	---	
0805	Inlet	1510	9.7	1970	1590	10.2	1980	86.5
0805	Outlet	189	10.0	240	235	10.1	295	
0806	Inlet	1640	9.6	2170	1600	10.0	2030	82.2
0806	Outlet	289	9.8	374	284	9.7	371	
0807	Inlet	1590	9.8	2060	1360	8.4	2050	83.0
0807	Outlet	266	9.6	351	276	10.0	350	
0808	Inlet	1130	9.3	1540	1130	9.5	1510	55.6
0808	Outlet	487	9.6	643	543	9.7	710	
0809	Inlet	1500	9.2	2070	1490	9.8	1930	45.7
0809	Outlet	115*	7.9*	185*	796	9.3	1090	

[a]The duplicate EPA Method 6B sampling trains (Train A and Train B) operated from 1000 hours on the day indicated to 0900 hours on the next day to constitute a 24-hour sample.

TABLE 2-1 (Continued)

Average SO_2 Emission Rate		Comments	
ng/J	lbs/10^6 BTU	Sampling Problems	Boiler/FGD Upsets
1650	3.83	Outlet sample not collected--preliminary check-out of sampling system	---
---	---		
1880	4.35	---	---
245	.570		
2240	5.21	*Outlet B train impingers improperly recovered. Data not used in average.	---
303	.704		
1900	4.42	*Leak indicated across Inlet A train. Outlet B train impingers improperly recovered. Data not used in average.	---
150	.348		
1980	4.59	---	Outlet Contraves inoperable--poor system control.
267	.622		
2100	4.87	---	Outlet Contraves inoperable--poor system control.
373	.866		
2060	4.79	---	Outlet Contraves inoperable--poor system control.
350	.814		
1520	3.54	---	Outlet Contraves inoperable--poor system control.
681	1.57		
2000	4.64	*High pressure drop across dririte impinger. Data indicate leak in system. Data not used in average.	High absorber pressure--flue gas bypasses FGD system--no scrubbing.
1090	2.52		

TABLE 2-1 (Continued)

Date[a] (MMDD)	Sampling Location	Sample Train A Results SO_2 (ppm)	Sample Train A Results CO_2 (%)	Sample Train A Results Emission Rate (ng/J)	Sample Train B Results SO_2 (ppm)	Sample Train B Results CO_2 (%)	Sample Train B Results Emission Rate (ng/J)	Average SO_2 Removal Efficiency
0810	Inlet	1530	9.3	2090	1590	10.0	2020	54.7
0810	Outlet	736	9.6	972	669	9.6	884	
0811	Inlet	1440	9.6	1900	1490	10.0	1890	8.2
0811	Outlet	579*	7.9*	931*	1340	9.8	1730	
0812	Inlet	1320	8.6	1950	1360	8.8	1960	72.6
0812	Outlet	366	9.2	505	412	9.2	568	
0813	Inlet	1400	8.9	2000	1330	8.5	1980	88.9
0813	Outlet	182	9.0	257	133	9.1	185	
0814	Inlet	1400	8.6	2060	1430	8.9	2040	83.6
0814	Outlet	222	9.1	308	249	8.7	363	
0815	Inlet	1470	9.1	2050	1430	8.9	2040	83.8
0815	Outlet	242	9.0	341	229	9.0	323	
0816	Inlet	1470	9.3	2000	1530	9.6	2020	91.8
0816	Outlet	130	9.8	168	120	9.5	160	
0817	Inlet	1660	10.4	2020	1600	9.9	2050	88.4
0817	Outlet	165	10.2	205	210	10.0	266	
0818	Inlet	1610	10.0	2040	1660	10.2	2060	85.2
0818	Outlet	236	10.3	291	254	10.1	319	

[a]The duplicate EPA Method 6B sampling trains (Train A and Train B) operated from 1000 hours on the day indicated to 0900 hours on the next day to constitute a 24-hour sample.

TABLE 2-1 (Continued)

Average SO_2 Emission Rate		Comments	
ng/J	lbs/10^6 BTU	Sampling Problems	Boiler/FGD Upsets
2060	4.77	---	High absorber pressure--flue gas bypasses FGD system--no scrubbing
928	2.15		
1900	4.41	*Obstruction in sampling system resulted in low sample volume and possible leak. Data not used in average.	High absorber pressure--flue gas bypasses FGD system--no scrubbing.
1730	4.01		
1960	4.55	---	High absorber pressure--flue gas bypasses FGD system--no scrubbing.
536	1.25		
1990	4.62	---	---
221	.51		
2050	4.76	---	---
334	.779		
2040	4.73	---	---
332	.771		
2010	4.66	---	---
164	.380		
2040	4.73	---	---
236	.548		
2050	4.76	---	---
305	.708		

(Continued)

TABLE 2-1 (Continued)

Date[a] (MMDD)	Sampling Location	Sample Train A Results SO_2 (ppm)	Sample Train A Results CO_2 (%)	Sample Train A Results Emission Rate (ng/J)	Sample Train B Results SO_2 (ppm)	Sample Train B Results CO_2 (%)	Sample Train B Results Emission Rate (ng/J)	Average SO_2 Removal Efficiency
0819	Inlet	1710	10.4	2090	1600	9.9	2050	86.9
0819	Outlet	215	10.4	262	228	10.2	283	
0820	Inlet	1580	9.7	2070	1600	10.0	2030	89.1
0820	Outlet	169	9.8	219	179	9.9	229	
0821	Inlet	1670	10.2	2080	1590	9.9	2040	87.3
0821	Outlet	204	10.1	256	209	10.0	265	
0822	Inlet	1580	9.9	2020	1610	9.9	2060	87.5
0822	Outlet	195	10.1	245	205	9.8	265	
0823	Inlet	1610	9.9	2060	1530	9.6	2020	84.2
0823	Outlet	249	9.9	319	252	9.7	329	
0824	Inlet	1630	9.9	2090	1620	9.8	2100	87.7
0824	Outlet	207	10.1	260	201	10.1	252	
0825	Inlet	1690	10.4	2060	1610	10.0	2040	64.4
0825	Outlet	588	10.2	731	585	10.2	727	
0826	EPA Method 6B samples are not collected because an electrical short circuit caused a damper to become maligned resulting in flue gas bypassing the FGD system.							
0827	On-site Method 6B audit sample no. 1 collected. Damper still misaligned.							
0828	On-site Method 6B audit sample no. 2 collected. Damper still misaligned.							
0829	On-site Method 6B audit sample no. 3 collected. Damper still misaligned.							

[a]The duplicate EPA Method 6B sampling trains (Train A and Train B) operated from 1000 hours on the day indicated to 0900 hours on the next day to constitute a 24-hour sample.

TABLE 2-1 (Continued)

Average SO_2 Emission Rate		Comments	
ng/J	lbs/10^6 BTU	Sampling Problems	Boiler/FGD Upsets
2070	4.80	---	---
273	.633		
2050	4.77	---	---
224	.521		
2060	4.79	---	---
261	.607		
2040	4.75	---	---
255	.594		
2040	4.73	---	---
324	.752		
2100	4.86	---	---
256	.594		
2050	4.76	---	Low slurry feed to spray dryer--reduced SO_2 removal.
729	1.69		

TABLE 2-2. SUMMARY OF ANL UNIT 5 BOILER AND FGD 24-HOUR[a] AVERAGE PROCESS DATA COLLECTED FROM AUGUST 2 THROUGH AUGUST 29, 1983

Parameter	Units	Date: 0802		Date: 0803		Date: 0804		Date: 0805		Date: 0806		Date: 0807		Date: 0808	
		24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation
Boiler Load	10^3 lbs/hr	107	(21)	113	(21)	112	(21)	110	(22)	100	24	103	24	100	20
Boiler Exit Gas O_2 Concentration	%	7.9	(21)	7.6	(21)	7.5	(21)	7.7	(22)	7.8	(23)	7.5	(23)	6.9	(20)
Baghouse Outlet Temperature	°F	158	(21)	158	(21)	159	(21)	160	(22)	164	24	165	24	167	20
Spray Dryer Inlet Temperature	°F	324	(21)	325	(21)	325	(21)	324	(22)	313	24	316	24	309	20
Spray Dryer Outlet Temperature	°F	155	(21)	155	(21)	155	(21)	155	(22)	155	24	156	24	159	20
Spray Dryer Slurry Feed	gpm	10.0	(21)	10.6	(21)	10.4	(21)	10.5	(22)	9.2	24	9.4	24	8.1	20
Spray Dryer Inlet Pressure	inches H_2O	-.09	(21)	-.08	(21)	-.09	(21)	-.08	(22)	-.09	(23)	-.08	(23)	-.09	(20)
Baghouse ΔP	inches H_2O	3.3	(21)	3.9	(21)	3.6	(21)	3.8	(22)	3.6	(23)	3.6	(23)	3.0	20
Lime Milk Flow	gpm	6.0	(21)	7.6	(21)	6.6	(21)	6.7	(22)	7.0	24	6.4	24	6.1	20
Central Gas Disperser ΔP	inches H_2O	0.2	(13)	0.5	(21)	0.5	(21)	0.4	(22)	0.2	(23)	0.3	(16)	0.1	(16)
Baghouse Outlet Dewpoint	°F	126	(20)	128	(20)	126	(20)	128	(22)	138	(23)	133	(23)	130	(20)
Atomizer Motor Amps	amps	50	(21)	52	(21)	52	(21)	54	(22)	50	(23)	52	(23)	50	(20)
Lime Milk Tank Level	%	76	(21)	78	(21)	75	(21)	74	(22)	72	(23)	75	(23)	75	(20)
Slurry Density	grams/cc	1.12	(21)	1.12	(21)	1.13	(21)	1.13	(22)	1.10	24	1.11	24	1.12	20
Slaking Dilution Water Flow	gpm	4.2	[12]	5.1	[12]	4.5	[11]	4.6	[10]	4.5	[12]	4.3	[11]	3.9	[12]
Lime Milk Flow	gpm	6.3	[12]	7.2	[12]	7.3	[11]	7.5	[10]	6.4	[12]	7.1	[11]	6.1	[12]
Lime Milk Density	grams/cc	1.28	[12]	1.29	[12]	1.28	[11]	1.27	[10]	1.28	[12]	1.29	[11]	1.29	[12]
Slurry Dilution Water Flow	gpm	--	--	--	--	--	--	--	--	2.8	24	2.9	24	2.9	20
Recycle Feed Rate	lbs/hr	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Contraves Outlet CO_2	%	--	--	--	--	--	--	--	--	5	23	6	23	5.4	20
Contraves Outlet SO_2	ppm	--	--	--	--	--	--	--	--	--	--	--	--	506	20
SO_2 Emission Rate	lbs/10^6 BTU	1.26	(21)	1.25	(20)	1.24	(20)	1.10	5	--	--	--	--	1.407	20
Slurry Mix Tank Level	%	76	(21)	76	(21)	75	(21)	75	(22)	73	24	73	24	75	20

[a] The 24-hour average represents the average of data collected from 1000 hours on the day indicated to 1000 hours the following day.

( ) dry panel log

[ ] wet panel log

-- Data not available because the monitor was not functioning properly or the process was not operating during that time period.

(Continued)

TABLE 2-2 (Continued)

Parameter	Units	Date: 0809		Date: 0810		Date: 0811		Date: 0812		Date: 0813		Date: 0814		Date: 0815	
		24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation
Boiler Load	10^3 lbs/hr	95	24	--	--	92	24	90	24	90	24	95	24	98	24
Boiler Exit Gas O_2 Concentration	%	7.8	(9)	--	--	--	--	8.7	(18)	7.9	(21)	9.1	(22)	8.7	(22)
Baghouse Outlet Temperature	°F	247	24	--	--	203	24	160	24	163	24	163	24	163	24
Spray Dryer Inlet Temperature	°F	300	24	--	--	313	24	310	24	311	24	312	24	313	24
Spray Dryer Outlet Temperature	°F	227	24	--	--	180	24	154	24	156	24	156	24	156	24
Spray Dryer Slurry Feed	gpm	2.1	24	--	--	--	--	6.7	24	9.0	24	9.1	24	9.4	24
Spray Dryer Inlet Pressure	inches H_2O	-.03	(9)	--	--	--	--	-.09	24	-.10	24	-.10	24	-.10	24
Baghouse ΔP	inches H_2O	2.9	24	--	--	--	--	2.2	24	3.7	24	3.7	24	4.4	24
Lime Milk Flow	gpm	1.9	24	--	--	--	--	1.8	24	4.0	24	6.0	24	4.8	24
Central Gas Disperser ΔP	inches H_2O	0.2	(9)	--	--	--	--	.01	(14)	0.2	(21)	0.3	(22)	0.4	(22)
Baghouse Outlet Dewpoint	°F	130	(9)	--	--	--	--	123	(18)	127	(21)	127	(22)	128	(22)
Atomizer Motor Amps	amps	52	(9)	--	--	--	--	49	(18)	52	(21)	50	(22)	51	(22)
Lime Milk Tank Level	%	77	(9)	--	--	71	24	68	24	68	24	70	24	69	24
Slurry Density	grams/cc	1.28	24	--	--	--	--	1.14	24	1.14	24	1.14	24	1.16	24
Slaking Dilution Water Flow	gpm	4.2	[5]	--	--	--	--	4.4	[9]	3.0	[12]	3.0	[11]	2.5	[12]
Lime Milk Flow	gpm	6.9	[5]	--	--	--	--	1.8	[9]	4.0	[12]	5.7	[11]	5.5	[12]
Lime Milk Density	grams/cc	1.29	[5]	--	--	--	--	1.25	[9]	1.27	[12]	1.27	[11]	1.28	[12]
Slurry Dilution Water Flow	gpm	--	--	--	--	--	--	1.3	24	3.0	24	3.0	24	2.5	24
Recycle Feed Rate	lbs/hr	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Contraves Outlet CO_2	%	8.2	23	--	--	8.6	23	8.1	23	7.9	23	8.3	23	8.5	23
Contraves Outlet SO_2	ppm	903	23	--	--	1234	23	463	23	310	23	349	23	352	23
SO_2 Emission Rate	lbs/10^6 BTU	1.749	23	--	--	2.016	23	1.323	23	1.113	23	1.205	23	1.212	23
Slurry Mix Tank Level	%	85	24	--	--	86	24	73	24	68	24	70	24	69	24

( ) dry panel log
[ ] wet panel log
-- Data not available because the monitor was not functioning properly or the process was not operating during that time period.

(Continued)

TABLE 2-2 (Continued)

Parameter	Units	Date: 0816		Date: 0817		Date: 0818		Date: 0819		Date: 0820		Date: 0821		Date: 0822	
		24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation	24 Hour Average	Number of Obser-vation
Boiler Load	10^3 lbs/hr	104	24	109	(22)	115	21	121	(23)	106	(23)	115	(23)	106	(23)
Boiler Exit Gas O_2 Concentration	%	8.7	(22)	8.1	(22)	6.6	(23)	6.8	(23)	7.7	(23)	7.4	(23)	7.1	(23)
Baghouse Outlet Temperature	°F	164	24	160	(22)	151	21	147	(23)	146	(23)	146	(23)	147	(23)
Spray Dryer Inlet Temperature	°F	310	24	321	(22)	313	21	326	(23)	322	(23)	322	(23)	322	(23)
Spray Dryer Outlet Temperature	°F	157	24	156	(22)	157	21	155	(23)	155	(23)	155	(23)	155	(23)
Spray Dryer Slurry Feed	gpm	9.9	24	10.3	(22)	11.1	21	12.6	(23)	11.4	(23)	11.1	(23)	10.0	(23)
Spray Dryer Inlet Pressure	inches H_2O	-1.0	24	-.09	(22)	-0.9	21	-.09	(23)	-.10	(23)	-.10	(23)	-.10	(23)
Baghouse ΔP	inches H_2O	4.6	24	4.8	(22)	3.7	21	4.0	(23)	3.8	(23)	3.8	(23)	3.7	(23)
Lime Milk Flow	gpm	7.0	24	7.7	(22)	8.5	21	8.7	(23)	7.5	(23)	7.7	(23)	8.2	(23)
Central Gas Disperser ΔP	inches H_2O	0.45	(22)	0.5	(22)	0.6	(23)	0.7	(23)	0.3	(23)	0.5	(23)	0.3	(23)
Baghouse Outlet Dewpoint	°F	129	(22)	130	(22)	129	(23)	132	(23)	129	(23)	131	(23)	128	(23)
Atomizer Motor Amps	amps	52	(22)	53	(22)	57	(23)	57	(23)	52	(23)	55	(23)	52	(23)
Lime Milk Tank Level	%	67	24	70	(22)	69	21	73	(23)	73	(23)	74	(23)	74	(23)
Slurry Density	grams/cc	1.19	24	1.21	(22)	1.15	21	1.17	(23)	1.18	(23)	1.19	(23)	1.19	(16)
Slaking Dilution Water Flow	gpm	4.4	[12]	4.9	[11]	5.0	[10]	4.8	[12]	4.2	[12]	3.9	[12]	3.9	[12]
Lime Milk Flow	gpm	5.1	[12]	7.8	[11]	8.6	[10]	7.7	[12]	7.8	[12]	6.6	[12]	7.4	[12]
Lime Milk Density	grams/cc	1.27	[12]	1.29	[11]	1.14	[10]	1.15	[12]	1.15	[12]	1.16	[12]	1.14	[12]
Slurry Dilution Water Flow	gpm	1.6	24	3.6	7	3.6	21	3.5	1	3.8	19	4.8	4	3.5	21
Recycle Feed Rate	lbs/hr	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Contraves Outlet CO_2	%	8.9	23	9.5	6	9.5	21	8.2	1	8.8	19	9.6	3	9.3	21
Contraves Outlet SO_2	ppm	319	23	319	6	400	21	297	1	375	19	372	3	374	21
SO_2 Emission Rate	lbs/10^6 BTU	1.017	23	1.02	(22)	1.201	21	1.09	(23)	1.10	(23)	1.12	(23)	1.11	(23)
Slurry Mix Tank Level	%	68	24	72	(22)	71	21	72	(23)	72	(23)	71	(23)	72	(23)

( ) dry panel log
[ ] wet panel log

-- Data not available because the monitor was not functioning properly or the process was not operating during that time period.

