

Characterization Of Particulate Emissions From Refinery Process Heaters And Boilers

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CHARACTERIZATION OF PARTICULATE EMISSIONS
FROM REFINERY PROCESS HEATERS AND BOILERS

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1.0 EXECUTIVE SUMMARY

This report presents the results of a field testing effort to characterize particulate emissions from refinery combustion sources. The effort included 155 tests on two process heaters and three boilers over a one year period. The units are described in Table 1-1 along with process conditions and number of tests by category.

The major objective of this program was to determine emission factors, size distribution, and chemical composition of particulates from refinery combustion sources. This was accomplished by measuring and analyzing source emissions from several types of units under a variety of fuel firing and excess air conditions. The tests were run under steady load conditions.

Key study findings and data interpretation are presented in Section 4. A brief discussion of major study findings is given below.

1.1 Particulate Emission Rates

Particulate emission rates for heaters and boilers on 100 percent gas or 100 percent oil were less than those predicted by EPA emission factors (AP-42).¹ Emission rates for 100 percent gas or 100 percent oil firing ranged from 7 to 87 percent of the values predicted by AP-42. EPA particulate emission factors are shown on pages 8 and 12 in the report and compared to our test data. Emission rates for the two units firing 100 percent gas ranged from 7 to 65 percent of the lower range predicted by AP-42 estimates. Emission rates for the two units firing 100 percent oil ranged from 52 to 87 percent of the AP-42 estimates. Fuel oil emission test results are compared with AP-42 data in Figure 4-1 of the text. Although survey data are lower than the

¹The U.S. Environmental Protection Agency developed emission factors from tests conducted on industrial process boilers firing either 100 percent gas or 100 percent fuel oil. These factors were published in AP-42, "Compilation of Air Pollution Emission Factors," Third Edition, with Supplements 1 through 13. During this project, tests were conducted under both single- and mixed-fuel-firing conditions. Results from tests completed under single fuel conditions are compared directly herein with the AP-42 factors. For those tests performed under mixed-fuel-firing conditions, comparison emission factors were calculated by prorating the AP-42 emission factors for oil and gas based on the heat rate of each fuel.

Table 1-1
UNIT DESCRIPTIONS AND DATA BASE

Description of Conditions					No. of Tests by Type					
Refinery	Source	Type of Unit	Max. Design Rating 10 ⁶ BTU/hr	Condition No.	Fuel Firing	% O ₂ at Test Site (Boiler)	Particulate ¹	PSD ²	NO _x ³	
					Ratio % Gas : % Oil					
A	1	Process Heater	315	1	97:3	2.3	3	1	3	
				2	93:7	4.3	3	1	3	
				3	51:49	4.0	3	1	3	
				4	54:46	5.4	3	1	3	
B	1	Process Heater	60.1	1	100:0	4.1	3	-	3	
				2	100:0	6.0	3	-	3	
A	2	Boiler	215	1	100:0	6.8 (2.9)	3	1	3	
				2	100:0	8.6 (4.7)	3	-	3	
				3	69:31	8.9 (5.2)	2	2	2	
				4	75:25	9.7 (6.5)	2	2	2	
				5	40:60	8.7 (5.5)	3	3	3	
				6	40:60	10.0 (6.8)	3	3	3	
B	2	Boiler	576	1	31:69	5.0	3	3	3	
				2	29:71	6.7	3	3	3	
				3	0:100	4.9	3	3	3	
				4	0:100	6.6	3	3	3	
C	1	Boiler	200	1	43:57	9.1 (5.4)	3	3	3	
				2	37:63	10.1 (6.5)	3	3	3	
				3	0:100	7.3 (3.7)	3	3	3	
				4	0:100	9.6 (5.4)	3	3	3	
TOTALS								58	39	58

¹EPA Method 5 as specified in Code of Federal Regulations, Title 40, Part 60, Appendix A, "Standards of Performance for New Stationary Sources," August 18, 1977.

²PSD = particle size distribution. Testing was performed according to Operating Manual for Andersen 2000, Inc., "Mark III Particle Sizing Stack Samplers," Andersen 2000 Inc., P. O. Box 20769, Atlanta, GA.

³EPA Method 7. Code of Federal Regulations, Title 40, Part 60, Appendix A, "Standards of Performance for New Stationary Sources," August 18, 1977.



AP-42 predicted values, the data are within the range of data used to develop the AP-42 correlation.

Emission rates for mixed-fuel-firing ranged from 9 percent of the AP-42 lower limit to 125 percent of the AP-42 upper limit. Emissions from three of the four units were below those predicted by AP-42.

The effect of excess air on mass emissions was examined. Over the range of excess air conditions tested, no significant effects were observed.

1.2 Particle Size Distribution

The particle size distribution (PSD) test results indicate that relatively small particles are produced during both gas and oil firing. The data show that ~ 50 weight (wt) percent of the particles for most tests were submicron ($<1 \mu\text{m}$). An average of about 75 percent of the particles by weight were $<10 \mu\text{m}$ effective aerodynamic diameter. Excess air showed no effect on size distributions. The data show that a greater weight percentage of small particles is formed during gas firing than for oil- and mixed-fuel-fired conditions.

1.3 Chemical Composition

Particles were analyzed for heavy metals, extractable organics, sulfates, nitrates, and elemental carbon, hydrogen, and nitrogen. The particles generally contained small quantities of metals ($<2 \text{ wt percent}$) and no nitrates ($<0.1 \text{ wt percent}$). Organics content varied widely from less than 1 percent to over 50 percent. Sulfate content ranged from 25 to 85 wt percent. The remaining chemical constituents were not identified in this study.

1.4 Nitrogen Oxides

Results of limited oxides of nitrogen testing indicated that NO_x emissions increased with rising excess air levels and also with the proportion of oil fired in those sources.

2.0 INTRODUCTION

2.1 Background

The importance of airborne particulate size and chemical composition is being examined by EPA as the Agency considers revising the National Ambient Air Quality Standard for particulate matter. The impact of discrete size fractions and fine or respirable particles is being considered rather than the currently controlled total suspended particulate (TSP) matter.

As mandated by the Federal Clean Air Act, the promulgation of a revised particulate standard could have impact on control strategies and revisions to the existing State Implementation Plans. This would affect many source types, including refinery combustion sources (i.e., steam generators and process heaters) and non-fired sources (e.g., FCC stacks and cokers). The purpose of this test program is to provide a preliminary data base of particulate emission rates, size distributions, and chemical compositions.

2.2 The Study Objectives

The objectives of this program were:

1. To determine particulate emission factors.
2. To obtain particle size distribution data.
3. To determine the chemical composition of the particulate.

2.3 The Project Organization

The test program determined the particulate mass emission rates, particle size distribution, and chemical composition (i.e., sulfates, heavy metals, nitrates, and elemental analyses) from process heaters and steam-generating boilers. These data were related to fuel composition and to predicted AP-42 emission rates. Nitrogen oxides emission rates were measured and compared to predicted AP-42 values to demonstrate the relationship between particulates generation and nitrous oxide formation. The effects of excess air levels were examined for each test unit. Testing on the first unit started 14 July 1981, and on 19 May 1982 all testing was completed. A total of 155 tests on two heaters and three boilers were conducted.



2.4 Field Test Methods

Standard test methods were employed in the program as follows:

1. Mass emissions - EPA Method 5.
2. Particle size distribution - Andersen impactor.
3. NO_x - EPA Method 7.



3.0 DESCRIPTIONS OF UNITS TESTED

Five sources (two heaters and three boilers) were surveyed under this contract. A brief description of each unit is presented below. Additional information on each unit is provided in Appendix B.

3.1 Process Heaters

3.1.1 Refinery A - Source 1

This source is a 1978 Foster Wheeler side-fired horizontal radiant-tube crude process heater. It has a maximum gross fired duty of 315×10^6 Btu/hr; fuel ratios can be varied from 0 to 100 percent gas or oil.

3.1.2 Refinery B - Source 1

This source is a 1978 G.C. Broach Company vertical-fired process heater on a hydrotreating unit used for desulfurization of diesel distillate. Unit processing capacity is 25,000 barrels per operating day (bpod). Its maximum fired duty is 60.1×10^6 Btu/hr and it is typically operated at 25 percent of maximum duty. It is designed to only fire 100 percent plant fuel gas.