(Continued)

TABLE 2-2 (Continued)

Parameter	Units	Date: 0823		Date: 0824		Date: 0825		Date: 0826*		Date: 0827*		Date: 0828*		Date: 0829*	
		24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation	24 Hour Average	Number of Observation
Boiler Load	10^3 lbs/hr	99	24	108	24	113	24	--	--	--	--	--	--	--	--
Boiler Exit Gas O_2 Concentration	%	7.1	(23)	7.5	(23)	7.7	(23)	--	--	--	--	--	--	--	--
Baghouse Outlet Temperature	°F	148	24	150	24	182	24	--	--	--	--	--	--	--	--
Spray Dryer Inlet Temperature	°F	309	24	311	24	312	24	--	--	--	--	--	--	--	--
Spray Dryer Outlet Temperature	°F	156	24	156	24	183	24	--	--	--	--	--	--	--	--
Spray Dryer Slurry Feed	gpm	9.4	24	10.3	24	7.2	24	--	--	--	--	--	--	--	--
Spray Dryer Inlet Pressure	inches H_2O	-.10	24	-.10	24	-.09	24	--	--	--	--	--	--	--	--
Baghouse ΔP	inches H_2O	3.0	24	3.2	24	3.0	24	--	--	--	--	--	--	--	--
Lime Milk Flow	gpm	8.2	(23)	8.3	(23)	8.8	(23)	--	--	--	--	--	--	--	--
Central Gas Disperser ΔP	inches H_2O	0.3	(23)	0.2	(23)	0.5	(23)	--	--	--	--	--	--	--	--
Baghouse Outlet Dewpoint	°F	128	(23)	130	(23)	130	(23)	--	--	--	--	--	--	--	--
Atomizer Motor Amps	amps	52	(23)	51	(23)	53	(23)	--	--	--	--	--	--	--	--
Lime Milk Tank Level	%	73	24	73	24	67	24	--	--	--	--	--	--	--	--
Slurry Density	grams/cc	1.15	24	1.14	24	1.13	24	--	--	--	--	--	--	--	--
Slaking Dilution Water Flow	gpm	3.9	[12]	4.1	[11]	4.4	[12]	--	--	--	--	--	--	--	--
Lime Milk Flow	gpm	7.4	[12]	6.5	[11]	7.4	[12]	--	--	--	--	--	--	--	--
Lime Milk Density	grams/cc	1.14	[12]	1.13	[11]	1.14	[12]	--	--	--	--	--	--	--	--
Slurry Dilution Water Flow	gpm	3.0	24	3.4	24	3.0	24	--	--	--	--	--	--	--	--
Recycle Feed Rate	lbs/hr	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Contraves Outlet CO_2	%	9.1	23	9.5	23	9.2	23	--	--	--	--	--	--	--	--
Contraves Outlet SO_2	ppm	398	23	370	23	588	23	--	--	--	--	--	--	--	--
SO_2 Emission Rate	lbs/10^6 BTU	1.253	23	1.103	23	1.329	23	--	--	--	--	--	--	--	--
Slurry Mix Tank Level	%	70	24	70	24	73	24	--	--	--	--	--	--	--	--

( ) dry panel log
[ ] wet panel log

*FGD system not operating/engineering process data sheets not available.

-- Data not available because the monitor was not functioning properly or the process was not operating during that time period.

TABLE 2-3. SUMMARY OF ULTIMATE AND PROXIMATE ANALYSES PERFORMED ON THE COAL USED AT THE ANL UNIT 5 BOILER DURING AUGUST 1 THROUGH AUGUST 26, 1983.

Type of Analysis	Parameter	8-1-83 to 8-23-83 Kentucky		8-24-83 to 8-26-83 Illinois	
		Concentration			
		(Wet Basis)	(Dry Basis)	(Wet Basis)	(Dry Basis)
Proximate	% H_2O	7.91	---	1.43	---
	% Ash	7.34	7.96	10.33	10.48
	% Volatile	37.5	40.7	34.93	35.44
	% Fixed Carbon	47.2	51.3	53.31	54.08
	Btu/Pound	12,320	13,380	13,113	13,303
	% Sulfur	3.37	3.66	3.36	3.41
Ultimate	% H_2O	7.91	---	1.43	---
	% Carbon	68.1	74.0	73.05	74.11
	% Hydrogen	4.81	5.22	4.76	4.83
	% Nitrogen	1.41	1.53	1.45	1.47
	% Chlorine	0.05	0.05	0.25	0.25
	% Sulfur	3.37	3.66	3.36	3.41
	% Ash	7.34	7.97	10.33	10.48
	% Oxygen	6.99	7.60	5.37	5.45
	F_c-factor (dry basis)	1775 SCF/10^6 Btu 4.768 x 10^{-8} SCM/J		1788 SCF/10^6 Btu 4.804 x 10^{-8} SCM/J	

2.2 DISCUSSION OF RESULTS

This section includes a brief discussion of the results presented in Section 2.1. The overall precision and reliability of the EPA Method 6B sampling and analytical procedure, used during this program, are discussed briefly in Section 2.2.1. The effect of boiler and FGD system upsets on SO_2 emission rates are presented in Section 2.2.2. The efficiency of the ANL Unit 5 FGD system during periods of "Trouble Free" operation are included in Section 2.2.3. Finally, the quality of the ANL Unit 5 boiler and FGD process data is briefly discussed in Section 2.2.4.

2.2.1 EPA Method 6B Precision and Reliability

During this program, the EPA Method 6B sampling and analytical procedure proved to be a precise and reliable means of collecting SO_2 emission rate data. The measured precision (replicability), based on observed variability in results for duplicate samples collected using collocated sampling trains was 6.2% overall during this program. Of the total of 96 sampling train days (i.e., four trains per day for 24 days, excluding the trial run at the inlet on the first day), SO_2 emission rate data were lost or invalidated in only five instances, resulting in a sampling/analytical reliability of 94.8%. A more detailed assessment of the precision and reliability of the EPA Method 6B sampling and analytical procedure, used during this program, is provided in Section 3.

2.2.2 Unit Availability--Effect on SO_2 Removal

From August 2[a] through August 29, 1983 the ANL Unit 5 boiler did not experience any major upsets in operation. During this same time period, the ANL Unit 5 FGD system experienced system upsets, of one form or another, on 13 of 28 days (46 percent). Table 2-4 presents a summary of the ANL Unit 5 FGD system upsets that occurred during this program. The upsets that had

[a] Data collected on August 1 is not included in the data assessment because no outlet SO_2 emission rate data were collected on this day.

an effect on the performance of the FGD system can be classified in four categories. These include:

- SO_2 monitor failure,
- High central gas disperser pressure drop,
- Low slurry feed rate to the spray dryer, and
- Electric short-circuits within the control panel.

On August 5, 1983 (Friday night), the outlet Contraves-Goerz SO_2 monitor suffered a power failure. The ANL instrument technician was off-duty and could not be contacted. Therefore, the outlet Contraves monitor was inoperable from late Friday afternoon until Monday morning (August 8, 1983). During this time period, the scrubber was placed in the manual mode and the scrubber operator(s) controlled the scrubber by using a chart that relates the required milk of lime flow needed to achieve sufficient SO_2 removal at a given boiler load. This approach to scrubber control assumes that the sulfur content of the coal and the reactivity of the lime do not change appreciably. The average SO_2 removal efficiency for August 5, 6, and 7, during manual operation of the scrubber, was approximately 84%. This compares to an average SO_2 removal efficiency of approximately 88% during August 2, 3, and 4 when the scrubber system operated in the automatic mode. Although the SO_2 removal efficiency decreased slightly (from 88 to 84%) during manual operation of the scrubber, the average scrubber SO_2 emission rate (~330 ng/J) did not rise above the maximum allowable Illinois state SO_2 emission limit (520 ng/J) during this period.

On Tuesday morning (August 9, 1983), a high pressure drop was detected across the FGD system and the operators bypassed the FGD system for a period of time. The high FGD pressure drop remained a problem until the morning of August 12, 1983 when an 18-inch plug of solids was removed from the central gas disperser. The maximum allowable SO_2 emission rate (520 ng/J) was exceeded on each of the four days that pluggage was a problem. During this period, the 24-hour average SO_2 emission rate ranged from 536 ng/J to

1730 ng/J. The exact cause for pluggage developing in the central gas disperser is not known.

On Thursday, August 25, 1983 low slurry feed rate (∿7.2 gpm) to the spray dryer (compared to a normal 9-12 gpm rate) resulted in an SO_2 emission rate (∿729 ng/J) higher than the maximum (520 ng/J) allowed by the State of Illinois. The exact cause for the low slurry feed rate to the spray dryer is not known.

On Friday morning, August 26, 1983, an electrical short developed in the "dry" control panel resulting in a damper becoming misaligned. The FGD system was bypassed resulting in almost no SO_2 control during this period. The electrical short was not corrected until after August 29, 1983.

2.2.3 SO_2 Removal Efficiency During "Trouble Free" Operation

From August 2 through August 29, 1983 the ANL Unit 5 FGD system operated in a "trouble free" mode during 18 of the 28 days (64 percent). The term "trouble free" is used here to denote periods of time when the FGD system did not encounter documented process upsets.

Table 2-5 presents a summary of the EPA Method 6B 24-hour average SO_2 removal and emission rate data collected during periods of "trouble free" operation. As shown in the table, the average SO_2 removal efficiency ranged from 82.2% to 92.1%, with an overall average of 86.8%. The average SO_2 emission rate ranged from 150 ng/J (0.348 lbs/10^6 Btu) to 373 ng/J (0.866 lbs/10^6 Btu), with an overall average of 271 ng/J (0.629 lbs/10^6 Btu).

Also included in Table 2-5 is the corresponding 24-hour average spray dryer approach to saturation temperature (ΔT_{AS}) for each period of "trouble free" operation. The ΔT_{AS} is calculated based on the difference between the spray dryer outlet process gas temperature and the baghouse outlet dew point temperature. Except for August 6, 1983, ΔT_{AS} ranged from 23 to 29°F with an

average of 27°F during "trouble free" operation. On August 6, 1983, the average ΔT_{AS} was 17°F and the emission rate (0.866 lbs/10^6 Btu) was the highest for any of the "trouble free" days. The spray dryer is designed to maintain a ΔT_{AS} of 22°F at the spray dryer outlet. It is not known if the difference between the design ΔT_{AS} value of 22°F and the average value of 27°F is due to inaccurate gas temperature and/or gas dew point measurements or if the system was not operating at the designated ΔT_{AS} conditions.

2.2.4 ANL Process Data Quality

The quality (precision) of the EPA Method 6B data collected during this program was carefully determined and the results are discussed in detail in Section 3. Assessment of the quality of the ANL Unit 5 boiler and FGD process data, summarized in Table 2-2, was beyond the scope of this program. Therefore, the quality of these data is subject to conjecture. One possible exception to this is the Contraves/Goerz continuous emission monitoring system (CEMS) data collected from the stack during this program. The relative accuracy of the Contraves/Goerz CEMS was not determined directly using EPA-accepted methodology, during this program. However, by comparing EPA Method 6B results to Contraves/Goerz CEMS results obtained during the same time period, the relative accuracy of the Contraves/Goerz can be estimated.

Table 2-6 presents a summary of the EPA Method 6B and Contraves/Goerz SO_2 and CO_2 concentration data and the SO_2 emission rate data. The Contraves/Goerz SO_2 and CO_2 concentration data are reported on a wet basis. The EPA Method 6B SO_2 and CO_2 concentration data are reported on a dry basis because the moisture content of the flue gas was not determined during this program. Therefore, EPA Method 6B and Contraves/Goerz SO_2 and CO_2 concentration data cannot be compared directly. However, if you assume a moisture content of about 15 percent (dew point temperature $\sim$130°F) in the stack, a basis of comparison can be established. The percent difference between the EPA Method 6B and the Contraves/Goerz SO_2 and CO_2 concentration data should approach the fraction of moisture ($\sim$15%) in the flue gas if the two sources of SO_2 and CO_2

data agree with each other. Based on the data in Table 2-6, the Contraves/Goerz CO_2 data compare within ±13% of the EPA Method 6B data on all days except August 6, 7, and 9, 1983.

The Contraves/Goerz SO_2 concentration data and SO_2 emission rate data, in Table 2-6, do not compare favorably with thecorresponding EPA Method 6B SO_2 data collected during periods of SO_2 compliance (1.2 lbs $SO_2/10^6$ Btu). The Contraves/Goerz SO_2 monitor on the stack does not appear to be very linear below about 400 ppm SO_2 (dry basis). In most cases, as the actual SO_2 concentration (based on EPA Method 6B) decreases below 400 ppm, the error in the Contraves/Goerz monitor increases substantially. For example, on August 12, 1983 the Contraves/Goerz average SO_2 value (463 ppm) was approximately 40% higher than the corresponding EPA Method 6B SO_2 concentration (389 ppm) after adjusting the Contraves/Goerz SO_2 data for 15% moisture. On August 26, 1983 the Contraves/Goerz average SO_2 value (319 ppm) was approximately 200% higher than the corresponding EPA Method 6B SO_2 concentration (125 ppm) after adjusting the Contraves/Goerz SO_2 data for 15% moisture. The high Contraves/Goerz SO_2 concentrations resulted in the Contraves/Goerz SO_2 emission rates being proportionately higher than SO_2 emission rates based on EPA Method 6B data.

TABLE 2-4. ANL UNIT 5 SPRAY DRYER-BAGHOUSE SYSTEM UPSET SUMMARY FOR THE PERIOD OF AUGUST 1 THROUGH AUGUST 29, 1983

Date	Approximate Time Period	Type of Upset	Effect on Performance
0805	1700 hrs - 2400	Outlet Contraves Inoperable	Poor System Control
0806	0000 hrs - 2400	Outlet Contraves Inoperable	Poor System Control
0807	0000 hrs - 2400	Outlet Contraves Inoperable	Poor System Control
0808	0000 hrs - 1100	Outlet Contraves Inoperable	Poor System Control
0809	0245 hrs - 0600	High Absorber Pressure	Flue Gas Bypasses FGD System--No Scrubbing
0809	1900 hrs - 2400	High Absorber Pressure	Flue Gas Bypasses FGD System--No Scrubbing
0810	0000 hrs - 1400	High Absorber Pressure	Flue Gas Bypasses FGD System--No Scrubbing
0810	2200 hrs - 2400	High Absorber Pressure	Flue Gas Bypasses FGD System--No Scrubbing
0811	0000 hrs - 2400	High Absorber Pressure	Flue Gas Bypasses FGD System--No Scrubbing
0812	0000 hrs - 1300	High Absorber Pressure	Flue Gas Bypasses FGD System--No Scrubbing
0825		Low Slurry Feed	Reduced SO_2 Removal and Higher Spray Dryer Exit Gas Temperature
0826	Approximately 0500-2400	Electrical Short Circuit	Flue Gas Bypasses FGD System--No Scrubbing
0827	0000 hrs - 2400	Electrical Short Circuit	Flue Gas Bypasses FGD System--No Scrubbing
0828	0000 hrs - 2400	Electrical Short Circuit	Flue Gas Bypasses FGD System--No Scrubbing
0829	0000 hrs - 2400	Electrical Short Circuit	Flue Gas Bypasses FGD System--No Scrubbing

TABLE 2-5. SUMMARY OF EPA METHOD 6B 24-HOUR AVERAGE SO_2 REMOVAL AND EMISSION RATE DATA COLLECTED AT ANL FROM AUGUST 2 THROUGH AUGUST 26, 1983 DURING PERIODS OF "TROUBLE FREE" OPERATION

Date[a] (MMDD)	Average SO_2 Removal Efficiency	Average SO_2 Emission Rate		Spray Dryer Approach To Saturation (°F)[b]
		ng/J	lbs/10^6 Btu	
0802	86.9	245	0.570	29
0803	86.5	303	0.704	27
0804	92.1	150	0.348	29
0805	86.5	267	0.622	27
0806	82.2	373	0.866	17
0807	83.0	350	0.814	23
0813	88.9	221	0.510	29
0814	83.6	334	0.779	29
0815	83.8	332	0.771	28
0816	91.8	164	0.380	28
0817	88.4	236	0.548	26
0818	85.2	305	0.708	28
0819	86.9	273	0.633	23
0820	89.1	224	0.521	26
0821	87.3	261	0.607	24
0822	87.5	255	0.594	27
0823	84.2	324	0.752	28
0824	87.7	256	0.594	26
Overall Average	86.8	271	0.629	27[c]

[a]The EPA Method 6B sampling trains were operated from 1000 hours on the day indicated to 0900 hours on the next day to constitute a 24-hour sample.
[b]Based on the difference between the spray dryer outlet process gas temperature and the baghouse outlet dew point temperature.
[c]Does not include value for August 6, 1983.

TABLE 2-6. COMPARISON OF PROCESS DATA COLLECTED USING THE EPA METHOD 6B AND THE CONTRAVES/GOERZ CEMS ON THE STACK AT ANL FROM AUGUST 2 THROUGH AUGUST 25, 1983

	Stack CO_2 Concentration (%)			Stack SO_2 Concentration (ppm)			SO_2 Stack Emission Rate ($lbs/10^6$ Btu)		
Date (MMDD)	Contraves/ Goerz[a]	EPA Method 6B[b]	Δ%[c]	Contraves/ Goerz[a]	EPA Method 6B	Δ%[c]	Contraves/ Goerz	EPA Method 6B	Δ%[d]
0802	--	9.2	--	--	180	--	1.26	0.570	121
0803	--	8.7	--	--	208	--	1.25	0.704	78
0804	--	10.0	--	--	116	--	1.24	0.348	256
0805	--	10.0	--	--	212	--	1.10	0.622	77
0806	5	9.8	-40	--	286	--	--	0.866	--
0807	6	9.8	-28	--	271	--	--	0.814	--
0808	5.4	9.6	-34	506	515	16	1.41	1.57	- 10
0809	8.2	9.3	3.7	903	796	33	1.75	2.52	- 31
0810	--	9.6	--	--	702	--	--	2.15	--
0811	8.6	9.8	3.2	1230	1340	8.0	2.02	4.01	- 50
0812	8.1	9.2	3.6	463	389	40	1.32	1.25	5.6
0813	7.9	9.0	-3.3	310	158	131	1.11	0.510	118
0814	8.3	8.9	9.7	349	236	74	1.20	0.779	54
0815	8.5	9.0	11.1	352	236	75	1.21	0.771	57
0816	8.9	9.6	9.1	319	125	200	1.02	0.380	168
0817	9.5	10.1	10.7	319	188	100	1.02	0.548	86
0818	9.5	10.2	9.6	400	245	92	1.20	0.708	69
0819	8.2	10.3	-6.3	297	222	57	1.09	0.633	72
0820	8.8	9.8	5.6	375	174	154	1.10	0.521	111
0821	9.6	10.0	12.9	372	206	112	1.12	0.607	85
0822	9.3	10.0	9.4	374	200	120	1.11	0.594	87
0823	9.1	9.8	9.2	398	250	87	1.25	0.752	66
0824	9.5	10.1	10.7	370	204	113	1.10	0.594	85
0825	9.2	10.2	6.1	588	586	18	1.33	1.69	-21

[a] Contraves/Goerz SO_2 and CO_2 values are on wet basis.

[b] EPA Method 6B data are on dry basis.

[c] $$\frac{\left(\frac{\text{Contraves}}{1-.15\ \text{Moisture Fraction}}\right) - \text{EPA}}{\text{EPA}} \times 100 = \Delta\%$$

[d] $$\frac{\text{Contraves} - \text{EPA}}{\text{EPA}} \times 100 = \Delta\%$$

SECTION 3

DATA QUALITY

The test approach used during this project for FGD system characterization incorporated a comprehensive quality assurance/quality control (QA/QC) program as an integral part of the overall sampling and analytical efforts. The QA/QC program was designed, in part, to ensure that the SO_2 emission rate/removal efficiency data collected during the test program were complete, representative, and comparable to other similar data. It was also designed to control measurement data quality within prescribed limits of acceptability, and to ensure that the resulting data were of known quality with respect to precision and accuracy. The QA/QC efforts addressed only efforts associated with Method 6B sampling and analysis. Control and assessment of process data quality were not within the scope of work for this project.

This section presents an assessment of the quality of measurement data collected during this test program. This assessment is based upon QC data and quality assurance audit results, and provides estimates of the uncertainty associated with the measurement data. Section 3.1 presents conclusions and a summary of QA/QC results. A discussion of the objectives of the QA/QC efforts, and the general approach used in achieving these objectives, is presented in Section 3.2. Methods used in quantitating data quality, along with definitions and explanations of QA/QC and statistical terminology are discussed in Section 3.3. Audit procedures and results are presented and discussed in Section 3.4, while Section 3.5 addresses QC procedures and results used to assess precision of the Method 6B data. Section 3.6 contains a brief discussion of reliability of the Method 6B sampling system and the impact upon data capture (completeness).

3.1 SUMMARY AND CONCLUSIONS

Quality control data collected throughout the course of the measurement program, along with performance audit results, provide the basis for assessing the quality of the SO_2 emission rate/removal efficiency data. These qualifying data indicate that the measurement data are of adequate quality to fulfill the program objectives. Table 3-1 presents measured values for precision and accuracy (bias) of the SO_2 emission rate data and the measurement parameters required to calculate emission rate. Precision and accuracy objectives which were presented in the Quality Assurance Project Plan (4) for this project are shown for comparison.

As indicated in Table 3-1, precision and accuracy of the emission rate data were well within the objectives presented in the QA Project Plan. SO_2 and CO_2 concentrations and sample volume are not separate measurement parameters as such, but rather are component parts of the SO_2 emission rate determination. Data quality for each of these individual components was also within the specified objectives. Based on measured precision and bias for the various components of the measurement system, 95% of the removal efficiency data would be expected to be in error by less than ±5% of the reported value (i.e., for at least 95% of the data, the "true" value should be within ±5% of the reported value).

The data quality measurements presented in Table 3-1 are average values and, as such, provide only a cursory glimpse of the data quality assessment performed for this project. The QA/QC program was designed to provide detailed information pertaining to the limitations associated with the measurement data. For instance, results for duplicate samples indicate that precision of the emission rate data at the inlet of the FGD system (2.8%) was considerably better than that at the outlet (8.3%). While the performance audit results and QC data presented in the remainder of this section provide the primary basis for evaluation of uncertainty in the emission rate measurements, this evaluation requires careful interpretation of the audit and QC data in the context of the measurement data and the manner in which the individual measurement parameters are related.

TABLE 3-1. SUMMARY OF ESTIMATED VS. MEASURED DATA QUALITY

Measurement Parameter	Precision[a]		Accuracy[b]	
	Estimated[c]	Measured[d]	Estimated[c]	Measured[e]
SO_2 Emission Rate	8.0%	6.2%	±7.7%	0.0% ± 1.6%
SO_2 Concentration[f]	5.0%	0.5%	±5.0%	-0.2% ± 0.1%
CO_2 Concentration	5.0%	3.0%	±5.0%	0.0% ± 0.2%
Sample Volume	2.0%	---	±5.0%	-2.6% ± 1.7%

[a]Coefficient of variation for replicate samples

[b]Bias (systematic error), expressed as a percentage of the measured value (i.e., relative error)

[c]Data quality objective presented in the Quality Assurance Project Plan

[d]Measured precision (replicability) based on observed variability in results for duplicate samples collected using colocated sampling trains

[e]95% confidence interval for mean relative error (bias) based on performance audit results

[f]Precision and bias of analytical phase of the method (i.e., barium-thorin titrations)

3.2 QA/QC PROGRAM OBJECTIVES

For any measurement effort, there always exists some degree of uncertainty associated with the measurement data due to inherent limitations of the measurement system. Usefulness of the measurement data is dependent upon the degree to which the magnitude of this uncertainty is known and upon its relative impact. The industrial boiler FGD system testing described in this report included a comprehensive quality assurance/quality control (QA/QC) program. The objectives of the QA/QC efforts were twofold. First, they provided the mechanism for controlling data quality within acceptable limits. Second, they form the basis for estimates of uncertainty by providing the necessary information for defining error limits associated with the measurement data.

The quality assurance function was organized to provide independent review and assessment of project activities and their ability to achieve the stated data quality objectives. The QA Coordinator for the project had the responsibility of evaluating the adequacy and effectiveness of the QC system and providing assurance that it was, in fact, responsive to the specific needs of the program.

In addition to reviewing the test plan and providing input into design of the QC efforts, the QA Coordinator conducted both performance and systems audits during the test program. The performance audits were designed to provide a direct, quantitative, point-in-time assessment of data quality in terms of accuracy. This was achieved by using equipment and standards which were independent of those used by the field personnel. The systems audit was designed to provide a systematic, qualitative review and assessment of the critical elements of the various measurement systems and associated internal quality control (QC) systems, with emphasis upon procedures and documentation.

A quality control system is a system of routine internal procedures for assuring that the data output of a measurement system meets prescribed criteria for data quality. Inherent and implied in this control function is a parallel function of measuring and defining the quality of the data output. A well-designed internal QC program must be capable of controlling and measuring the quality of the data in terms of precision and accuracy, as well as ensuring that the data are complete, representative, and comparable. Precision reflects the influence of the inherent variability in any measurement system. Accuracy reflects the degree to which the measured value represents the actual or "true" value for a given parameter, and includes elements of both bias and precision. The precision and bias of the final data are related to the precision and bias of the component parts of the measurement system. While the QA activities served an evaluative function which was independent of the testing efforts per se, the QC system was an integral part of the daily technical effort. Together, the QC data and the audit results may be used to qualify the measurement data, as discussed in the remainder of this section.

3.3 METHODS OF QUANTITATING DATA QUALITY

Internal quality control data associated with sampling/analytical aspects of this project, along with performance audit results and the measurement data themselves, provide the basis for a quantitative assessment of measurement data quality. The two aspects of data quality which are of primary concern are precision and accuracy. Accuracy reflects the degree to which a measured value represents the actual or "true" value for a given parameter, and includes elements of both bias and precision. Precision is a measure of the variability associated with the measurement data.

The quality control system for this measurement effort, in its broadest sense, included all procedures which ensured that the resulting measurement data were of adequate quality to fulfill the program objectives. Some procedures which fall into the category of QC were primarily intended to control

data quality within acceptable limits (e.g., adherence to specified sampling and analytical procedures, calibration of instrumentation, careful documentation of field data and results, etc.). Other QC procedures were intended to provide data pertaining to precision (variability) and accuracy of the measurement data. In some cases, a single QC procedure might fulfill both control and assessment functions.

The data necessary for assessment of precision and accuracy were obtained in several ways. The performance audits for the various measurements parameters were meant to address accuracy of the measurement systems and consisted of challenging component parts of the system with audit samples or standards. Variability (precision) associated with the measurement system was measured and documented using QC procedures such as control sample analyses, duplicate analyses, and collection of duplicate samples. These procedures are discussed in more detail in Sections 3.4 and 3.5. This section is devoted to discussion of the procedures and operating definitions used in quantitating data quality.

3.3.1 Definitions of Precision, Accuracy, and Bias

Precision, by the definition presented in the EPA Quality Assurance Handbook (3), is "a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions." Different measures of precision exist, depending upon these "prescribed similar conditions." Radian typically uses the EPA definitions for replicability, repeatability, and reproducibility, as summarized in Table 3-2.

Accuracy is a measure of the degree of agreement between a measured value and the true value of the measured parameter. For single measurements, accuracy includes components of both bias and precision, i.e., both systematic and random error. Accuracy of the average of individual measurements equates accuracy with bias and represents an attempt to quantitate systematic error (bias) independent of random error (precision). The validity or significance of the estimate of bias is directly related to the number of individual

TABLE 3-2. MEASURES OF PRECISION

Source of Variability	Replicability	Repeatability	Reproducibility
Specimen (subsample)	Same or different	Same or different	Most likely different
Sample	Same	Same	Same
Analyst	Same	At least one of these must be different	Different
Apparatus	Same		Different
Day	Same		Same or different
Laboratory	Same	Same	Different

measurements used to compute the average. It is based on the principle that, as the number of individual measurements is increased indefinitely, the sample mean, $\bar{X}$, approaches a definite value, μ. The difference between μ and the true value, T, represents the magnitude of the measurement bias, or systematic error. The error in each individual measurement reflects this systematic error plus random error due to imprecision.

3.3.2 Assessment of Accuracy and Bias

Performance audits represent the primary mechanism for assessing accuracy of a measurement system and, by extrapolation, accuracy of the resulting measurement data. When a measurement system is challenged with an audit sample, the true value of which is known, the degree of agreement between the measured value and the true value reflects the accuracy of the measurement. The difference between the two is due to measurement error and includes both random error (imprecision) and systematic error (bias). This difference, expressed as "percentage of the true value," is often referred to as "relative accuracy," or simply "accuracy," although technically it represents inaccuracy.

Typically, repeated measurements are made of the parameter of interest for the same audit sample, or for additional samples at different levels, and the average error is then calculated. As discussed in Section 3.3.1 above, this error value represents an estimate of measurement bias or systematic error, although it is also often labeled "accuracy."

The significance of this bias estimate may be evaluated using confidence intervals. An approximate 95% confidence interval for the mean error can be calculated using:

$$CI_{\text{mean error}} = \text{Mean}(\bar{X}) \pm t_{0.025,(n-1)} \left(\frac{\text{Standard Deviation}}{\sqrt{n}} \right)$$

where n is the number of measurements used to compute the average and standard deviation and t is a table statistical value (0.025 confidence level, n-1 degrees of freedom; where n is greater than 10, t approaches 2.0).

As an example, for a particular set of nine measurements, an overall mean of 20 ppm is reported, and the standard deviation of these data is 10 ppm. Also, the true concentration if 30 ppm. for these measurements, the 95% confidence interval is:

$$95\%\ CI_{mean} = 20 \pm 2.3 \left(\frac{10}{\sqrt{9}}\right)$$

$$\text{or } 20 \pm 7.7$$

which is the interval ranging from 12 ppm to 28 ppm. Since this interval does not include the true value, 30 ppm, a conclusion of bias is justified. The magnitude of this bias is between 2 and 18 ppm. The uncertainty in the bias estimate is due to variability arising from random error.

For the audit data presented in Section 5.4, results are presented in terms of relative error where:

$$\text{Relative Error} = \frac{\text{Measured Value - True Value}}{\text{True Value}} \times 100$$

Results for a given set of audit data are typically summarized in terms of "mean relative error," which represents an estimate of the bias of the measurement system. Variability among the individual error values used to calculate mean relative error reflects one aspect of the overall precision associated with the measurement system. This variability is typically quantitated in terms of the standard deviation of the relative error, which is also presented.

The confidence interval approach may also be applied to audit results expressed in terms of mean relative error. For example, consider a set of

audit data for which a mean relative error of -5.0% is reported with a standard deviation of 6.0%, based on five observations (i.e., five audit sample analyses). For these measurements, the 95% confidence interval for the mean is:

$$95\%\ CI = -5.0\% \pm 2.8\ \frac{6.0\%}{5} \quad \text{or } -5.0\% \pm 7.5\%$$

Since the confidence interval (-12.5%, 2.5%) includes zero, conclusion of bias is not justified and the audit data indicate that the measurements are accurate within the limits of precision.