3.2 Boilers

3.2.1 Refinery A - Source 2

This source is a Riley Stoker boiler constructed in 1948. It is a balanced draft, end-horizontal-fired boiler with radiant tubes and horizontal section convection tubes. It has a maximum gross fired duty of 215×10^6 Btu/hr; fuel ratios can be varied from 0 to 100 percent refinery fuel gas or oil.

3.2.2 Refinery B - Source 2

This horizontal-fired steam generator, built in 1978 by Riley Stoker, is of a natural circulation, water tube-type design. Its steam production capacity is 440×10^3 lb/hr at a maximum heat rating of 576×10^6 Btu/hr. Its fuel-firing ratio is infinitely adjustable but is currently limited to about 30 percent gas based on the availability of process fuel gas.

3.2.3 Refinery C - Source 1

This boiler was designed by Babcock and Wilcox and constructed in 1942. It is a balanced draft, horizontal-fired unit with a maximum steam rating of 125,000 lb/hr at 750°F and 700 psig. The boiler has a design efficiency of 86 percent and is rated at 200×10^6 Btu/hr. It can be fired on gas or oil or any combination thereof.



4.0 RESULTS OF MEASUREMENTS

4.1 Mass Emissions

4.1.1 Process Heaters

Process heater emission factors based on the front-half catch¹ are compared to those from AP-42 in Table 4-1. Key particulate data and results are listed, by run, in Tables 4-2 and 4-3 for Refinery A Source 1 and Refinery B Source 1, respectively. Detailed data are included in Appendix A.

Data for Refinery A process heater were obtained while the source fired a combination of process gas and a No. 4 fuel oil (0.09 wt percent S, <0.01 wt percent ash) ranging from 51 to 97 percent gas on a Btu basis. The measured particulate emission factors were all less than the lower limits of the prorated EPA emission factor ranges for all combinations of fuel-firing and excess air. The average measured particulate emission factor was 0.0024 ± 0.0006 lb/10⁶ Btu. The lower limits of the prorated EPA emission factor ranges varied from 0.0055 to 0.027 lb/10⁶ Btu.

Refinery B process heater operated on 100 percent fuel gas at its typical firing rate during the survey. The measured particulate emissions factors were an order of magnitude less than the lower limit of the AP-42 predicted range. As expected, the average measure particulate emission factor, 0.0004 lb/10⁶ Btu, was significantly less than the value obtained for the mixed-oil-gas-firing of Refinery A process heater.

Particulate emissions were measured at two excess air levels for each source. Excess air levels were monitored by stack percent O₂. The stack O₂ level varied from 2.0 to 5.5 percent for Refinery A Source 1 and from 4.1 to 6.0 percent for Refinery B Source 1. Two of the three tests indicated insignificant effects of excess air on particulate emissions. One test on the Refinery A heater, at very low excess air, showed increased emission rates.

Front-half and total (front-half plus back-half) particulate were measured.¹ For Refinery A heater (mixed-fuel-fired), the front-half catch averaged 62 percent of the total particulate. For Refinery B heater (gas-fired), the front-half particulate averaged 17 percent of the total catch.

¹Terms are defined in Appendix C.

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Table 4-1

Summary of Particulate Emission Factors from Process Heaters

Refinery	Source	Test Run Numbers ⁴	Fuel Firing Ratio % Gas : % Oil	Percent O ₂ at Test Location	Heat Input Rate 10 ⁶ BTU/hr	Particulate Emission Factors ¹								
						Fuel Firing Rate		Measured		EPA ²		Measured		EPA ³
						Gas 10 ⁶ ft ³ /hr	Oil 10 ³ gph	lb/10 ⁶ BTU	lb/10 ⁶ SCF gas	lb/10 ⁶ BTU	lb/10 ⁶ BTU	lb/10 ⁶ SCF gas	lb/10 ⁶ SCF gas	lb/10 ³ gal oil
A	1	1,2,3	97:3	2.0	262	0.212	0.054	0.0031	0.0055-0.014	---	---	5-15:7		
		4,5,6	93:7	4.0	257	0.200	0.125	0.0017	0.0073-0.015	---	---	5-15:7		
		7,9,11	51:49	4.0	270	0.115	0.914	0.0023	0.027-0.031	---	---	5-15:7		
		8,12,13	54:46	5.5	252	0.113	0.802	0.0023	0.025-0.029	---	---	5-15:7		
B	1	4,5,6	100:0	4.1	15	0.015	---	0.0004	0.0049-0.015	0.39	0.39	5-15:---		
		1,2,3	100:0	6.0	16	0.016	---	0.0003	0.0049-0.015	0.35	0.35	5-15:---		

¹Particulate is defined in this section as that material collected by EPA Method 5 (front-half catch).

²Values shown for single fuel firing conditions were calculated using AP-42 Emission Factors and actual fuel firing rates and fuel sample analysis results. Those shown for mixed fuel firing were calculated by prorating the AP-42 Emission Factors for gas and oil based on the heat rate of each fuel using the following equation:

$$\frac{\text{lb Particulate}}{10^6 \text{ BTU}} = \frac{\text{Gas Emission}}{\text{Gas Fired Duty (AP-42 Factor)}} + \frac{\text{Oil Emission}}{\text{Oil Fired Duty (AP-42 Factor)}}$$

³Values obtained from AP-42 Third Edition. Grade 4 oil was fired in Refinery A process heater.

⁴Run 10 was discounted because of process swings during test.

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REFINERY A

SOURCE NO. 1

Table 4-2

SUMMARY OF TEST RESULTS

Test Run Number ¹	One	Two	Three	Four	Five	Six	Seven	Nine	Eleven	Eight	Twelve	Thirteen
Fuel Firing Ratio % Gas : % Oil	100:0	100:0	91:9	94:6	91:9	94:6	46:54	46:54	61:39	48:52	57:43	58:42
Percent O ₂ at Test Location	2.3	2.3	2.3	4.4	4.3	4.3	3.8	4.1	4.1	5.2	5.5	5.4
<u>Particulate Results</u>												
<u>Front-Half</u>												
Concentration, grains/dscf, x10 ⁻³	3.0	1.6	2.2	0.7	1.3	1.3	1.9	1.3	1.1	1.6	1.5	0.8
Mass Emission Rate, pounds/hour	1.1	0.56	0.78	0.26	0.50	0.57	0.80	0.54	0.52	0.70	0.64	0.38
Series Average Mass Emission Rate, lbs/hr		0.81			0.44			0.62			0.57	
<u>Total</u>												
Concentration, grains/dscf, x10 ⁻³	4.0	2.5	3.3	1.3	2.1	2.3	2.5	3.0	2.1	2.2	2.3	1.6
Mass Emission Rate, pounds/hour	1.4	0.91	1.2	0.50	0.81	0.99	1.1	1.3	0.97	0.95	1.0	0.75
Series Average Mass Emission Rate, lbs/hr		1.2			0.77			1.1			0.90	
<u>NO_x Emissions, as NO₂²</u>												
Concentration, ppm by Volume, dry basis	30.	51.	42.	64.	59.	77.	112.	142.	138.	126.	162.	136.
Concentration, lbs/dscf, x 10 ⁻⁶	3.6	6.1	5.0	7.6	7.0	9.2	13.	17.	17.	15.	19.	16.
Mass Emission Rate, pounds/hour	8.8	15.	12.	21.	19.	28.	40.	51.	53.	45.	60.	52.
Series Average Mass Emission Rate, lbs/hr		12.			23.			48.			52.	

¹Run 10 was discounted because of process swings during test.²Results shown are averages of three (3) grab samples.

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REFINERY B

SOURCE 1

TABLE 4-3

SUMMARY OF TEST RESULTS

Test Run Number	Four	Five	Six	One	Two	Three
Fuel Firing Ratio, %gas:oil	100:0	100:0	100:0	100:0	100:0	100:0
Percent O ₂ at test location	4.0	4.0	4.4	6.3	5.8	5.9
<u>Particulate Results</u>						
<u>Front-Half</u>						
Concentration, grains/dscf, x 10 ⁻⁵	11.8	2.23	21.5	5.68	18.6	10.1
Mass Emission Rate, lbs/hr, x 10 ⁻³	5.76	1.04	10.2	2.74	9.06	4.99
Series Average Mass Emission Rate, lbs/hr, x 10 ⁻³		5.67			5.60	
<u>Total</u>						
Concentration, grains/dscf, x 10 ⁻⁵	64.6	62.7	77.6	54.7	84.0	58.8
Mass Emission Rate, lbs/hr, x 10 ⁻³	31.5	29.3	36.6	26.4	41.0	29.0
Series Average Mass Emission Rate, lbs/hr, x 10 ⁻³		32.5			32.1	
<u>NO_x Emissions, as NO₂¹</u>						
Concentration, ppm by volume, dry basis	48.5	50.6	68.4	64.8	55.1	58.2
Concentration, lbs/dscf, x 10 ⁻⁶	5.79	6.05	8.16	7.74	6.58	6.95
Mass Emission Rate, lbs/hr	1.97	1.98	2.69	2.62	2.25	2.40
Series Average Mass Emission Rate, lbs/hr		2.21			2.42	

¹Results shown are averages of three (3) grab samples.