3.3.3 Assessment of Precision

As stated above, accuracy of measurement data is a function of both bias (systematic error) and precision (random error). If a particular measurement method is known or assumed to be unbiased, i.e., free of systematic error, then accuracy of the results is limited only by random variability, i.e., by the precision of the measurements. For most standard or accepted source test methods, random error is the major source of measurement error.

For the sampling/analytical procedures used in this program, the measurement data precision (i.e., random error, exclusive of temporal variability) is a function of the combined effects of analytical variability and sampling variability. Each of these two sources of variability could be further subdivided into numerous specific components of variability such as that associated with standardization of the barium chloride titrant, sample handling, etc.

The precision estimates presented in Section 3.5 are based on observed variability among replicate or repeat measurements made under various "prescribed similar conditions," selected for specific purposes. This variability was quantitated by first calculating the standard deviation for each set of

measurements. The standard deviation is a measure of the average distance of individual observations from the mean. It is usually denoted s and defined as:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1}}$$

where: n is the sample size,

X_i is the i^{th} observation in the sample, and

$\bar{X}$ is the sample mean.

In order to facilitate comparison of variability at different concentration levels, measured variability is reported in terms of the coefficient of variation (also known as relative standard deviation) which is defined as:

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\%$$

When individual measurements of variability (i.e., CV) were combined (pooled) to obtain an overall measure of variability for a given set of conditions or measurements, the following technique was used:

$$\text{Pooled CV} = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 \, DF_i}{\sum_{i=1}^{n} DF_i}}$$

where X_i = CV of data set i (e.g., CV for one duplicate pair, i),

DF_i = degrees of freedom for data set i (k_i-1),

n = total number of data sets (e.g., total number of duplicate pairs),

k_i = number of data points in set i (e.g., k=2 for duplicates),

i = data set 1,2,3 ... n

In Section 5.5, variability in the Method 6B data is evaluated in terms of that arising from various components of the method. Magnitudes and relative contributions of each component or source of variability are presented. This evaluation of the measurement data was performed using a statistical technique known as analysis of variance (ANOVA). This technique separates the variation present in a set of data into independent components and then tests hypotheses about these components. A complete discussion of the ANOVA technique is given by Cochran and Cox (5).

Also presented in Section 3.5 are results for paired t-tests performed using Method 6B SO_2, CO_2, and emission rate data. These tests were performed to evaluate the statistical significance of observed differences in results between the colocated sampling trains. This statistical procedure consisted of calculating the difference between results for Train A and Train B, at both inlet and outlet locations, for each test run (i.e., each day). For each pair of trains, and each parameter, mean differences and standard deviations were calculated. The hypothesis that the mean difference was equal to zero was then tested at the 95% confidence level using a t-test. The formula for the t-test is:

$$t = \frac{\bar{d} - \mu_d}{S_d / \sqrt{n}}$$

where $\bar{d}$ = mean of the observed paired difference,

μ_d = hypothesized mean difference, i.e., zero,

S_d = standard deviation of the paired differences, and

n = number of paired differences in the sample set.

For the hypothesis test, if the calculated value of t is greater than the table value of t for the sample size n (i.e., n-1 degrees of freedom), the null hypothesis must be rejected. Rejection of the null hypothesis (mean difference is equal to zero) would indicate that the difference between results for the paired trains was statistically significant. If the calculated value of t is less than the table value, we must fail to reject the null hypothesis. This is equivalent to saying that there is no reason to

believe that observed differences in results between the trains are significant (i.e., there is no reason to believe they are not equal to zero).

3.4 QUALITY ASSURANCE AUDITS

A quality assurance audit of measurement efforts associated with this test program was conducted August 27-29, 1983 at Argonne National Laboratory in Argonne, Illinois. This audit was performed by the project QA Coordinator and included performance audits of selected components of the measurement system, as well as a systems audit of the overall test effort. Audit procedures and results are discussed in this section.

3.4.1 Performance Audits

Performance audits for this program provided a direct, point-in-time evaluation of the capability of the measurement system to generate data of acceptable quality. In its broadest sense, the measurement system consisted of numerous components, including the equipment, apparatus, calibration standards, and personnel used to perform the testing, as well as the associated procedures and techniques used for sample collection, sample analysis, and data reduction. The primary measurement parameters for this program were SO_2 emission rate and removal efficiency. These parameters cannot be measured directly, but rather are calculated based upon measurements of SO_2 and CO_2 concentrations in flue gas, and carbon content and gross caloric value of the fuel. The performance audits were therefore designed to address the measurement parameters used in calculating SO_2 emission rates and removal efficiencies.

The emission rate/removal efficiency "measurement system" may be considered to have consisted of two subsystems. The primary subsystem was that used for measuring SO_2 and CO_2 concentrations in the flue gas. The other subsystem was that used for determining carbon content and gross caloric value of the fuel, which were in turn used to calculate the CO_2 F-factor. Performance audit activities addressed both of these subsystems.

Since the fuel analyses represented a relatively minor component of the overall measurement effort, the performance audit of that subsystem consisted merely of submitting a standard coal sample for analysis along with one of the actual coal samples. The performance audit of the flue gas SO_2 and CO_2 measurements was considerably more involved, commensurate with the level of effort involved and complexity of the measurement system. As discussed in Section 5, EPA Method 6B was used for determination of SO_2 and CO_2 concentrations in the inlet and outlet flue gases. This measurement system as a whole was audited using standard atmospheres of SO_2 and CO_2 in nitrogen. Major components of the Method 6B measurement system were also audited individually. These included the analytical phase of the SO_2 determinations (i.e., barium-thorin titrations), the dry gas meters used for gas volume measurements, and the balance used for gravimetric determination of CO_2. Performance audit results are summarized in Table 3-3. Audit procedures and detailed results are presented and discussed in the remainder of this section.

3.4.1.1 Method 6B Measurements--

The Method 6B sampling and analytical system as a whole was audited by challenging the system with test atmospheres of SO_2 and CO_2 in nitrogen. These test atmospheres were collected using the four sampling trains (two trains at the inlet and two at the outlet of the spray dryer/fabric filter FGD system) in their normal configuration. The only difference between normal sample collection procedures and those used for the audit test runs was the sampling interval. For the audit, sampling was performed continuously over intervals of approximately one hour duration, as opposed to the normal procedures of intermittent sampling over a 24-hour period.

Test atmospheres for the first two audit runs were generated by blending two compressed gas mixtures, one containing CO_2 (and O_2) in nitrogen, and the second containing SO_2 in nitrogen. The third test run used only an SO_2 mixture. A total of three gas mixtures were used to generate different SO_2 and CO_2 concentrations for the three test runs. Two SO_2 mixtures were used, both of which were EPA Traceability Protocol mixtures obtained from

TABLE 3-3. SUMMARY OF PERFORMANCE AUDIT RESULTS

Parameter	Analytical Method	Instrument	Audit Standard(s)	Mean Relative Error[a]
SO_2 (Sampling and Analysis)	EPA Method 6B	--	Scott Environmental Technology SO_2 Cyl. #AAL 11426 and Cyl. #AAL 11470	0.15%
CO_2 (Sampling and Analysis)	EPA Method 6B	--	Scott Environmental Technology O_2/CO_2 Cyl. #AAL 6541	0.00%
SO_2 (Analysis Only)	Barium-Thorin Titration	--	EPA Stationary Source QA Reference Standards Lot #0980	-0.20%
Gas Volume	Dry Gas Meter	Singer #K418992	GCA/Precision Scientific Wet Test Meter #14AES	-2.80%
		Singer #H988524	GCA/Precision Scientific Wet Test Meter #14AES	-1.30%
		Singer #H988523	GCA/Precision Scientific Wet Test Meter #14AES	-3.91%
		Singer #H988525	GCA/Precision Scientific Wet Test Meter #14AES	-2.55%
Weight	Balance	Mettler PC 4400 Serial No. 816571	Ainsworth 4254-S Class S Weights Serial No. 36697	±0.02g[b]
% Carbon in Coal	ASTM D3178	--	Alpha Resources Coal Standard AR 2781 Lot #315	-0.35%
Btu/lb Coal	ASTM D2015	--	Alpha Resources Coal Standard AR 2781 Lot #315	-0.72%

[a] Average percentage error, unless otherwise indicated.

[b] Error range, in grams.

Scott Environmental Technology, Inc. One mixture (Cylinder #AAL 11426) had an SO_2 concentration of 1630 ppm while the other (Cylinder #AAL 11470) contained 612.6 ppm SO_2. The third mixture (Cylinder #AAL 6541) was a "certified" standard (analytical accuracy ±2%) also obtained from Scott, containing 30% CO_2 and 40% O_2 in nitrogen.

The CO_2/O_2 mixture was blended with the SO_2 mixtures using a Radian-modified Bendix Model 8861-DA gas dilution system. This sytem uses precision pressure regulators to control flow through a series of capillary flow restrictors. Various ratios of two gas mixtures are obtained using different capillary combinations. Capillary flows (i.e., mixing ratio) were measured immediately before each test run using an NBS-traceable Hastings HBM 1A soap bubble flow meter. Audit gas mixtures were introduced to the sampling trains using a manifold system which incorporated a tee for venting excess flow to the atmosphere, preventing pressurization of the manifold. Duplicate samples were collected during each of the three audit test runs using either inlet or outlet sampling train pairs. Two runs were conducted using the inlet trains and one using the outlet train, for a total of six samples.

Results for the Method 6B audit runs are presented in Table 3-4. As discussed in Section 3.3 above, individual values for relative error include both systematic and random error components (i.e., error due to both bias and imprecision). By averaging relative error values for a given parameter to obtain mean relative error, variability due to imprecision tends to be "averaged out." Thus, mean relative error is the best available estimate of measurement bias. The 95% confidence interval is a range which takes into account variability among the observations and the number of observations in the sample set to define the uncertainty of the bias estimate. It represents the interval within which we can be 95% confident that the "true" mean value (i.e., the population mean) falls. If, as is the case for the Method 6B audit data, the 95% confidence interval for mean relative error includes zero, a conclusion of bias is not justified and the measurement data are judged to be accurate within the limits of its precision. Precision of the Method 6B data is discussed in Section 3.5 below.

TABLE 3-4. METHOD 6B AUDIT RESULTS

Test Run	Train ID	SO_2			CO_2			Emission Rate[a]		
		Actual SO_2 Concentration (ppm)	Measured SO_2 Concentration (ppm)	Relative Error[b] (%)	Actual CO_2 Concentration (% v/v)	Measured CO_2 Concentration (% v/v)	Relative Error[b] (%)	Actual Emission Rate (ng/J)	Measured Emission Rate (ng/J)	Relative Error[b] (%)
1	Inlet A	1311	1312	0.08	5.86	5.78	-0.08	2838	2879	1.44
1	Inlet B	1311	1279	-2.44	5.86	5.74	-0.12	2838	2826	-0.42
2	Outlet A	425.5	427.1	0.38	9.16	9.16	0.00	589	591	-0.34
2	Outlet B	425.5	431.4	1.39	9.16	9.35	0.19	589	585	-0.68
3	Inlet A	1630	1643	0.80	0.0	0.0	--	--	--	--
3	Inlet B	1630	1641	0.68	0.0	0.0	--	--	--	--
			Mean Relative Error[c]	0.15%			0.00			0.00
			Standard Deviation[d]	1.34%			0.14			0.97
			95% C.I.[e]	(-1.19%, 1.56%)			(-0.22%, 0.22%)			(-1.55%, 1.55%)

[a] Emission rate values calculated from corresponding SO_2 and CO_2 concentrations using a carbon dioxide F-factor (F_c) of 4.772×10^{-8} Nm^3/J, where Emission Rate = $C_s \times F_c \times \left(\frac{100}{\% CO_2}\right) \times 10^6$, when C_s = SO_2 concentration, mg/Nm^3

[b] Difference between measured and actual concentrations, expressed as a percentage of the actual concentration, i.e., Relative Error = $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$

[c] Estimate of bias, or systematic error

[d] Standard deviation of relative error; indicative of variability about the mean

[e] 95% confidence interval for mean relative error

The emission rate values in Table 3-4 were calculated from the SO_2 and CO_2 concentrations using a carbon dioxide F-factor value of 4.772×10^{-8} Nm^3/J. "Actual emission rates" for each run were calculated using corresponding values for "actual SO_2 concentration" and "actual CO_2 concentration." "Measured emission rates" were calculated in the same manner, using SO_2 and CO_2 results for each run. These data and corresponding error values are presented to illustrate error propagation in calculating emission rates from SO_2 and CO_2 measurements. As shown in the table, the 95% confidence interval for mean relative error of the emission rate values is larger than the corresponding intervals for SO_2 and CO_2 concentrations. At ±1.55%, it is, however, well within the ±7% objective specified in the Quality Assurance Project Plan (4).

3.4.1.2 SO_2 Analyses--

The audit test runs described above provide estimates of total measurement error for Method 6B sampling and analysis. A performance audit was also performed on the analytical phase of the Method 6B SO_2 determination, to assess error associated with the barium-thorin titrations. This audit consisted of submitting for analysis a set of five Stationary Source Quality Assurance SO_2 Reference Samples. These audit samples were obtained from the U.S. Environmental Protection Agency, Quality Assurance Division, EMSL/RTP.

Results for the SO_2 analytical audit samples are presented in Table 3-5. Although the magnitude of the mean relative error value (i.e., bias estimate) for the analytical phase of the method is slightly larger than the corresponding value for sampling and analysis (Table 3-5), the standard deviation and 95% confidence intervals are smaller indicating less variability (i.e., better precision). Since the 95% confidence interval for mean relative error does not include zero, a slight negative bias is indicated. Overall, however, these results are excellent, with no observed relative error greater than 0.4%. Using these audit data to calculate statistical tolerance limits, it may be shown that, at the 95% confidence level, at least 90% of the

TABLE 3-5. SO_2 ANALYTICAL AUDIT RESULTS

Sample Number (Lot 0980)	Actual SO_2 Concentration (mg/Nm^3)	Measured SO_2 Concentration (mg/Nm^3)	Relative Error[a] (%)
8286	381.3	381.1	-0.05
4442	762.6	760.7	-0.25
1823	1143.9	1140.2	-0.32
2357	1906.5	1902.5	-0.21
5565	2287.8	2284.4	-0.15
		Mean Relative Error[b]	-0.20
		Standard Deviation[c]	0.10
		95% C.I.[d]	(-0.32,-0.07)

[a]Difference between measured and actual concentrations, expressed as a percentage of the actual concentration, i.e.,

$$\text{Relative Error} = \frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$$

[b]Estimate of bias, or systematic error

[c]Standard deviation of relative error; indicative of variability about the mean

[d]95% confidence interval for mean relative error

analytical data would be expected to have relative errors in the interval ranging from -0.62% to 0.23%.

3.4.1.3 Dry Gas Meters--

Each of the four dry gas meters (DGMs) used for Method 6B sampling were audited using a GCA/Precision Scientific wet test meter (0.1 ft^3 per revolution, Serial Number 14 AES). Two calibration check runs were performed for each DGM. Nominal flow rates of one liter per minute were used, corresponding to the normal sampling flow rates. A minimum of 8 liters of air was drawn during each test run. Gas volumes measured by the wet test meter and the DGMs were used to calculate dry gas meter correction factors (DGMCFs) for each DGM. These audit values are presented in Table 3-6. As indicated in the table, audit correction factors for all four meters agreed with the pretest calibration factors within the ±5% acceptance criterion.

3.4.1.4 Balance--

The Mettler Model PC 4400 top loader balance (Serial Number 816571) used for gravimetric determination of CO_2 was audited using a set of Class S standard weights (Ainsworth 4254-S, Serial Number 36697). As shown in Table 3-7, the balance was accurate within ±0.02 g over the audit range of 0.02 g to 210.00 g. Since the Ascarite® columns were weighed only to the nearest 0.1 g, errors of less than ±0.05 g would have no measureable impact upon the CO_2 data. By way of comparison, a weighing error of 0.1 g would result in an error of about 0.14% CO_2, for a sample volume of 0.04 Nm^3. With a nominal CO_2 concentration of 10%, this would represent a relative error of less than 1.5% in the CO_2 measurement, or the emission rate measurement, as well.