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4.1.2 Boilers

Boiler particulate emissions factors, based on the front-half catch, are compared with AP-42 emission factors in Table 4-4. Summarized data can be found in Tables 4-5, 4-6, and 4-7 for Refinery A, B, and C boilers, respectively. Detailed data are included in Appendix A.

During 100 percent gas-firing conditions for Refinery A boiler, the average emission rate, $0.0022 \pm .0012$ lb/10⁶ Btu, was less than the lower limit of the predicted EPA emission factor (0.0045 lb/10⁶ Btu). During 100 percent oil-firing conditions for Refinery B and C boilers, the average measured emission rates were also less than the EPA-predicted rates:

Refinery	Average Emission Factor, lb/10 ⁶ Btu	Predicted EPA AP-42 Value*, lb/10 ⁶ Btu
B	$0.035 \pm .003$	0.069
C	$0.071 \pm .022$	0.10

*Based on fuel composition and firing rates

Although the survey data are lower than the AP-42 predicted values, the data are within the range of data used to develop the AP-42 correlation (see Figure 4-1).

Particulate emission factors were estimated for mixed-fuel-firing on Refinery boilers A, B, and C by prorating AP-42 values based on fuel heat contents and firing rates. These prorated AP-42 values are compared to average measured emission rates below:

Refinery	Average Emission Factor, lb/10 ⁶ Btu	Range of Prorated EPA AP-42 Values, lb/10 ⁶ Btu
A	$0.012 \pm .004$	0.012 - 0.027
B	$0.030 \pm .005$	0.049 - 0.053
C	$0.078 \pm .009$	0.059 - 0.068

The test data, shown in Table 4-4, generally indicated that mass emissions increased with the proportion of oil fired but showed no correlation with excess air over the range of excess air conditions studied.

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TABLE 4-4
Summary of Particulate Emission Factors from Boilers

Refinery Source	Test Run Numbers	Fuel Firing Ratio Gas : % Oil	Percent O ₂ at Test Location (Boiler)	Particulate Emission Factors ¹						
				Fuel Firing Rate			Measured			
				Heat Input Rate 10 ⁶ BTU/hr	Gas	Oil	Measured lb/10 ⁶ BTU	EPA ² lb/10 ⁶ BTU	lb/10 ³ gal oil	lb/10 ³ gal oil
					10 ⁶ ft ³ /hr	10 ³ gal				
A	2	7,8,9	100:0	199	0.181	---	0.0030	0.0045-0.014	3.3	5-15:---
		10,11,12	100:0	204	0.185	---	0.0013	0.0045-0.014	1.5	5-15:---
		13,14	69:31	196	0.123	0.411	0.0066	0.014-0.020	---	5-15:5.2
		15,16	75:25	194	0.132	0.328	0.0072	0.012-0.019	---	5-15:5.2
		1,2,3	40:60	182	0.066	0.737	0.016	0.023-0.027	---	5-15:5.2
	4,5,6	40:60	187	0.068	0.758	0.014	0.023-0.027	---	5-15:5.2	
B	2	1,2,3	31:69	549	0.114	2.53	0.028	0.049-0.052	---	5-15:10
		4,5,6	29:71	541	0.103	2.59	0.032	0.050-0.053	---	5-15:10
		10,11,12	0:100	560	---	3.75	0.035	0.069	(5.2)	---
		7,8,9	0:100	567	---	3.80	0.035	0.069	(5.2)	---
C	1	7,8,9	43:57	172	0.072	0.653	0.079	0.059-0.063	---	5-15:15
		10,11,12	37:63	160	0.057	0.674	0.076	0.065-0.068	---	5-15:15
		1,2,3	0:100	203	---	1.36	0.054	0.10	(8.0)	---
		4,5,6	0:100	155	---	1.04	0.088	0.10	(13)	---

¹Particulate is defined in this section as that material collected by EPA Method 5 (front-half catch).

²Values shown for single fuel firing conditions were calculated using AP-42 Emission factors and actual fuel firing rates and fuel sample analysis results. Those shown for mixed fuel firing were calculated by prorating the AP-42 Emission Factors for gas and oil based on the heat rate of each fuel using the following equation:

$$\frac{\text{lb Particulate}}{10^6 \text{ BTU}} = \frac{(\text{Gas Fired Duty})(\text{AP-42 Gas Emission Factor}) + (\text{Oil Fired Duty})(\text{AP-42 Oil Emission Factor})}{\text{TOTAL FIRED DUTY}}$$

³The AP-42 Particulate Emission Factors for residual oil combustion are best described, on the average, as a function of fuel oil grade and sulfur content, as shown below: Grade 6 oil: 1b/10³ gal = 10 (S) + 3, where S is the percentage, by weight, of sulfur in the oil.

Grade 5 oil: 10 lb/10³ gal.

Grade 4 oil: 7 lb/10³ gal.

⁴Grade 6 oil was fired in all boiler sources. For Refinery A, wt. % S in the oil = 0.22

For Refinery B, wt. % S in the oil = 0.73

For Refinery C, wt. % S in the oil = 1.19

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REFINERY A
SOURCE 2
TABLE 4-5
SUMMARY OF TEST RESULTS

Test Run Number	Seven	Eight	Nine	Ten	Eleven	Twelve	Thirteen	Fourteen	Fifteen	Sixteen	One	Two	Three	Four	Five	Six	
Fuel Firing Ratio, % Gas : % Oil	100:0	100:0	100:0	100:0	100:0	100:0	68:32	70:30	75:25	74:26	40:60	40:60	40:60	41:59	40:60	39:61	
Percent O ₂ Exiting Boiler	2.9	3.0	2.9	4.8	4.6	4.6	5.3	5.1	6.5	6.4	5.5	5.3	5.5	6.8	6.8	6.8	
Percent O ₂ at Test Location	7.0	7.0	6.6	8.6	8.7	8.5	8.8	9.0	9.6	9.8	8.7	8.6	8.9	10.0	10.0	10.0	
Particulate Results																	
Front-half																	
Concentration, grains/ dscf, x 10 ⁻³	1.9	1.3	2.7	0.7	0.5	1.2	3.5	3.9	3.3	4.3	8.3	8.0	8.5	6.5	7.2	7.1	
Mass Emission Rate, pounds/hour	0.57	0.39	0.80	0.24	0.19	0.39	1.2	1.4	1.2	1.5	2.9	2.7	3.0	2.3	2.8	2.9	
Series Average Mass Emission Rate, lbs/hr	0.59			0.27			1.3			1.4			2.9			2.7	
Total																	
Concentrations, grains/ dscf, x 10 ⁻³	3.8	3.9	7.7	1.8	2.0	3.3	5.5	8.5	7.0	10.3	15.9	13.6	15.5	11.4	14.9	13.7	
Mass Emission Rate, pounds/hour	1.1	1.2	2.3	0.65	0.70	1.1	1.9	2.9	2.4	3.6	5.5	4.6	5.4	4.0	5.9	5.5	
Series Average Mass Emission Rate, lbs/hr	1.5			0.82			2.4			3.0			5.2			5.1	
NO _x Emissions as NO ₂ ¹																	
Concentration, ppm by volume, dry basis	76.	102.	69.	131.	125.	117.	215.	203.	189.	202.	200.	211.	211.	194.	212.	206.	
Concentration, lbs/dscf, x 10 ⁻⁶	9.0	12.2	8.2	15.7	14.9	14.0	25.6	24.2	22.5	24.2	23.8	25.2	25.2	23.2	25.3	24.6	
Mass Emission Rate, lbs/hr	19.	26.	17.	39.	37.	32.	61.	59.	55.	59.	58.	60.	61.	57.	70.	69.	
Series Average Mass Emission Rate, lbs/hr	21.			36.			60.			57.			60.			65.	

¹Results shown are averages of three (3) grab samples.

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REFINERY B
SOURCE 2
TABLE 4-6

SUMMARY OF TEST RESULTS

Test Run Number	One	Two	Three	Four	Five	Six	Ten	Eleven	Twelve	Seven	Eight	Nine
Fuel Firing Ratio, % Gas : % Oil	27:73	33:67	33:67	31:69	27:73	27:73	0:100	0:100	0:100	0:100	0:100	0:100
Percent O ₂ at Test Location	4.8	5.0	5.1	6.7	6.7	6.6	4.9	5.0	4.7	6.5	6.7	6.6
<u>Particulate Results</u>												
<u>Front-Half</u>												
Concentration, grains/dscf	0.017	0.013	0.011	0.013	0.015	0.014	0.019	0.019	0.015	0.017	0.017	0.016
Mass Emission Rate, pounds/hour	18.2	14.7	12.3	16.2	18.8	17.5	20.4	21.3	16.6	19.9	20.7	19.1
Series Average Mass Emission Rate, lbs/hr		15.1			17.5			19.4			19.9	
<u>Total</u>												
Concentration, grains/dscf	0.019	0.014	0.014	0.013	0.016	0.015	0.019	0.020	0.019	0.018	0.018	0.016
Mass Emission Rate, pounds/hour	20.3	15.0	15.0	16.3	19.3	18.9	20.9	21.9	20.3	21.2	21.3	19.9
Series Average Mass Emission Rate, lbs/hr		16.8			18.2			21.0			20.8	
<u>NO_x Emissions, as NO₂¹</u>												
Concentration, ppm by volume, dry basis	110.	106.	127.	125.	79.8	115.	131.	133.	140.	130.	132.	127.
Concentration, lbs/dscf, x 10 ⁻⁶	13.2	12.7	15.2	14.9	9.53	13.8	15.6	15.9	16.8	15.5	15.8	15.2
Mass Emission Rate, lbs/hr	98.0	98.1	117.	131.	81.2	118.	121.	123.	129.	130.	135.	129.
Series Average Mass Emission Rate, lbs/hr		104.			110.			124.			131.	

¹Results shown are averages of three (3) grab samples.

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REFINERY C
SOURCE 1

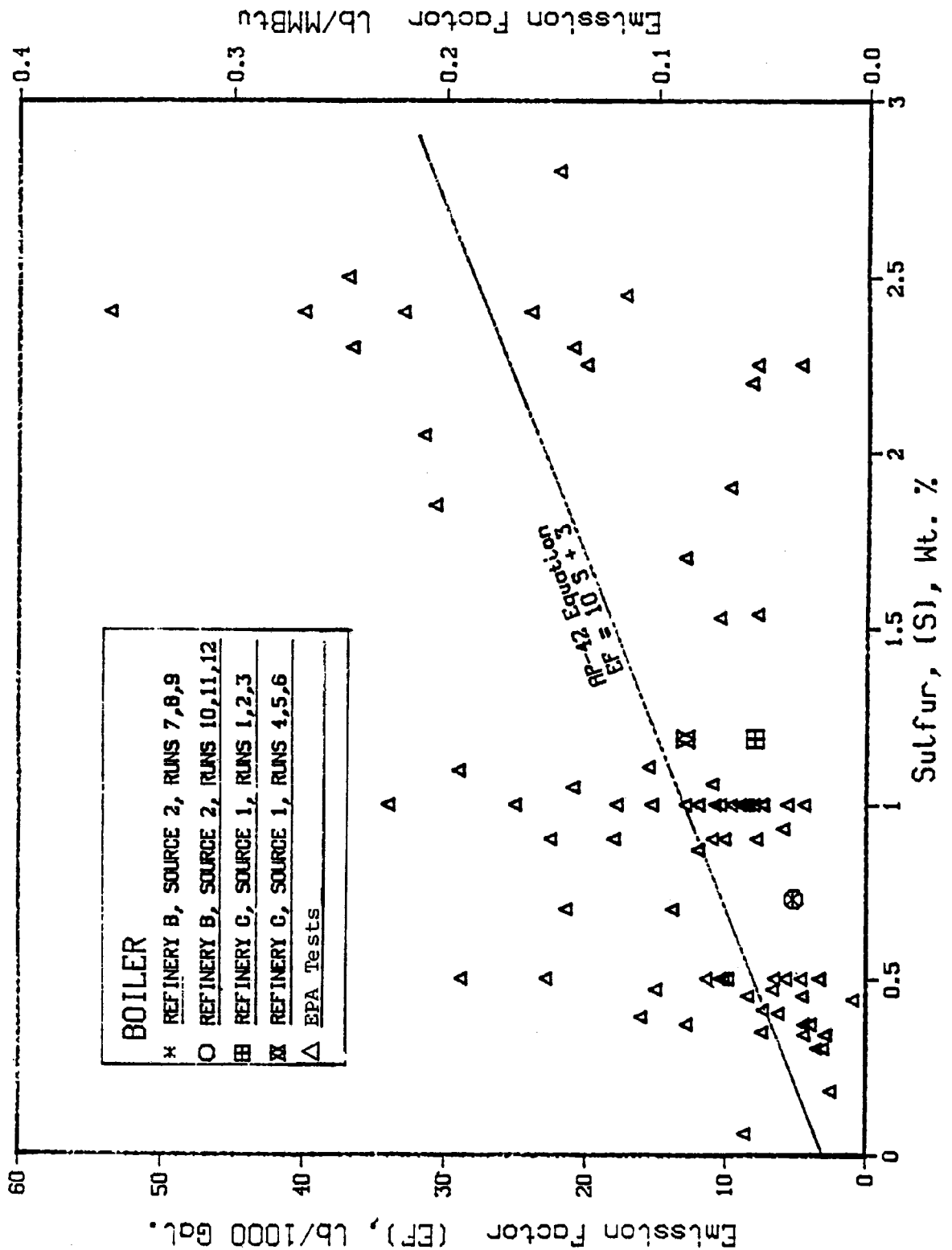
TABLE 4-7

SUMMARY OF TEST RESULTS

Test Run Number	Seven	Eight	Nine	Ten	Eleven	Twelve	One	Two	Three	Four	Five	Six
Fuel Firing Ratio, % Gas : % Oil	47:53	36:64	48:52	43:57	33:67	35:65	0:100	0:100	0:100	0:100	0:100	0:100
Percent O ₂ at Test Location	9.2	9.1	9.1	10.5	10.2	9.7	7.5	7.5	7.2	9.7	9.5	9.6
Percent O ₂ Exiting Boiler	5.5	5.4	5.4	6.4	6.6	6.5	3.5	4.0	3.5	5.4	5.4	5.5
<u>Particulate Results</u>												
<u>Front-Half</u>												
Concentration, grains/dscf	0.030	0.037	0.035	0.034	0.027	0.029	0.021	0.030	0.027	0.038	0.039	0.031
Mass Emission Rate, pounds/hour	12.2	14.9	13.8	13.2	11.1	12.0	8.29	12.9	11.4	14.6	14.8	11.8
Series Average Mass Emission Rate, lbs/hr		13.6			12.1			10.9			13.7	
<u>Total</u>												
Concentration, grains/dscf	0.031	0.042	0.040	0.035	0.028	0.031	0.027	0.032	0.038	0.041	0.049	0.034
Mass Emission Rate, pounds/hour	12.5	16.8	15.5	13.3	11.3	13.0	10.9	13.5	16.0	15.7	18.5	13.1
Series Average Mass Emission Rate, lbs/hr		14.9			12.5			13.5			15.8	
<u>NO_x Emissions, as NO₂¹</u>												
Concentration, ppm by volume, dry basis	134.	121.	118.	130.	127.	109.	157.	123.	191.	170.	162.	158.
Concentration, lbs/dscf, x 10 ⁻⁶	16.0	14.4	14.1	15.5	15.1	13.0	18.8	14.7	22.8	20.3	19.3	18.9
Mass Emission Rate, lbs/hr	45.1	40.1	38.6	41.9	43.3	37.9	52.7	43.8	67.4	54.9	51.1	51.0
Series Average Mass Emission Rate, lbs/hr		41.3			41.0			54.6			52.3	

¹Results shown are averages of the three (3) grab samples.