3.4.1.5 Proximate/Ultimate Fuel Analyses--

The CO_2 F-factor used for calculating SO_2 emission rates from Method 6B SO_2 and CO_2 data was calculated based upon proximate/ultimate analyses of the coal used for firing the boiler. These coal analyses were performed by Commercial Testing and Engineering, Inc. The performance audit of these analyses consisted of submitting a standard coal sample for analysis

TABLE 3-6. DRY GAS METER AUDIT RESULTS

Meter S/N	DGM Correction Factor, Y, from Pretest Calibration	Measured DGM Correction Factors (Audit Results)		Mean Measured DGMCF	Mean Difference[a] (%)
		Run 1	Run 2		
K418992	0.9846	1.0135	1.0126	1.0130	-2.80
H988524	0.9980	1.0097	1.0126	1.0112	-1.30
H988523	1.0212	1.0666	1.0589	1.0628	-3.91
H988525	0.9924	1.0272	1.0095	1.0184	-2.55

[a]Difference between pretest calibration DGMCF (Y) and that measured during audit expressed as a percentage of the mean audit value, where

$$\text{Mean \% Difference} = \frac{\text{Mean Measured DGMCF} - \text{Pretest Calibration DGMCF}}{\text{Mean Measured DGMCF}} \times 100$$

TABLE 3-7. BALANCE AUDIT RESULTS

Standard Weight (grams)	Measured Weight (grams)	Error[a] (grams)
210.00	210.01	0.01
200.00	200.02	0.02
180.00	180.01	0.01
150.00	150.01	0.01
100.00	100.01	0.01
50.00	50.01	0.01
30.00	30.01	0.01
20.00	20.00	0.00
10.00	9.99	-0.01
5.00	5.00	0.00
3.00	3.00	0.00
2.00	2.00	0.00
1.00	1.00	0.00
0.50	0.50	0.00
0.30	0.30	0.00
0.20	0.19	-0.01
0.10	0.10	0.00
0.05	0.05	0.00
0.02	0.02	0.00
	Mean Error[b]	0.003
	Standard Deviation[c]	0.007
	95% C.I.[d]	(0.000, 0.007)

[a]Error, in grams (measured weight - standard weight)

[b]Average of individual errors, in grams

[c]Standard deviation of individual errors, in grams

[d]95% confidence interval for mean error, in grams

along with an actual sample. The audit standard (Part Number AR 2781, Lot Number 315) was obtained from Alpha Resources, Inc.

Results for the fuel audit analyses are presented in Table 3-8. Although a total of nine parameters are included in the proximate/ultimate analyses, only two of these, percent carbon from the ultimate analyses and Btu/lb from the proximate analysis, are used in calculating CO_2 F-factors. As indicated in the table, results for both of these parameters were accurate within ±1.0%. If the actual % CO_2 and Btu/lb values for the audit sample are used to calculate a CO_2 F-factor, a value of 1771 standard cubic feet (SCF) per million Btu is obtained (4.757×10^{-8} Nm^3/J). Using the measured values, an F-factor of 1796 $SCF/10^6$ Btu (4.824×10^{-8} Nm^3/J) is obtained. Thus, the audit results correspond to an F-factor relative error of about 1.4% (i.e., the difference between the two values represents 1.4% of the value obtained using the "actual" % carbon and Btu/lb values).

3.4.2 Systems Audit

A systems audit is an on-site qualitative review of the various aspects of a total sampling and/or analytical system to assess its overall effectiveness. It represents a subjective evaluation of a set of interactive systems with respect to strengths, weaknesses, and potential problem areas. The audit provides an evaluation of the adequacy of the overall measurement system(s) to provide data of known quality which are sufficient, in terms of quantity and quality, to meet the program objectives.

A systems audit of the measurement system used for the FGD system characterization testing was conducted at the time of the on-site performance audit. Prior to the field audit, a checklist was prepared which delineated the critical aspects of the test methodology, using the Quality Assurance Project Plan (4) as a guide. The checklist served as a tool to direct the focus of the systems audit and to document relevant observations. A copy of the completed checklist is shown in Figure 3-1.

TABLE 3-8. PERFORMANCE AUDIT RESULTS FOR COAL ANALYSES

Parameter	Actual Value	Measured Value	Relative Error[a]
Proximate Analysis			
% Ash	6.03%	6.07%	0.66%
% Volatile	42.39%	42.37%	-0.05%
% Fixed Carbon	51.58%	51.56%	-0.04%
Btu/lb.	13561	13419	-0.72%
% Sulfur	3.14%	3.08%	-1.91%
Ultimate Analysis			
% Carbon	74.81%	75.07%	0.35%
% Hydrogen	5.64%	5.26%	-6.73%
% Nitrogen	1.52%	1.46%	-3.94%
% Chlorine	0.01%	0.01%	0.00%

[a] $\text{Relative Error} = \frac{\text{Measured Value} - \text{Actual Value}}{\text{Actual Value}} \times 100$

RADIAN CORPORATION

METHOD 6B--DETERMINATION OF SO_2 AND CO_2

SYSTEMS AUDIT FORM

Site: ARGONNE NAT'L LAB Date: 8/28/83

Contract: 222 018 10 Auditor: DLLewis

Yes	No	Comments	Operation
			PRESAMPLING
✓			1. Knowledge of process conditions.
✓		4 METERS - PRETEST CALIBRATION IN SPECS.	2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test.
✓			3. Adequate facilities.
✓			4. Spare parts and support equipment available.
✓			5. Qualified personnel.
	✓	NOT YET PERFORMED	6. Peroxide efficiency test conducted.
✓			7. Ascarite® cylinder properly packed, with no open spaces or channels.
			SAMPLING
✓			1. Proper preparation and addition of absorbing solutions to impingers.
✓		OCCASIONAL PROBLEMS WITH PLUGGING OF ASCARITE COLUMN -- INVALIDATED RUNS	2. Sampling performed at constant rate (±10%).
✓			3. Pertinent data recorded before and after sample collection.
✓		2 MINUTES PER HOUR, EACH HOUR	4. Sampling performed at least 2 minutes continuously during each cycle of operation.
✓		24 TWO MINUTE PERIODS	5. Minimum of 12 equal, evenly spaced periods of sampling per 24 hours.
✓			6. Probe maintained at proper temperature.
✓		ENCLOSED WITH TARP	7. Sampling train shielded from direct sunlight.
✓			8. Sample train leak checked at conclusion of run.
✓			9. Total sample volume between 25 and 60 liters.

Figure 3-1. Systems Audit Checklist

Method 6B Systems Audit Form (Continued)

Yes	No	Comments	Operation
			POSTSAMPLING
✓		0.1N H_2SO_4	1. Control sample analysis performed.
✓			2. Impingers and connecting tube rinsed.
✓			3. Proper sample aliquoting technique.
✓		EXCELLENT	4. Proper titration technique, particularly endpoint precision.
✓			5. Blank analysis performed with each sample set.
✓			6. Calculation procedure/check.
✓		STANDARDIZED DAILY; BARIUM CHLORIDE USED	7. Barium perchlorate solution standardized in appropriate manner.
✓			8. Appropriate data recording format.
✓			9. Blanks used to correct field sample results.
✓		100% DUPLICATE TITRATION	10. Minimum of ten percent of samples analyzed in duplicate.

COMMENTS: ANALYTICAL NOTEBOOK VERY GOOD, COMPLETE, WELL ORGANIZED. MASTER SAMPLE LOGBOOK NOT CURRENT -- SEVERAL DAYS BEHIND. CAREFUL ATTENTION TO SAMPLING AND ANALYTICAL TECHNIQUE. CAREFUL ATTENTION TO QC ACCEPTANCE CRITERIA FOR DUPLICATES, CONTROL SAMPLE ANALYSES; CONTROL CHART USED FOR CONTROL SAMPLE ANALYSES.

Figure 3-1. (Continued)

The systems audit conducted for this program consisted of observing and documenting activities associated with the overall sampling/analytical system employed in the FGD system testing. In addition to providing an on-site evaluation of sampling and analytical procedures and techniques, the systems audit included review of all record keeping and data handling systems, including:

- documentation of equipment calibration and reagent standardization,
- completeness of sampling data forms,
- data review and validation procedures,
- data storage and filing procedures,
- sample logging procedures,
- sample custody procedures,
- documentation of quality control data (control charts, etc.), and
- documentation of equipment maintenance activities.

Overall, the systems audit indicated an effective, well-organized sampling/analytical effort which was judged to be adequate for achieving the program objectives. Attention to details of the internal QC program and careful compliance with specified procedures were generally observed for both sampling and analytical activities. The quality control chart for SO_2 control sample analyses was current and the analytical notebook included provisions for noting whether acceptance criteria were met for duplicate analyses and control sample analyses. The only notable deficiency in the overall test effort was in regard to completeness of the master sample logbook and the DART logbook, entries in both of which were several days behind. However, both of these logbooks were used as backup systems. Sample data were current in both the analytical notebook and on the sampling data sheets, and the DART hardcopy provided a detailed record of system operations.

3.5 QUALITY CONTROL DATA

Internal QC procedures for this program were designed to control data quality within acceptable limits and provide a basis for data quality assessment. A complete overview of the internal QC program is in the Quality Assurance Project Plan prepared for this program (4). As with any measurement effort, a primary data quality consideration is measurement variability, or data precision. In this program, quality control sample analyses, duplicate samples, and duplicate analyses provided the mechanism for quantitating sampling/analytical variability. The use of specific acceptance criteria for QC analyses provided the mechanism for controlling measurement data quality. A discussion of the QC procedures used for quantitating Method 6B measurement data variability (precision) is presented in this section, along with summaries of the QC data.

3.5.1 Control Sample Analyses

The analytical phase of the Method 6B procedure, involving the barium-thorin titrimetric determination of SO_2 (as $SO_4^{=}$) is a critical part of the overall method. In order to control precision and accuracy of these analyses within acceptable limits, a 0.100 N sulfuric acid (H_2SO_4) solution was used as a control standard. As prescribed in the QC protocol, the analyst analyzed a control sample prior to analysis of each set of Method 6B impinger solution samples. Before sample analyses could proceed, the analyst was required to demonstrate acceptable accuracy by analysis of the control sample. The acceptance criterion for this control check was agreement of the measured concentration within ±5% of the actual concentration. Additionally, as a check on analytical precision, duplicate analyses of a 0.01 N H_2SO_4 standard solution, performed prior to each set of sample analyses to standardize the barium chloride ($BaCl_2$) titrant, were required to differ by less than or equal to 1% or 0.2 ml of titrant, whichever was less.

Results for the daily control sample analyses were plotted using a control chart, shown in Figure 3-2. As shown in the figure, measured values

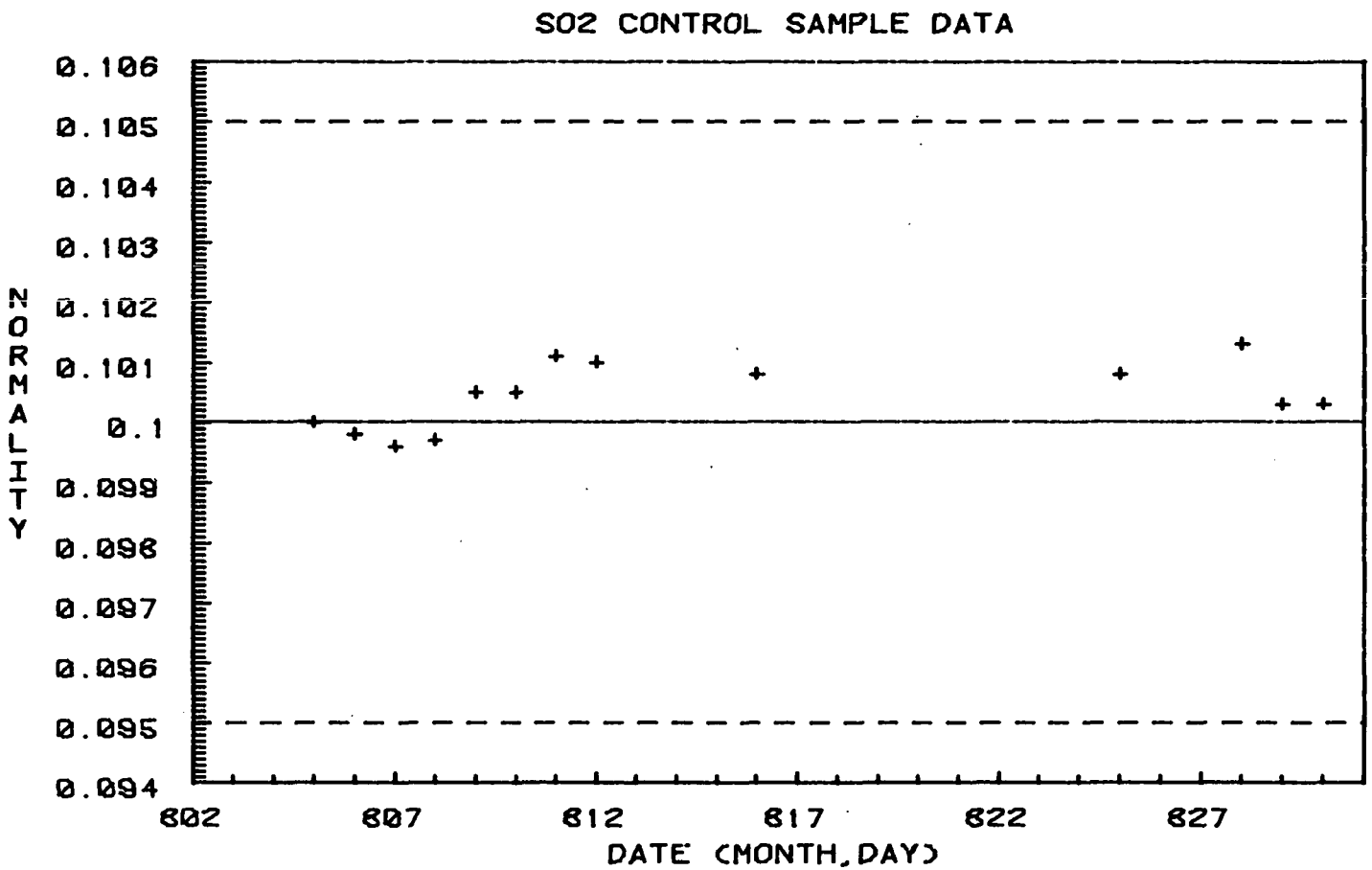

Figure 3-2. SO_2 Control Sample Data

ranged from 0.0988 N to 0.1013 N, or from -1.2% to 1.3%, well within the ±5% QC limit. Agreement for duplicate standard titrations ranged from a difference of 0.10 ml to a difference of 0.00 ml for titrant volumes of approximately 20 ml. Again this was easily within the 1%/0.2 ml titrant acceptance criterion.

In addition to controlling analytical accuracy within acceptance limits, the control sample analyses provide a data base for evaluating precision of the SO_2 analyses in terms of day-to-day variability (repeatability). These data indicate repeatability of 0.7%, expressed in terms of the coefficient of variation (i.e., relative standard deviation).

3.5.2 Duplicate Analyses

As a continuing check on analytical precision, duplicate analyses of Method 6B impinger solution samples were subject to the same acceptance criterion as specified for duplicate standard titrations (i.e., difference less than or equal to 1% or 0.2 ml of titrant volume). All impinger solution samples were analyzed in duplicate. Evaluation of these data indicate within-day precision (replicability) of 0.27% for inlet samples and 0.67% for outlet samples, both expressed in terms of the pooled (i.e., average) coefficient of variation (CV). These results represent an overall pooled CV of 0.51% for duplicate analyses.

3.5.3 Duplicate Samples

In addition to SO_2 control sample analyses and duplicate analyses of all SO_2 samples, all Method 6B samples (both SO_2 and CO_2) were collected in duplicate using collocated sampling trains at both the inlet and outlet of the spray dryer/fabric filter FGD system. A major QC function of the duplicate, collocated sampling trains was to maximize data capture by providing a backup sampling system at both sampling locations. However, results for duplicate samples may be used to assess total (i.e., sampling

plus analytical) measurement variability for both CO_2 and SO_2 data, as well as variability of SO_2 emission rates calculated using these data.

Results for SO_2 and CO_2 concentration measurements and for SO_2 emission rates calculated using these measurement data were statistically evaluated using analysis of variance (ANOVA) techniques. This evaluation provides information pertaining to the following aspects of the Method 6B data:

- Statistical significance of differences between SO_2, CO_2, and emission rate values for the paired sampling trains (i.e., determination of relative bias between Train A and Train B at both locations),

- Statistical significance of observed day-to-day differences (i.e., temporal variability) in SO_2, CO_2, and emission rate values as compared to differences between paired sampling trains,

- Magnitude of measurement variability (precision) for the various components of variability in the SO_2, CO_2, and emission rate determinations, and

- Relative contribution of each component of variability (e.g., analytical, sampling, and temporal) to total variability for the SO_2, CO_2, and emission rate measurements.

Paired t-tests were used to evaluate Method 6B data for both inlet and outlet locations to determine the statistical significance of observed differences in results for the collocated sampling trains. This evaluation indicated that, at the 5% significance level (i.e., 95% confidence level), there was no significant difference (i.e., no relative bias) between SO_2 or CO_2 concentrations measured using Train A and those measured using Train B.