FIGURE 4-1
COMPARISON OF MEASURED PARTICULATE EMISSIONS
TO EPA'S AP-42 CORRELATION FOR
NO. 6 OIL-FIRED FURNACES



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The impact of fuel mixture on front-half/back-half particulate catches was examined. The percentage front-half to total particulate catch was inversely related to the proportion of gas fired in the boilers:

Refinery	Average % Gas Fired	Front Half:Total Particulate Catch,%
B	15	94
C	20	89
A	71	47

4.2 Size Distribution

4.2.1 Process Heaters

Particle size distribution (PSD) data were obtained only for Refinery A heater (see Table 4-8 below for results summary). Single tests were performed at 70 percent gas : 30-percent oil-firing condition at two different oxygen levels. No PSD data were obtained for Refinery B heater because the extremely low particulate loading (average of 1.2×10^{-4} gr/dscf) prevented the attainment of sufficient mass with the impactor over a reasonable sampling period.

Additional PSD data are included in Appendix A.

TABLE 4-8

REFINERY A SOURCE 1 PARTICLE SIZE DISTRIBUTION DATA

Fuel-Firing Ratio % Gas: % Oil	Percent O ₂ at Test Location	Mass Percent Less Than Stated Size			
		0.3 um	1.0 um	3.0 um	10.0 um
70:30	3.9	84	86	87	88
70:30	5.5	70	72	73	76

The above data are presented graphically in Figure 4-2.

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REFINERY A SOURCE 1

PARTICLE SIZE DISTRIBUTION TEST RESULTS AT 70% GAS : 30% OIL

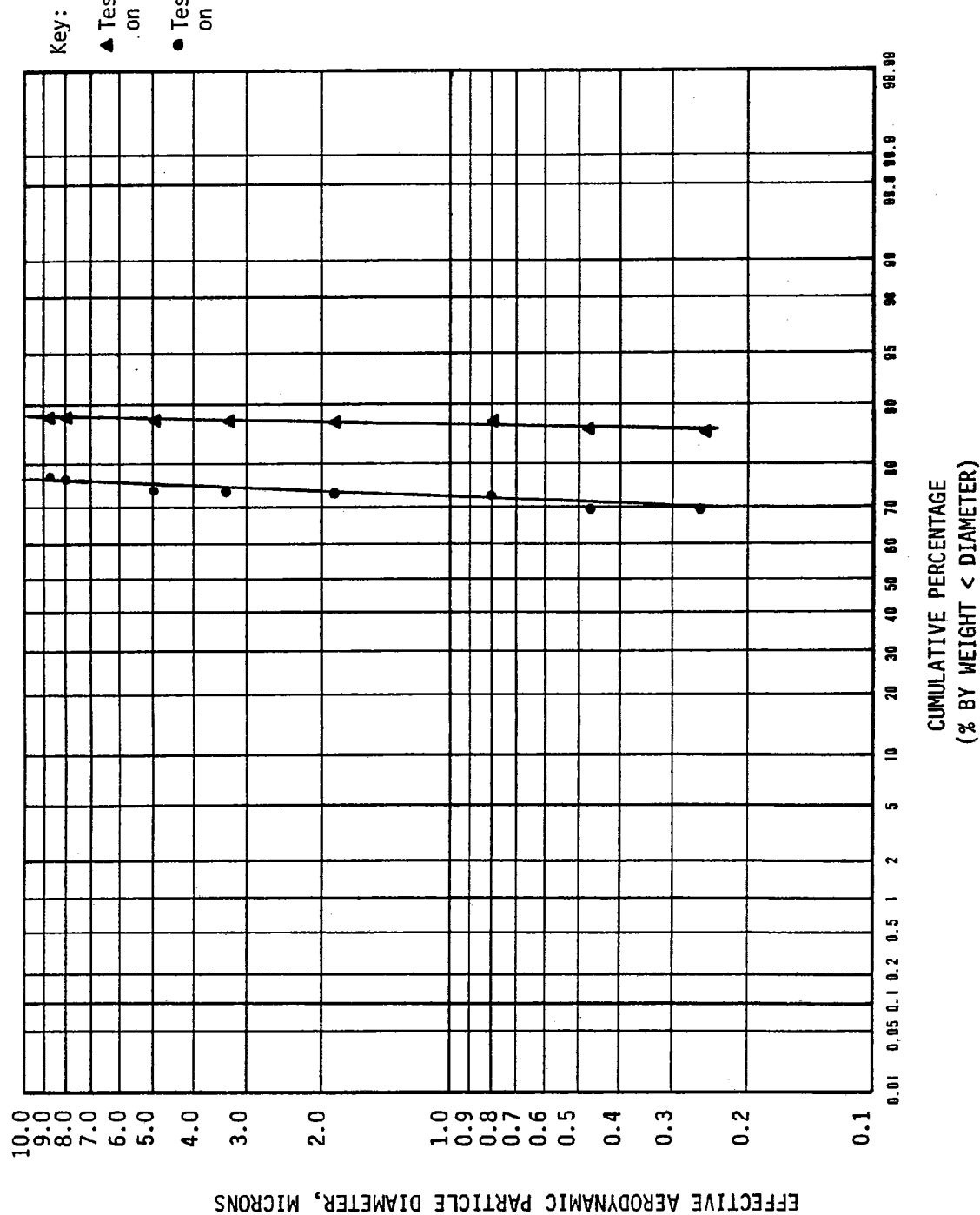


FIGURE 4-2



4.2.2 Boilers

Average PSD data for the three boilers are presented in Table 4-9. Mean mass percent less than 0.3, 1.0, 3.0, and 10 μm data are shown for tests performed at each process condition. De-tailed information for all PSD tests is contained in Appendix A.

Data from the single PSD test conducted under 100 percent gas-firing conditions are plotted in Figure 4-3. The range, mean, standard deviation, and quartile groups of the PSD data for all mixed fuel and for all 100 percent oil-firing conditions are shown graphically in Figures 4-4 and 4-5, respectively.

The size distributions are combined by fuel fired as shown in Table 4-10:

TABLE 4-10

CUMULATIVE WEIGHT PERCENTAGE LESS
THAN DIAMETER BY FUEL CONDITION

Particle Size Range, μm	100% Gas	100% Oil	Mixed
≤ 0.3	73	44 $\pm$ 11	44 $\pm$ 14
≤ 1.0	78	55 $\pm$ 9	53 $\pm$ 13
≤ 3.0	82	68 $\pm$ 7	63 $\pm$ 11
≤ 10.0	85	79 $\pm$ 6	72 $\pm$ 9

For submicron particles, the data show that a greater weight percentage of smaller particles is formed during gas-firing than for oil- and mixed-fuel-fired conditions. For particles greater than 1 μm , no significant differences between fuel types were observed.

Under 100 percent gas-firing conditions, ~ 73 percent of the particles by weight were ≤ 0.3 μm effective aerodynamic diameter (EAD). For oil, 40 to 50 percent of the particles by weight were ≤ 0.3 μm effective aerodynamic diameter. No consistent effects of excess air on PSD were found.

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TABLE 4-9

AVERAGE PARTICLE SIZE DISTRIBUTION DATA SUMMARY FOR BOILER SOURCES

Refinery/ Source	Fuel Firing Ratio % Gas : % Oil	Percent O ₂ at Boiler	Mass Percent Less than Stated Size and Standard Deviation			
			0.3 um	1.0 um	3.0 um	10.0 um
A/2	100:0	2.9	73	78	82	85
	69:31	5.2	49 ± 9	57 ± 11	63 ± 13	70 ± 12
	75:25	6.5	43 ± 4	55 ± 6	66 ± 8	76 ± 9
	40:60	5.4	38 ± 7	48 ± 6	58 ± 5	70 ± 3
	40:60	6.8	50 ± 3	57 ± 8	66 ± 5	73 ± 2
B/2	31:69	5.0	65 ± 7	61 ± 10	77 ± 11	82 ± 13
	28:72	6.7	28 ± 11	39 ± 11	51 ± 10	64 ± 7
	0:100	4.9	44 ± 17	54 ± 14	64 ± 11	75 ± 8
	0:100	6.6	42 ± 5	55 ± 8	67 ± 9	77 ± 9
C/1	44:56	5.4	29 ± 6	41 ± 8	53 ± 10	66 ± 9
	37:63	6.5	47 ± 4	59 ± 5	68 ± 7	78 ± 8
	0:100	3.7	40 ± 13	55 ± 9	70 ± 4	82 ± 1
	0:100	5.4	50 ± 11	62 ± 9	72 ± 6	82 ± 4

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REFINERY A SOURCE 2
PARTICLE SIZE DISTRIBUTION TEST RESULTS UNDER 100% GAS FIRING CONDITIONS

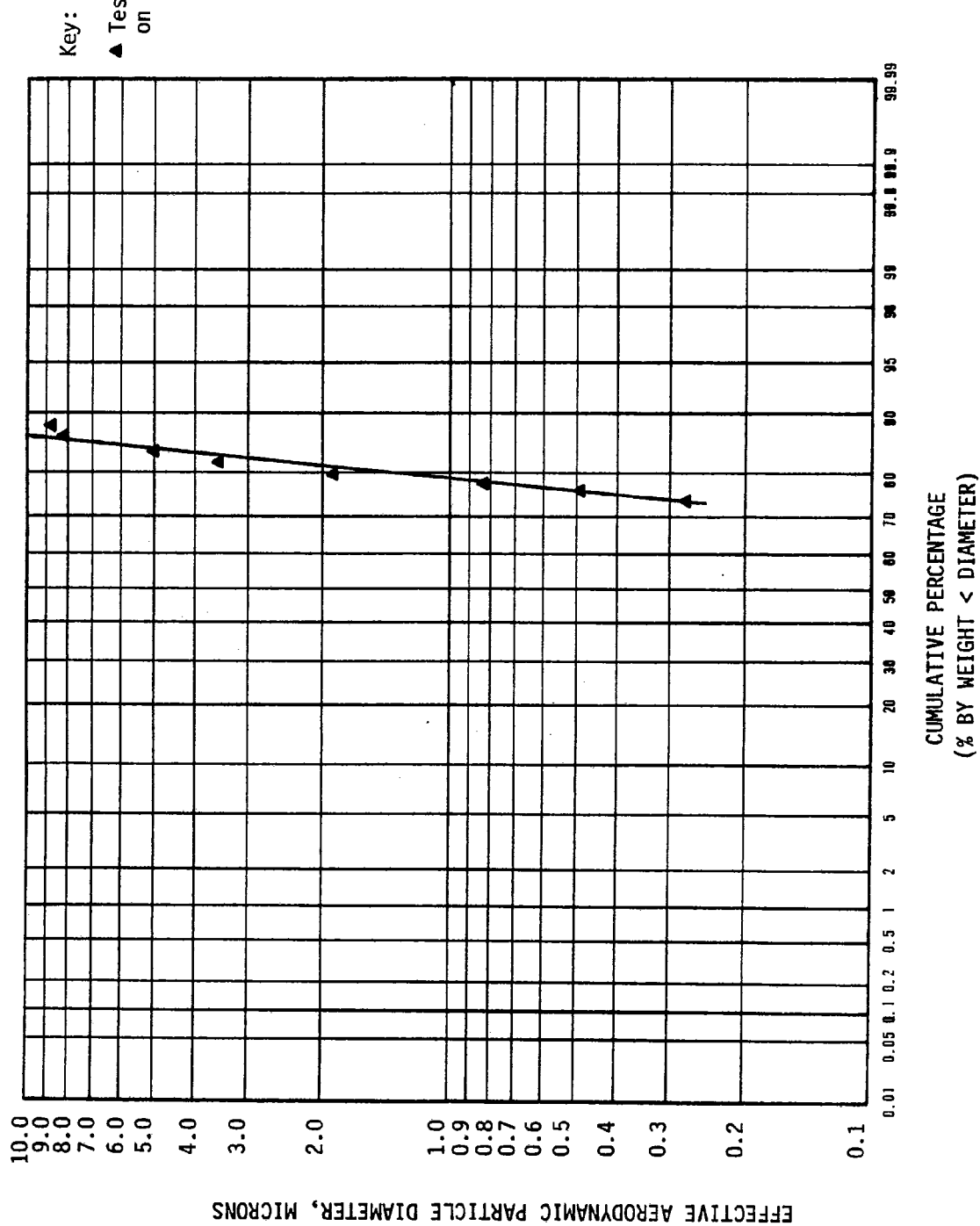


FIGURE 4-3

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SUMMARY OF PARTICLE SIZE DISTRIBUTION TEST RESULTS UNDER MIXED FUEL FIRING CONDITIONS

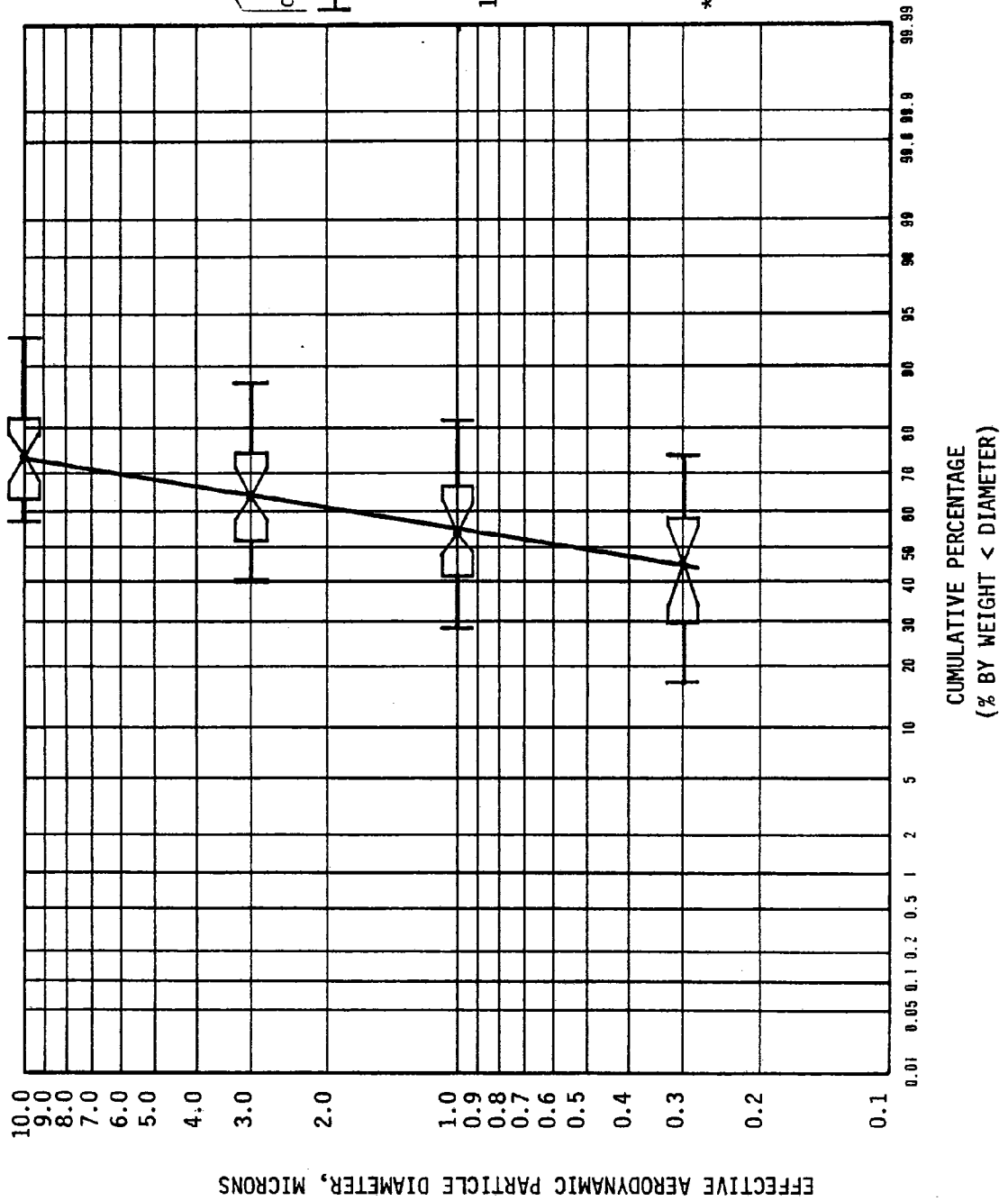
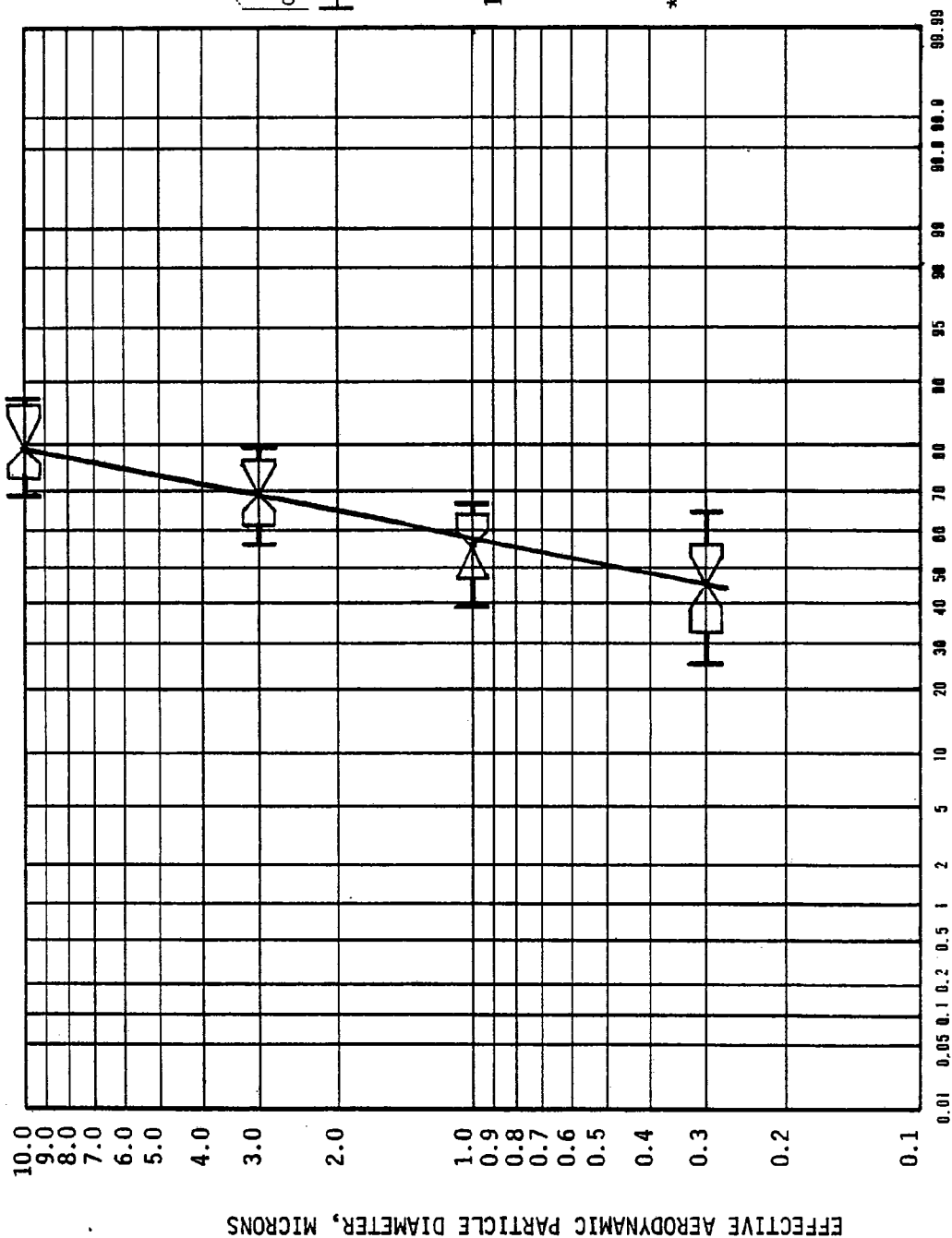