Differences between Train A and Train B emission rates were not statistically significant for the outlet data, but because of interaction between SO_2 and CO_2 results, the differences were significant for the inlet data.

The comparison of results for the paired trains is summarized in Table 3-9. The statistical significance of emission rate differences at the inlet may be attributed to a positive mean difference (i.e., Train A results tended to be greater than Train B results) for SO_2 concentration accompanied by a negative mean difference for CO_2 concentration. At the outlet, mean differences for both SO_2 and CO_2 were negative (i.e., Train B gave, on the average, higher results for both parameters). Although the relative bias between Train A and Train B emission rates at the inlet is statistically significant, the magnitude of this bias is relatively small, with the mean difference of 38.0 ng/J, representing only 1.9% of the mean measured inlet emission rate (2009 ng/J).

Similar tests, again at the 5% significance level, were performed to determine if observed day-to-day variation in measured values are statistically significant. In other words, the data were evaluated to determine whether day-to-day variations were "real" or were due to random variability arising from sampling and analytical imprecision. In all cases (i.e., for SO_2, CO_2, and emission rate values at both inlet and outlet) temporal or day-to-day variability was significantly greater than combined sampling and analytical variability.

For the Method 6B data as a whole, there were two major components of measurement data variability. One component was that due to day-to-day variability in process operation, or temporal variability. The second component was that due to random variability in sampling and analysis. Since the SO_2 samples were analyzed in duplicate, sampling and analytical variability may be evaluated as separate components. Using ANOVA techniques, both the magnitude and relative contribution of each component was determined for all three parameters (SO_2, CO_2, and emission rate) at both sampling

TABLE 3-9. SUMMARY OF SIGNIFICANCE TEST DATA FOR PAIRED RESULTS

Location	Parameter	Mean Difference for Paired Trains (Train A-Train B)	Standard Deviation	Number of Observations	Significant (95% Confidence Level)
Inlet	SO_2	17.9 ppm	70.0 ppm	23	No
	CO_2	-0.07 %	0.58 %	23	No
	Emission Rate	38.0 ng/J	72.0 ng/J	23	Yes
Outlet	SO_2	-11.3 ppm	35.3 ppm	20	No
	CO_2	-0.03 %	0.28 %	22	No
	Emission Rate	-14.5 ng/J	46.4 ng/J	20	No

locations. Table 3-10 summarizes results for the component of variance analysis. These data are presented in terms of coefficients of variation for day-to-day variability, duplicate samples, and duplicate analyses (SO_2) in Table 3-11.

3.6 METHOD 6B RELIABILITY AND DATA CAPTURE

Overall, the Method 6B sampling/analytical approach used during this program proved to be a reliable means of collecting SO_2 removal efficiency and emission rate data. The use of duplicate, collocated sampling systems is credited with achieving an overall data capture of 100% (i.e., valid SO_2 emission rate and removal efficiency data were collected on 24 out of 24 sampling days). Problems did occur on occasion, resulting in loss or invalidation of SO_2 and/or CO_2 data from one or more of the four sampling trains. However, in no case was data for both trains at either the inlet or outlet locations lost or invalidated on the same day.

Instances of Method 6B data loss during this program may be attributed to two causes:

- Sampling system problems such as leaks and/or high pressure drops which resulted in invalidation of results for the affected sampling train, and
- Operator error which resulted in loss of samples (and data).

Observed sampling problems were documented on the data collection sheet and are summarized in the comment section of Table 2-1. Of the total of 96 sampling train days (i.e., four trains per day for 24 days, excluding the trial run at the inlet on the first day), SO_2 and/or CO_2 data were lost or invalidated in five instances, for a sampling/analytical reliability of 94.8%.

Since both inlet and outlet measurement data are required to calculate removal efficiency, method reliability with respect to removal efficiency data must consider the relative frequency of data loss for either inlet or

TABLE 3-10. SUMMARY OF ANALYSIS OF VARIANCE RESULTS

Parameter	Source of Variability	Inlet			Outlet		
		Mean Measured Value	Variance Component[a]	Percent of Total Variance	Mean Measured Value	Variance Component[a]	Percent of Total Variance
SO_2	Temporal		14008.8	84.8		53326.0	98.8
	Sampling		2489.7	15.1		650.2	1.2
	Analytical		17.5	0.1		4.5	<0.1
	Total	1527 ppm	16516.0	100.0	310 ppm	53980.7	100.0
CO_2	Temporal		0.199	54.9		0.179	86.9
	Sampling/ Analytical		0.164	45.1		0.027	13.1
	Total	9.64%	0.363	100.0	9.7%	0.206	100.0
Emission Rate	Temporal		14425.3	81.8		91748.4	98.8
	Sampling/ Analytical		3202.8	18.2		1127.4	1.2
	Total	2009 ng/J	17628.2	100.0	406 ng/J	92875.8	100.0

[a]Variance components are equal to standard deviations squared and thus have units which are the squares of those used for the corresponding measurement parameter (e.g., ppm^2, etc.)

TABLE 3-11. COEFFICIENTS OF VARIATION FOR REPEAT AND DUPLICATE MEASUREMENTS

Parameter	Inlet			Outlet		
	Day-to-Day Variability (CV)	Duplicate Sample Precision (CV)	Analytical Precision (CV)	Day-to-Day Variability (CV)	Duplicate Sample Precision (CV)	Analytical Precision (CV)
SO_2	8.42%	3.28%	0.27%	75.0%	8.26%	0.68%
CO_2	6.25%	4.20%	--	4.68%	0.37%	--
Emission Rate	6.61%	2.82%	--	75.0%	8.27%	--

outlet trains of a given system. For system A (i.e., inlet Train A plus outlet Train A), there were three days of invalidated data (August 4, 9, and 11), for a reliability of 87.5% (21 of 24 days). For System B, samples were lost on August 3 and 9, for a reliability of 91.7%. This gives an average system reliability of 89.6%.

Of the five instances of lost or invalidated data, three were due to problems (e.g., leaks) with a sampling train, and two were due to operator error during sample recovery. Thus, sampling reliability alone was 96.9% (i.e., 93 of 96 sampling train days). It is also worth noting that all instances of lost or invalidated data occurred within the first ten of the 24 sampling days, indicating that operator familiarity with the sampling system and related procedures was probably a significant factor in method reliability. It is probably also true that general familiarity with the method must be combined with familiarity with the specific sampling systems used in order to maximize data capture.

SECTION 4

PROCESS DESCRIPTION

The FGD system characterization performed by Radian at Argonne National Laboratory was conducted on the Unit 5 spray dryer/baghouse system. This section describes the system configuration and sampling locations used during testing.

4.1 PLANT CONFIGURATION

The Argonne steam plant consists of five boilers that provide 200 psig steam throughout the entire 1500 acre facility for heating and evaporative cooling. Argonne's main boiler (Unit 5) is a coal-fired Wickes (now Combustion Engineering) spreader stoker unit designed to produce a maximum of 170,000 pounds of saturated steam per hour at 200 psig pressure. Control equipment was required on Unit 5 to comply with State of Illinois SO_2 and particulate emissions standards (refer to Table 4-1) when high sulfur, midwestern coal was burned in the unit. (A copy of Subpart D, as printed in the Federal Register, is included in Appendix D of Volume II).

TABLE 4-1. STATE OF ILLINOIS EMISSION LIMITS FOR ANL BOILER NO. 5

Pollutant	Limit
Sulfur Dioxide	1.2 lb/10^6 BTU (520 ng/J)
Particulate Matter	0.1 lb/10^6 BTU and $\leq$20% Opacity

The system installed on Argonne's No. 5 boiler to treat the flue gas is a Niro Atomizer/Joy Manufacturing industrial design. A simplified schematic of the process is shown in Figure 4-1.

The system consists of two parts, a wet end and a dry end. In the wet end, pebble lime is held in a 100 ton storage silo with a "live" cone bottom. From this vessel, lime is fed through a Wallace and Tiernan weighbelt feeder into the lime slaker. The weighbelt feeder is equipped with a feedrate indicator as well as a totalizer which allows ANL to measure lime consumption. In the slaker, careful addition of potable water causes the calcium oxide (CaO) to react and form calcium hydroxide ($Ca(OH)_2$), or milk of lime. The milk of lime, at about 15% solids, is passed through a rotary screen in order to remove the "grits," or inert particles, from the milk of lime. From the slaker, the milk of lime is sent to a covered, agitated, storage tank. This storage tank has a 30-minute hold time and serves two purposes: (1) to ensure completeness of the slaking reaction as well as to even out any inconsistencies in slaker operation, and (2) to ensure a temporary lime supply in case of slaker system failure.

The milk of lime is next pumped to the slurry mix tank. In this agitated vessel, recycled waste powder, milk of lime, and some dilution water are combined to form an approximately 35-40 percent (by weight) slurry. The mix ratio of recycled waste powder, milk of lime, and dilution water is controlled to maintain the desired SO_2 emission rate ($\leq$520 ng/J) and outlet spray dryer temperature ($\sim$150°F). The flow of milk of lime to the mix tank is dependent upon the liquid level in the mix tank and the SO_2 concentration. A decrease in the liquid level or an increase in the SO_2 concentration will cause the milk of lime flow to increase. Recycle solids flow to the mix tank is dependent upon the slurry feed density and the SO_2 concentration. A decrease in the slurry feed density or a decrease in the SO_2 concentration will cause the flow of recycle solids to increase. The dilution water flow rate is only dependent upon the liquid level in the feed tank.

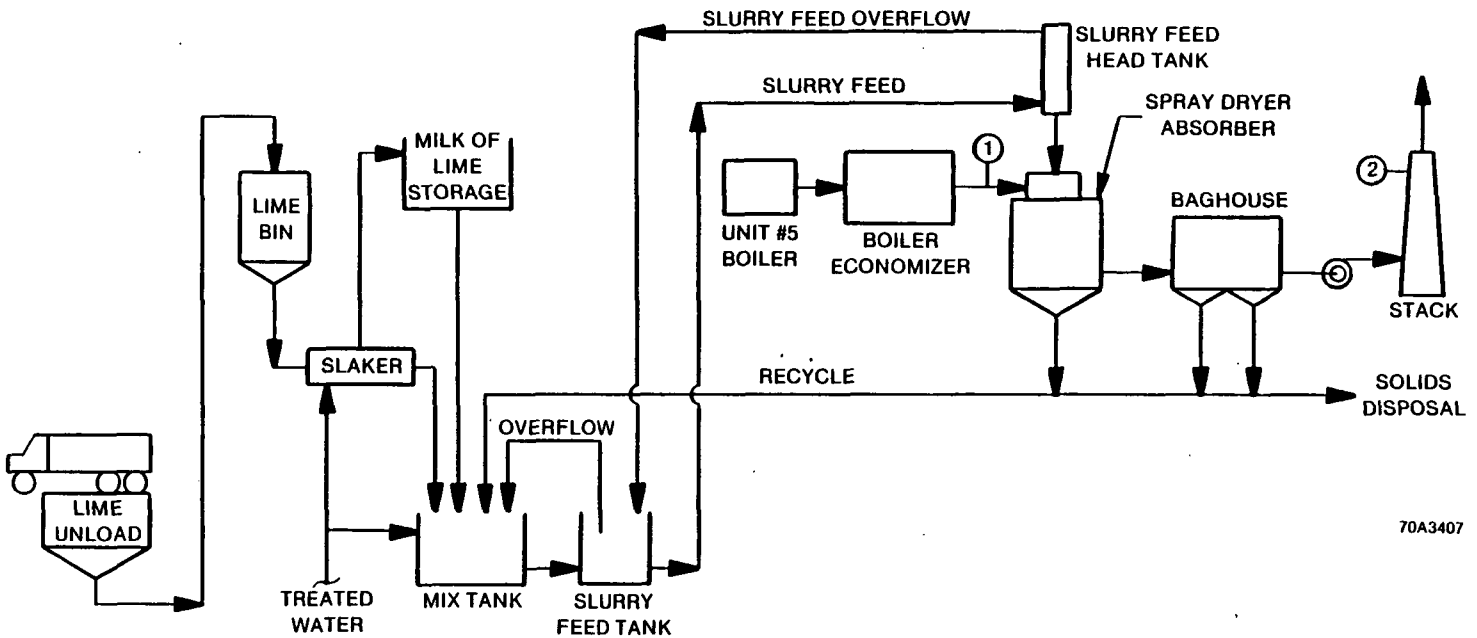

Figure 4-1. Schematic Diagram of the Argonne National Laboratory Unit 5 Boiler Spray Dryer/Baghouse Flue Gas Desulfurization System

From the mix tank, the slurry is transferred to the slurry feed tank via another rotary screen to ensure removal of any lumps which might clog the feed slurry piping system. Overflow from the slurry feed tank goes back into the slurry mix tank, so there is a continual circulation between the tanks. Slurry from the feed tank is pumped, at a constant high flow rate, to a head tank located above the atomizer. A control valve regulates the amount of slurry fed to the atomizer, with the excess being returned to the feed tank. This returned slurry also passes through the rotary screen that is filtering the stream from the slurry mix tank.

Flue gas, exiting the boiler's induced draft (ID) fan, passes into a modified breeching at the existing stack. A guillotine damper diverts the flue gas flow into the FGC system ductwork leading to the spray dryer. This inlet ductwork splits the flue gas into two streams. One stream, with about 60% of the gas flow, is directed into a roof gas disperser, located on the top of the spray dryer. The remainder of the gas stream enters a central gas disperser, located in the middle of the spray dryer. Both gas streams, upon entering the dryer, are given circular motions with their main directions of flow being opposed to each other. In the spray dryer, the slurry droplets contact the hot flue gases where two events happen somewhat simultaneously: (1) the sulfur oxides react with the lime to form calcium sulfite and calcium sulfate, and (2) water associated with the lime evaporates, thereby cooling the flue gas. The spray dryer is designed to control the temperature of the gas exiting the spray dryer to 22°F (or more) above the dew point. This temperature control is very important for several reasons including: (1) achieving consistent SO_2 control; (2) the necessity of protecting the baghouse from condensation; (3) minimization of the lime stoichiometry required for SO_2 removal; and (4) preventing the wetting of the walls of the spray dryer.

Some of the powder formed in the spray dryer settles to the bottom and is collected by a drag-line conveyer. The remainder of the powder, entrained in the gas stream, enters the baghouse where it is removed by filtration. Upon exiting the baghouse, the gas passes through a booster fan and then

into the existing stack. Tables 4-2 and 4-3 list some of the parameters related to the spray dryer and fabric filter.

TABLE 4-2. SPRAY DRYER PARAMETERS

- Niro Atomizer Incorporated
- 10 Second Residence Time
- 25' Diameter, 19' Straight Side
- Rotary Atomizer - 14,000 RPM
- Dual Gas Inlet - Roof and Central Gas Dispersers
- Carbon Steel Construction

TABLE 4-3. FABRIC FILTER PARAMETERS

- Joy Manufacturing Company
- 4 Compartment Pulse Jet
- 3.01:1 Air-to-Cloth Ratio
- 280 Bags/Compartment - 6" Diameter - 12' Long
- 16 Ounce Woven Fiberglass Fabric with Teflon® Coating
- 5278 Ft^2 Filter Area/Compartment

4.2 DESCRIPTION OF SAMPLING POINTS

Flue gas samples were collected at the inlet to the spray dryer and on the stack downstream of the baghouse (refer to Point (1) and (2) in Figure 4-1). The location and orientation of the two sampling locations are illustrated graphically in Figure 4-2.

Flue gas from the ANL Unit 5 boiler travels through a vertical duct to the roof where the duct splits and the flue gas can either exit through the stack or enter the FGD system. During normal operation, the guillotine valve (refer to Figure 4-2) is closed and the double louver dampers are open, forcing the boiler flue gas through the FGD system.

The FGD inlet sampling location was between the guillotine valve and the double louver damper and consisted of three, 3-inch, NPT, horizontally-oriented ports located one above another. Flue gas samples were collected using the top (Port A) and bottom (Port B) ports. During sampling at the FGD inlet, the two sampling probes were situated approximately 30 inches (mid-way) into the duct and the probe tips were approximately 36 inches from each other (refer to Figure 4-3).

Upon exiting the FGD system, the flue gas passes through an induced draft fan and is then vented to the atmosphere by means of a six-foot diameter stack. The FGD outlet flue gas samples were collected using the sampling ports on the stack sampling platform. Figure 4-4 illustrates the approximate orientation of the FGD outlet sampling ports and the two sampling probes. Four, 3-inch, NPT ports were located on two perpendicular diameters. Two of the four ports were used for sample collection. During sampling at the FGD outlet, the probe used at Port A was inserted approximately 18 inches into the stack, while the probe used at Port B was inserted approximately 24 inches into the stack.