FIGURE 4-4

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SUMMARY OF PARTICLE SIZE DISTRIBUTION TEST RESULTS UNDER 100% OIL FIRING CONDITIONS



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FIGURE 4-5



4.3 Chemical Composition of Particulates

Particulates were analyzed for metal content, sulfates, nitrates and carbon, hydrogen, and nitrogen. The chemical composition of composite fuel oil samples was determined.

4.3.1 Process Heaters

The fuel oil analysis for Refinery A process heater tests is shown in Table 4-11. The fuel was a No. 4 fuel oil and had a relatively low sulfur and ash content. Detailed fuel analysis results are shown in Appendix A.

Particulate chemical analyses are presented for Refinery A heater in Tables 4-12 and 4-13. There was insufficient sample (<20 mg/test) at Refinery B heater (from the 6 to 9 hour-long tests) to conduct tests other than gravimetric analyses.

The total heavy metals content of the front-half particulate sample residues was <1.4 percent by weight for Refinery A heater. Small amounts (0.02 to 0.85 percent by weight) of chromium, copper, nickel, and zinc were detected in the front-half samples residues during some of the tests. It is believed that most of the chromium and nickel found in the Test Run No. 1 sample originated from the stainless steel nozzle of the sampling train since these values were out of line with those determined in the other tests. Essentially no heavy metals were captured in the back-half catch samples. Some arsenic and mercury (0.39 and 0.12 ppm by weight, respectively) were detected in the composite fuel oil sample but not in the source samples. Since arsenic, mercury, and selenium are relatively volatile metals, it is expected that those compounds would not have been effectively captured by an EPA Method 5 particulate train.

Elemental analysis was performed on front- and back-half catches. The results are presented in Table 4-13.

Sulfate was the major component of both front-half and back-half sample residues. The sulfate content of the front-half samples averaged 53 percent (by weight) while the back-half catches averaged 68 percent. The data indicate no effect of excess air or fuel sulfur content on particulate sulfur content. The sulfur content of particulate collected during 100 percent gas-fired conditions was higher than expected based on the typical sulfur content of fuel gas. This could possibly be attributed to the flaking-off of stack sulfur particulate from previous oil-firing





TABLE 4-11

REFINERY "A" FUEL OIL COMPOSITE SAMPLE ANALYSIS

Analyte	Result
Ash, %	<0.01
Carbon, %	86.9
Hydrogen, %	12.3
Nitrogen, %	0.16
Oxygen, %	0.52
Sulfur, %	0.09
Metals, ppm by weight	
Arsenic	0.39
Barium	0.18
Cadmium	<0.04
Chromium	<0.04
Copper	0.10
Lead	<0.04
Mercury	0.12
Nickel	0.08
Selenium	0.19
Vanadium	0.04
Zinc	5.5

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REFINERY A

SOURCE 1

TABLE 4-12

MISCELLANEOUS ANALYTICAL RESULTS - METALS^{1,2}

TEST RUN NUMBER:	One		Four		Seven		Eight	
TEST DATE:	7/14/81		7/16/81		7/18/81		7/18/81	
FUEL FIRING RATIO, % GAS : % OIL:	100:0		94:6		46:54		48:52	
PERCENT O2 AT TEST LOCATION:	2.3		4.4		3.8		5.2	
RESIDUE CATCH FRACTION ANALYSIS:	Front- half	Back- half	Front- half	Back- half	Front- half	Back- half	Front- half	Back- half
PARTICULATE CATCH RATIO, % FRONT-HALF: BACK-HALF:	74:26		51:49		73:27		74:26	
HEAVY METALS CONTENT, % BY WEIGHT								
Cr	0.85	0.02	0.14	ND	0.09	ND	0.07	ND
Cu	0.03	ND	0.03	ND	ND	ND	0.02	ND
Ni	0.35	ND	ND	ND	0.04	ND	ND	ND
Zn	0.14	ND	0.12	ND	0.15	ND	0.15	ND

¹Note that barium, cadmium, lead and vanadium were not found in any of the samples.

²Key: ND = Not Detected (<0.01% by weight).

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REFINERY A SOURCE 1
STACK No. 1 (HEATER)

TABLE 4-13

SUMMARY OF ELEMENTAL AND ION CHROMATOGRAPHIC ANALYTICAL RESULTS

Test Run Number	Test Date	Fuel Firing Ratio % Gas : % O ₂	Residue Catch Fraction Analysis	Particulate Catch Ratio % Front-half : % Back-half	Parameter, % by Weight				
					Elemental Analysis (1)			Ion Chromatographic Analysis	
					C	H	N	Sulfate	Nitrate
Two	7/15/81	100:0/2.3	Front-half	61:39	<1	1.4	2.3	44	< 2
			Back-half		20	4.1	3.2	62	< 2
Five	7/16/81	91:9/4.3	Front-half	62:38	<1	2.7	1.4	60	< 2
			Back-half		10	3.1	1.4	73	< 2
Eleven	7/20/81	61:39/4.1	Front-half	54:46	<1	2.7	1.8	49	< 2
			Back-half		7.5	2.8	3.9	76	< 2
Thirteen	7/21/81	58:42/5.4	Front-half	51:49	4.6	3.3	3.1	57	< 2
			Back-half		1.8	3.1	4.4	61	< 2

(1) Elemental analysis results shown are questionable. Large errors due to working with small amounts of residue are probable.

operations. On the other hand, it might be attributed to artifact formation and weighing errors associated with small quantities of material analyzed. No nitrate particulate (<2 percent) was detected in any samples. The remaining chemical constituents of the particulate were not identified in this study.