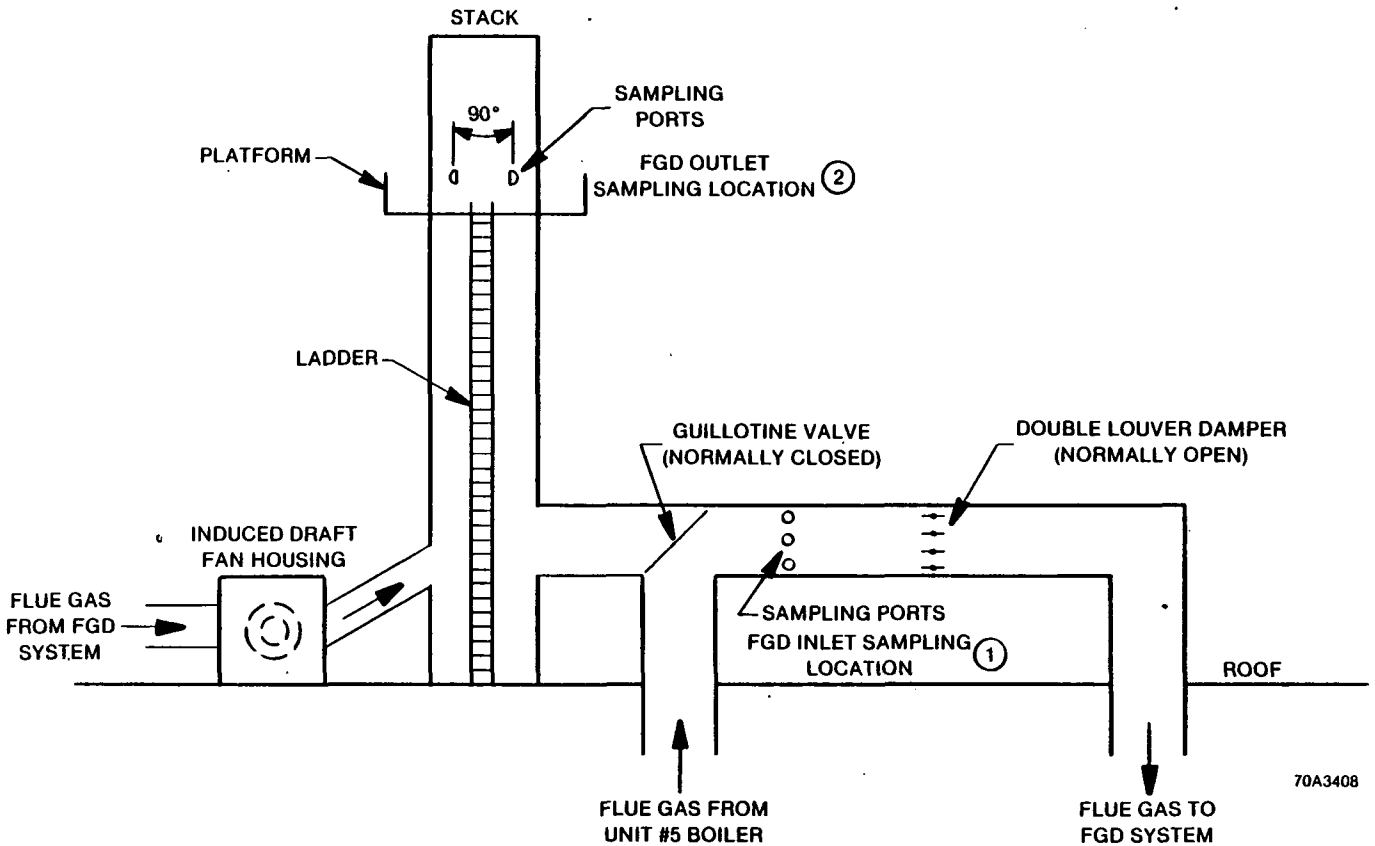

Figure 4-2. Schematic Diagram Illustrating the Location of the Inlet and Outlet Flue Gas Sampling Ports at the Argonne National Laboratory Unit 5 Spray Dryer Baghouse Flue Gas Desulfurization System

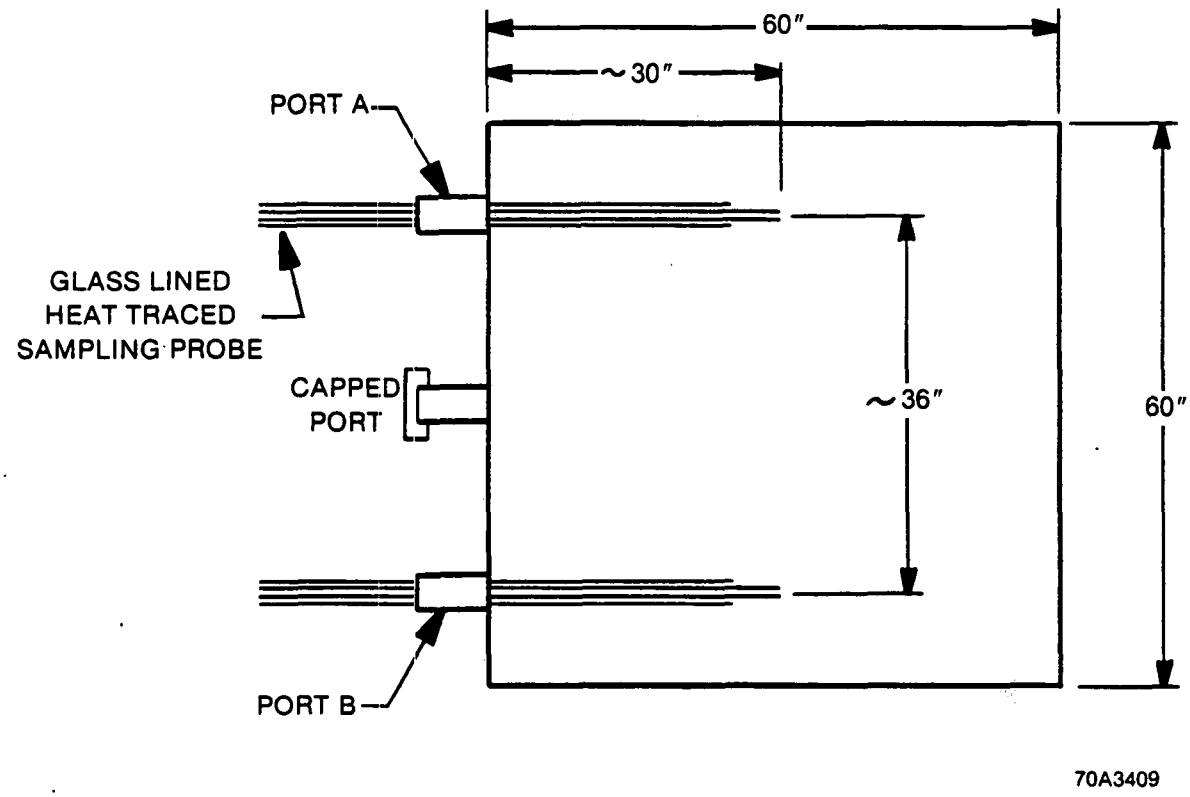

Figure 4-3. Diagram Illustrating the Relative Location of the Two Sampling Probes Used in Collecting the Duplicate EPA Method 6B Samples at the Inlet to the Argonne National Laboratory Unit 5 FGD System.

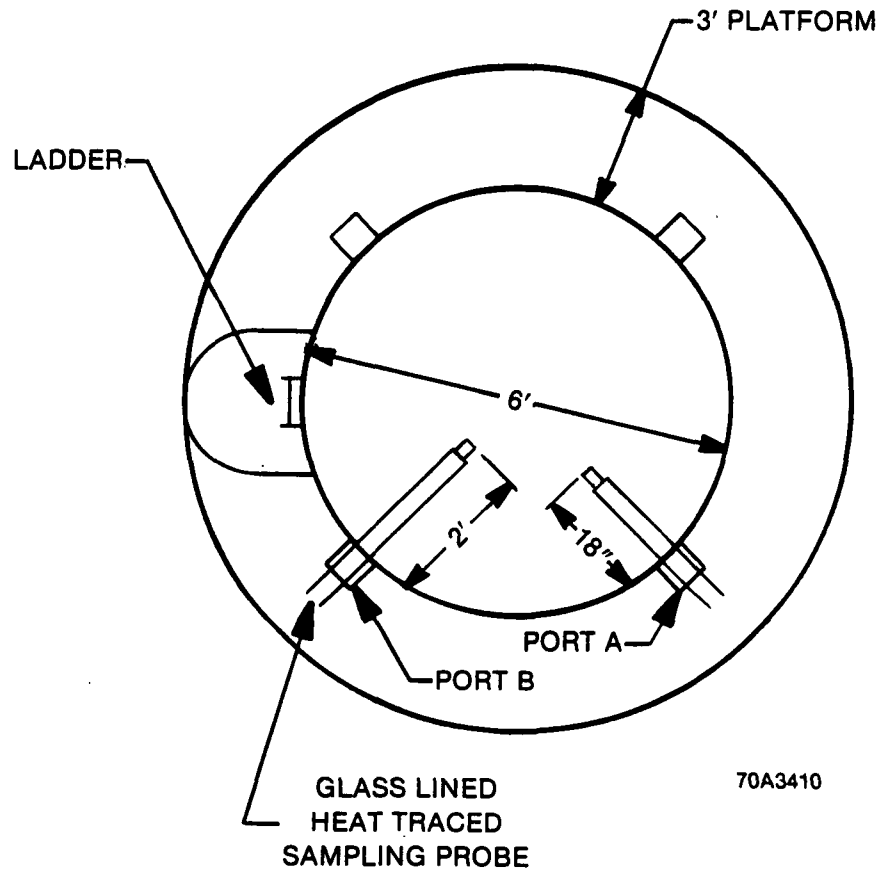

Figure 4-4. Diagram Illustrating the Location of the Two Sampling Probes Used in Collecting the Duplicate EPA Method 6B Samples at the Outlet of the Argonne National Laboratory Unit 5 FGD System.

SECTION 5

SAMPLING AND ANALYSIS

In order to determine the SO_2 removal efficiency of the FGD system at the Argonne test site, SO_2 emission rates were measured at the inlet and outlet of the system. This required measurement of the SO_2 content and CO_2 content of the flue gas, along with fuel analysis to derive CO_2 F-factors for the emission rate calculation. Sampling and analytical procedures are described below.

5.1 SAMPLING

The sampling procedure(s) used in the collection of flue gas samples and coal samples are described in this section.

5.1.1 Flue Gas Sampling

During this program, the SO_2 and CO_2 concentrations of the flue gas were determined using EPA Method 6B (1). (A copy of EPA Method 6A and 6B procedures are included in Appendix D of Volume II). The sampling system is illustrated in Figure 5-1 and briefly described below.

A glass-lined, heat-traced probe was used to extract a gas sample from the stack. An out-of-stack heated filter removed particulate from the gas stream prior to entering the impingers. The probe and filter oven temperatures were maintained at about 250°F. Gas exiting the probe entered a series of three midget impingers. The first two impingers had tapered stems and contained approximately 20 ml each of 6 percent H_2O_2 for SO_2 removal. The third impinger with a straight stem was filled with about 25 grams of

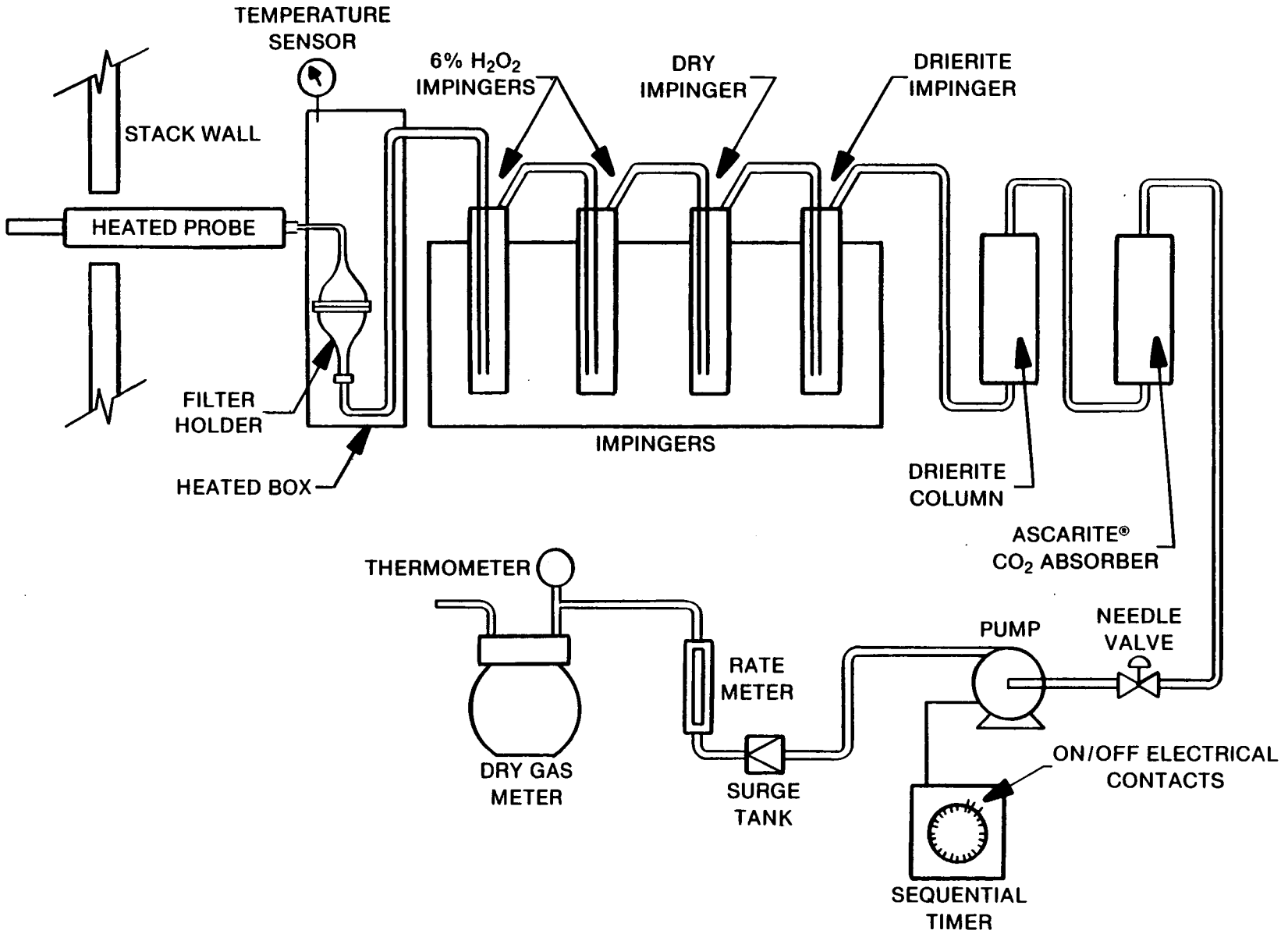

Figure 5-1. EPA Method 6B SO_2 and CO_2 Sampling Train

Drierite® to help prevent condensation in the sample line exiting the impinger train.

Gas exiting the impingers entered a canister containing about 200 grams of Drierite® for final moisture removal. After final moisture removal, the gas sample passed through a canister containing about 200 grams of Ascarite® for CO_2 absorption. A pump and dry gas meter were used to control and monitor the flow rate of the sample gas. The gas flow rate was maintained at approximately 1 liter per minute.

A sequential industrial timer regulated the operation of the sample pump during the 24-hour sampling period. The sample pump was on 2 minutes every hour resulting in a total daily sampling time of approximately 48 minutes (48 liters of sample gas). The 24-hour sampling period started at hour 1000 each day and ended at 0959 on the following day.

Prior to sampling, the impingers and Ascarite® canisters were weighed and the weights recorded. All weighings were made within ±0.1 grams. Filters were replaced in the heated filter holders every third day on the inlet samplers and weekly on the outlet sampling trains. This schedule was established after the first week of testing. The sampling system was leak-checked before sampling and leaks with rates of greater than 0.02 liters per minute were eliminated. Heating systems were operated continuously and cold water was placed around the impingers as needed. All pertinent sampling data (i.e., meter volumes, impinger weights, temperatures, etc.) were recorded on a standardized data form like the one illustrated in Figure 5-2.

During sampling, a tarpaulin cover protected the sampling system from direct sunlight and adverse weather. The sampling system was visually checked periodically during the day to ensure proper operation. Problems encountered during sampling were noted on the data sheet and in the sampling log notebook.

Method 6B

FIELD SAMPLING DATA SHEET

Plant Name _____

Sampling Location: _____ Run ID _____

Initial Leak Rate _____ Final Leak Rate _____

Meter ID _____ DGM Correction Factor: _____

Sampling Period: Start: Date _____ Time _____

Stop: Date _____ Time _____

Operator Initials _____ Duration: _____Hrs _____Minutes

SAMPLING DATA

	Dry Gas Meter Reading	Rotameter Setting	Dry Gas Meter Temperature		Barometric Pressure	Probe Temp. °F	Flex Connector Temp.	Train Outlet Temp.
			Inlet	Outlet				
Final								
Initial								
Average								

Net Sample Volume (ℓ) _____

SAMPLE RECOVERY DATA

	Impingers and Drierite	Ascarite Column
Final Wt. (g)	_____	_____
Initial Wt. (g)	_____	_____
Moisture Wt. (g)	_____	CO_2 Wt. (g) _____

Impinger Contents Sample ID _____

H_2O_2 Blank Sample ID _____

Sample Recovered By: _____ Date: _____

Remarks: _____

Figure 5-2. Method 6B Field Sampling Data Sheet

5.1.2 Coal Sample Collection

Approximately once a month, coal is shipped by barge to ANL. The coal is trucked from the barge to the ANL power plant for storage and use. While the coal is still on the barge, a sample is collected by ANL personnel for ultimate analysis and proximate analyses. No additional coal samples are collected on a routine basis. Radian originally planned to obtain a portion of each coal sample collected by ANL personnel and submit this fraction for independent analysis.

From August 1 through August 23, 1983, the ANL Unit 5 boiler operated using a subbituminous coal from Kentucky. On the morning of August 24, 1983, the ANL Unit 5 boiler started using a subbituminous coal from Illinois. At the end of the on-site sampling/analysis program, Radian tried to obtain a sample of the Kentucky and Illinois coal from ANL personnel. However, the two coal samples collected by ANL personnel were no longer available because they had already been shipped to the subcontractor for analysis. A grab sample of the Illinois coal used on August 30, 1983 was subsequently collected from the conveyer belt by Radian personnel. A sample of the original Kentucky coal could not be obtained.

5.2 SAMPLE ANALYSIS

Flue gas and coal sample analytical procedures used during this program are discussed briefly in this section.

5.2.1 Flue Gas Analysis

Test personnel performed a final system leak check after sampling. The Ascarite® canister was weighed to determine the mass CO_2 collected. The contents of the first two impingers were quantitatively transferred to a 100 ml volumetric flask, diluted to volume with distilled water, and

analyzed for SO_2 (as SO_4) by means of the barium-thorin titration procedure outlined in EPA Method 6 (2), using barium chloride ($BaCl_2$) as the titrant. (A copy of the EPA Method 6 procedure is included in Appendix D of Volume II). The SO_2 and CO_2 concentrations obtained from the analyses were used to calculate the emission rates in ng/J. All emission rate calculations followed the standardized calculation data forms (refer to Figure 5-3) located on the back of each EPA Method 6B data sheet.

5.2.2 Coal Analysis

Commercial Testing and Engineering, Inc. (CT&E), located near Chicago, Illinois, performed ultimate and proximate analysis of the Kentucky and Illinois coals used during this program, as well as a quality assurance audit sample. The Kentucky coal sample was collected and sent by ANL personnel to CT&E for analysis. The Illinois coal sample was collected by Radian personnel and shipped along with the audit coal sample to CT&E for analysis. The ultimate and proximate coal analysis results are presented in Table 2-3. The CO_2 F-factor (F_c) for each coal sample was derived from the ultimate and proximate analysis (dry basis) of the coal.

A. Standard Meter Volume, $V_{m(std)}$, Nm^3

$$V_{m(std)} = \frac{V_{m(act)}}{1000} \times \frac{528°R}{T_{m(avg)}} \times \frac{P_{bar}\ "Hg}{29.92\ "Hg} \times DGMCF$$

$$V_{m(std)} = \frac{\quad}{1000} \times \frac{528}{\quad + 460} \times \frac{\quad}{29.92} \times \quad = \quad Nm^3$$

B. CO_2 Volume Collected, Standard Conditions, Nm^3

$$V_{CO_2(std)} = 5.467 \times 10^{-4} (M_{af} - M_{ai})$$

$$V_{CO_2(std)} = 5.467 \times 10^{-4} (\quad - \quad) = \quad Nm^3$$

C. CO_2 Concentration, %

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_{m(std)} + V_{CO_2(std)}} \times 100$$

$$C_{CO_2} = \frac{\quad}{\quad + \quad} \times 100 = \quad \%$$

D. SO_2 Concentration, mg/Nm^3

$$C_{SO_2} = 32.03 \frac{(V_t - V_{tb})\ N\ (V_{soln}/V_a)}{V_{m(std)} + V_{CO_2(std)}}$$

$$C_{SO_2} = 32.03 \frac{(\quad - \quad) \times \quad \times (\quad/\quad)}{\quad + \quad} = \quad mg/Nm^3$$

(To convert mg SO_2/dscm to ppm, multiply by 3.762×10^{-1})

E. Moisture Volume Collected, Nm^3

$$V_{H_2O(std)} = 1.336 \times 10^{-3} (M_{wf} - M_{wi})$$

$$V_{H_2O(std)} = 1.336 \times 10^{-3} (\quad - \quad) = \quad Nm^3$$

F. Moisture Concentration, %

$$C_{H_2O} = \frac{V_{H_2O(std)}}{V_{m(std)} + V_{CO_2(std)} + V_{H_2O(std)}}$$

$$C_{H_2O} = \frac{\quad}{\quad + \quad + \quad} = \quad \%$$

G. SO_2 Emission Rate

$$E_{SO_2} = C_{SO_2}\ F_c \left(\frac{100}{C_{CO_2}}\right) \times 10^6$$

$$E_{SO_2} = \quad \quad \left(\frac{\quad}{\quad}\right) \times 10^6 = \quad ng/J$$

Remarks: _____

Figure 5-3. Method 6B Calculations Worksheet

SECTION 6

PROCESS MONITORING PROCEDURES

During this program, Radian collected pertinent boiler and FGD process data to allow for the evaluation of the system performance and to help determine the critical operating parameters and the system economics. Table 6-1 shows the parameters monitored during this program.

A Radian DART II data acquisition system provided the means for on-site, continuous collection of process data. The DART was directly connected with the main Unit 5 boiler and FGD control panels to obtain the instrument output signals of interest. The DART generated five minute averages from instantaneous signals from the monitors. The DART determined hourly averages and 24-hour averages for each of the parameters of interest from the 5-minute averages. The DART 24-hour averages coincided with the EPA Method 6B 24-hour sampling time period. The five-minute averages, hourly averages, and 24-hour averages were stored on a floppy disk, and the average values were also printed on site using an on-line printer. The DART used acronyms to represent each of the parameters of interest and their respective units of concentration. The DART acronyms are also included in Table 6-1.

Argonne personnel manually recorded boiler and FGD process data once an hour using prepared process log sheets. The manually recorded process data proved useful because not all of the pertinent process data were continually available from the DART. Certain process data were not available to the DART because of incompatible or nonexistent electronic signal or because the monitor signal was not available on the main control panel. Also, the DART malfunctioned several times during the program resulting in no recorded process data for short periods of time. Whenever the DART could not provide

process data, the Argonne process log sheets provided the data to calculate a 24-hour average.

TABLE 6-1. SUMMARY OF ANL UNIT 5 BOILER AND FGD PROCESS PARAMETERS OF INTEREST (INCLUDING DART ACRONYMS WHEN APPLICABLE)

Parameter	Units	DART Acronym
Unit 5 Boiler Load	10^3 lbs steam/hour	BLOAD/PPH
Unit 5 Boiler Exit Gas O_2 Concentration	%	---*
Baghouse Outlet Temperature	°F	BHOUT/DEGF
Spray Dryer Inlet Temperature	°F	SDIN/DEGF
Spray Dryer Outlet Temperature	°F	SDOUT/DEGF
Spray Dryer Slurry Feed Rate	gpm	SFR/TGPM
Spray Dryer Inlet Pressure	inches H_2O	SDINP/TI H_2O
Baghouse Pressure Drop	inches H_2O	BHDP/TI H_2O
Lime Milk Flow	gpm	LTMFR/TFPM
Central Gas Disperser Pressure Drop	inches H_2O	RGDIS/TI H_2O
Baghouse Outlet Dew Point Temperature	°F	---*
Atomizer Motor Amps	amps	---*
Lime Mix Tank Level	%	LMTL/%
Slurry Density	grams/cc	SFSG
Slaking Dilution Water Flow	gpm	---*
Lime Milk Flow	gpm	---*
Lime Milk Density	grams/cc	---*
Slurry Dilution Water Flow	gpm	DH_2O/TGPM
Recycle Feed Rate	lbs/hr	---*
Contraves Outlet CO_2	%	CO_2/T%
Contraves Outlet SO_2	ppm	SO_2/PPM
Contraves SO_2 Emission Rate	lbs/10^6Btu	SO_2/LB BTU
Slurry Mix Tank Level	%	SMTL/%

*Data collected from operator log sheet.
**Data not available.

SECTION 7

EXAMPLE CALCULATIONS

Included in this section are examples of calculations performed during this program.

Standard Meter Volume, $V_{m(std)}$

- Dry Standard Cubic Meter (dscm)

$$V_{m(std)} = \frac{\left(\begin{array}{c}\text{Actual Meter}\\ \text{Volume (liters)}\end{array}\right)(528°R)\left(\begin{array}{c}\text{Barometric}\\ \text{Pressure ("Hg)}\end{array}\right)\left(\begin{array}{c}\text{Dry Gas Meter}\\ \text{Correction Factor}\end{array}\right)}{(1000)\left(\begin{array}{c}\text{Average Meter}\\ \text{Temperature (°F)}\end{array} + 460°R\right)(29.92"Hg)}$$

Example: Based on ARG-0825-M6B-O/B data,

$$V_{m(std)} = \frac{(53.0 \text{ liters})(528°R)(29.52"Hg)(1.02)}{(1000)(84°F + 460°R)(29.92"Hg)}$$

$$V_{m(std)} = 0.0518 \text{ m}^3$$

CO_2 Volume Collected, Standard Conditions, $V_{CO_2(std)}$

- Dry Standard Cubic Meter (m^3)

$$V_{CO_2(std)} = \left(5.467 \times 10^{-4} \frac{\text{m}^3}{\text{gram } CO_2}\right)\left(\begin{array}{l}\text{Final mass}\\ \text{of ascarite}\\ \text{after sampling (g)}\end{array} - \begin{array}{l}\text{Initial mass of}\\ \text{ascarite before}\\ \text{sampling (g)}\end{array}\right)$$

Example: Based on ARG-0825-M6B-O/B data,

$$V_{CO_2(std)} = 5.467 \times 10^{-4} \frac{\text{m}^3}{\text{gram } CO_2} (533.0\text{g} - 522.2\text{g})$$

$$V_{CO_2(std)} = 0.0059 \text{ m}^3$$

CO_2 Concentration, C_{CO_2}

- Percent (%)

$$C_{CO_2} = \frac{CO_2 \text{ Volume Collected, Standard Conditions } (m^3) \times 100}{\text{Standard Meter Volume } (m^3) + CO \text{ Volume Collected, Standard Conditions } (m^3)}$$

Example: Based on ARG-0825-M6B-O/B data,

$$C_{CO_2} = \frac{(0.0059 \text{ m}^3)(100)}{0.0518 \text{ m}^3 + 0.0059 \text{ m}^3}$$

$$C_{CO_2} = 10.2\%$$

SO_2 Concentration, C_{SO_2}

- Milligrams per Dry Standard Cubic Meter (mg/sm^3)

$$C_{SO_2} = (32.03)\frac{\left(\begin{matrix}\text{Volume}\\ \text{Titrant (ml)}\end{matrix} - \begin{matrix}\text{Volume of}\\ \text{Blank (ml)}\end{matrix}\right)\left(\begin{matrix}\text{Normality of}\\ \text{Titrant}\end{matrix}\right)\left(\frac{\text{Total Volume Sample (ml)}}{\text{Volume of Aliquots (ml)}}\right)}{\text{Standard Meter Volume } (m^3) + CO_2 \text{ Collected at Standard Conditions } (m^3)}$$

Example: Based on ARG-0825-M6B-O/B data,

$$C_{SO_2} = (32.03)\frac{(24.47 \text{ ml} - 0.0 \text{ ml})(.0102 \text{ N})\left(\frac{100 \text{ ml}}{10 \text{ ml}}\right)}{.0518 \text{ m}^3 + .0059 \text{ m}^3}$$

$$C_{SO_2} = 1555 \text{ mg/sm}^3$$

- Parts per Million (ppm)

To convert mg SO_2/sm^3 to ppm, multiply by 3.762×10^{-1} million sm mg SO_2

Example: Based on ARG-0825-M6B-O/B data,

C_{SO_2} = 1555 mg SO_2/sm^3 x 3.762×10^{-1} million sm /mg SO_2

C_{SO_2} = 585 ppm

Carbon Dioxide F-Factor, F_c

- Standard Cubic Feet per Million BTU ($scf/10^6$ BTU)

$$F_c = \frac{321 \times 10^3 \ (\%C)}{\text{Gross Calorific Value}}$$

Example: Based on the results of the analysis of the Illinois coal presented in Table 6-3,

$$F_c = \frac{(321 \times 10^3)(74.1)}{13{,}303 \text{ BTU/pound}}$$

F_c = 1788 $scf/10^6$ BTU

- Standard Cubic Meters per Joule (sm^3/J)

To convert $scf/10^6$ BTU to sm^3/J, multiply by 2.686×10^{-5} $\frac{sm^3 - BTU}{SCF-J}$

Example: Based on the results of the analysis of the Illinois coal presented in Table 6-3,

$$F_c = (1788 \text{ scf}/10^6 \text{ BTU})\left(2.686 \times 10^{-5} \frac{sm^3 - BTU}{SCF-J}\right)$$

$F_c = 4.804 \times 10^{-8}$ sm^3/J

SO_2 Emission Rate, E_{SO_2}

- Nanogram per Joule (ng/J)

$$E_{SO_2} = \left(SO_2 \text{ Concentration } (mg/sm^3)\right)\left(CO_2 \text{ F-factor } (sm^3/J)\right)\left(\frac{100}{CO_2 \text{ Concentration } (\%)}\right)\left(10^6\right)$$

Example: Based on ARG-0825-M6B-O/B data,

$$E_{SO_2} = (1555 \text{ mg/sm}^3)\ (4.804 \times 10^{-8} \text{ sm}^3/J)\left(\frac{100}{10.24}\right)\left(10^6\right)$$

$$E_{SO_2} = 730 \text{ ng/J}$$

- Pounds per Million BTU (lbs/10^6 BTU)

To convert ng/J to lbs/10^6 BTU, multiply by 2.32×10^{-3} $\frac{\text{lb-J}}{\text{ng-}10^6 \text{ BTU}}$

Example: Based on ARG-0825-M6B-O/B data,

$$E_{SO_2} = (730 \text{ ng/J})\left(2.32 \times 10^{-3} \frac{\text{lb/J}}{\text{ng-}10^6 \text{ BTU}}\right)$$

$$E_{SO_2} = 1.69 \text{ lbs/}10^6 \text{ BTU}$$

SO_2 Control Efficiency, CE_{SO_2}

- Percent (%)

$$CE_{SO_2} = \frac{\left[\begin{array}{c}\text{Average Inlet } SO_2 \\ \text{Emission Rate (ng/J)}\end{array} - \begin{array}{c}\text{Average Outlet } SO_2 \\ \text{Emission Rate (ng/J)}\end{array}\right] \times 100}{\text{Average Inlet } SO_2 \text{ Emission Rate (ng/J)}}$$

Example: Based on ARG-0825-M6B-O/B data,

$$CE_{SO_2} = \frac{([2060 \text{ ng/J}) - [734 \text{ ng/J}])100}{2060 \text{ ng/J}}$$

$$CE_{SO_2} = 64.4\%$$

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1. EPA Method 6B--"Determination of Sulfur Dioxide and Carbon Dioxide Daily Average Emission from Fossil Fuel Combustion Sources," 40 CFR 60, Appendix A, Environment Reporter, Bureau of National Affairs, Inc., Washington, D.C., March 25, 1983.

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