4.3.2 Boilers

Metals content, sulfates, nitrates, extractable organics, and elemental analyses were determined. For comparison purposes, the chemical composition of test fuels is shown in Table 4-14. Detailed fuel analyses are presented in Appendix A.

No cadmium, silver, aluminum, calcium, magnesium, tin, or silica was detected in particulate samples from these test boilers (see Table 4-15). Small amounts (<1 percent) of barium, chromium, copper, lead, zinc, and potassium were found in some particulate residues. Greater amounts (up to 2 to 5 percent) of nickel, vanadium, sodium, and iron were measured in some particulate residues. Data from 100 percent oil tests were examined for a metals balance. Metals in the particulate residues were traceable to the fuel burned although a balance was not obtained in all cases. The metals contents of the process fuel gases were less than that of the fuel oils on a comparable Btu basis. As can be seen from Table 4-15, the front-half (filterable particulate) samples contained a greater percentage of metals than did the back-half (condensable particulate) catches in most instances.

The elemental analyses indicate that the carbon, hydrogen, and nitrogen content of the front-half samples is affected by excess air. As excess air was increased, the carbon, hydrogen, and nitrogen content was found to decrease. No such trend was evident for the back-half elemental analysis data. The back-half elemental analysis results for Refineries B and C are believed to contain large ($\pm$ 50 percent) errors. These errors are introduced from accumulative weighing errors on samples in the 1 to 10 mg range in large (100 to 150 mg) containers and from analyzer errors from working at or below the normal limit of quantitation of the instrument. See Table 4-16 for results.

Sulfate particulate was a significant (25 to 83 percent by weight) constituent of front- and back-half catch residues for both gas and oil firing. Excess air levels and the fuel composition had no effect on the wt percent sulfate in the particulate when firing fuel oil (see Table 4-17).

Nitrate was not detected in any sample (<0.1 percent by weight). Chloride analyses were performed on Refinery A particulate catch residues but none was found (<0.1 percent by weight). The remaining chemical constituents of the particulates were not identified.



TABLE 4-14

FUEL OIL COMPOSITE SAMPLES ANALYSIS FOR BOILER SOURCES

Analyte	Results		
	Refinery A	Refinery B	Refinery C
Ash, %	0.02	0.03	0.02
Carbon, %	87.0	86.8	86.8
Hydrogen, %	12.2	11.3	11.2
Nitrogen, %	0.30	0.22	0.18
Oxygen, %	0.26	0.87	0.61
Sulfur, %	0.22	0.73	1.19
Metals, ppm by weight			
Arsenic	<0.2	<0.2	<0.2
Barium	1.9	0.7	0.75
Cadmium	<0.5	<0.5	<0.5
Chromium	<0.5	0.7	<0.5
Copper	3.0	1.5	<0.5
Lead	<0.5	5.4	<0.5
Mercury	0.03	0.05	0.07
Nickel	21	11	11
Selenium	0.26	<0.1	0.49
Vanadium	<0.5	2.1	31
Zinc	10	6.7	1.7

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BOILER SOURCES

TABLE 4-15
MISCELLANEOUS ANALYTICAL RESULTS - METALS^{1,2}

Refinery/ Source	Test Run Number	Test Date	Fuel Firing Ratio % Gas : % Oil	Boiler % O ₂	Particulate Catch Fraction	Particulate Catch Ratio % FH : % BH	METALS CONTENT, % BY WEIGHT									
							Ba	Cr	Cu	Ni	Pb	V	Zn	K	Na	Fe
A/2	Seven	5/8/82	100:0	2.9	Front-half	52:48	ND	0.02	0.01	0.12	ND	0.07	0.16	ND	ND	1.1
	Ten	5/10/82	100:0	4.8	Front-half	35:65	0.48	ND	0.02	0.29	ND	0.18	0.34	ND	ND	0.88
	Thirteen	5/12/82	68:32	5.3	Front-half	63:37	0.53	0.02	0.09	3.1	ND	0.63	0.75	0.14	1.5	4.2
	Fifteen	5/13/82	75:25	6.5	Front-half	50:50	0.54	0.02	0.06	2.9	ND	0.61	0.69	0.34	2.3	4.7
	One	5/4/82	40:60	5.5	Front-half	53:47	0.27	0.05	0.06	3.2	ND	0.66	0.51	0.17	1.4	4.7
	Four	5/5/82	41:59	6.8	Front-half	58:42	0.36	0.02	0.05	3.6	ND	0.75	0.53	0.12	1.4	4.1
B/2	One	12/11/81	27:73	4.8	Front-half	90:10	0.29	0.04	0.07	0.86	0.51	0.96	0.39	---	---	---
	Four	12/13/81	31:69	6.7	Back-half	99:01	0.01	ND	0.14	ND	ND	ND	0.16	---	---	---
	Ten	12/17/81	0:100	4.9	Front-half	98:02	0.38	0.05	0.08	1.3	0.58	1.4	0.46	---	---	---
	Seven	12/15/81	0:100	6.5	Back-half	94:06	0.06	ND	0.36	ND	ND	ND	0.32	---	---	---
	Seven	12/15/81	0:100	6.5	Front-half	94:06	0.44	0.05	0.06	1.4	0.49	1.3	0.49	---	---	---
	Seven	12/15/81	0:100	6.5	Back-half	94:06	0.04	ND	0.24	ND	ND	ND	0.33	---	---	---
C/1	Seven	3/3/82	47:53	5.5	Front-half	98:02	0.34	0.05	0.07	0.14	0.50	1.3	0.48	---	---	---
	Ten	3/22/82	43:57	6.4	Back-half	99:01	0.02	ND	0.14	ND	ND	ND	0.24	---	---	---
	One	2/17/82	0:100	3.5	Front-half	76:24	0.02	0.02	0.01	0.63	0.02	1.4	0.06	---	---	---
	Four	2/22/82	0:100	5.4	Back-half	93:07	ND	ND	0.07	ND	ND	ND	0.11	---	---	---
	Four	2/22/82	0:100	5.4	Front-half	93:07	0.03	0.02	0.01	0.42	ND	1.7	0.04	---	---	---
	Four	2/22/82	0:100	5.4	Back-half	93:07	ND	ND	0.03	ND	ND	ND	0.06	---	---	---

¹Note that cadmium, silver, aluminum, calcium, magnesium, tin and silica were not found in any samples analyzed.

²key: ND = Not Detected (<0.01% by weight).
--- = Means parameter not run.

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BOILER SOURCES
TABLE 4-16
SUMMARY OF ELEMENTAL AND ION CHROMATOGRAPHIC ANALYTICAL RESULTS

Refinery	Test Run Number	Test Date	Fuel Firing Ratio % Gas : % Oil	Percent O2 Exiting Boiler (at test point)	Residue Catch Fraction Analysis	Particulate Catch Ratio % Front-half; % Back-half	PARAMETER, % BY WEIGHT						
							Analysis			Ion Chromatographic Analysis (1)			
							C	H	N	Sulfate	Nitrate	Chloride	
A	Eight	5/8/82	100:0	3.0 (7.0)	Front-half Back-half	32:68	24 13	6.9 4.2	0.9 1.8	41 49	ND ND	ND ND	
	Eleven	5/10/82	100:0	4.6 (8.7)	Front-half Back-half	27:73	23 12	7.2 4.0	6.9 1.2	42 32	ND ND	ND ND	
	Fourteen	5/12/82	70:30	5.1 (9.0)	Front-half Back-half	46:54	13 5.1	3.8 4.5	0.8 0.6	39 28	ND ND	ND ND	
	Sixteen	5/13/82	74:26	6.4 (9.8)	Front-half Back-half	42:58	8.5 3.3	2.4 3.8	0.1 1.0	32 43	ND ND	ND ND	
	Two	5/5/82	40:60	5.3 (8.6)	Front-half Back-half	59:41	6.9 3.1	2.0 4.1	0.4 0.9	31 46	ND ND	ND ND	
	Five	5/7/82	40:60	6.8 (10.0)	Front-half Back-half	48:52	5.9 2.4	2.3 4.2	0.3 0.8	30 46	ND ND	ND ND	
B	Two	12/12/81	33:67	--- (5.0)	Front-half Back-half	98:02	13 42	3.1 6.6	0.4 2.7	45 36	ND ND	ND ND	
	Five	12/14/81	27:73	--- (6.7)	Front-half Back-half	97:03	8.7 22	1.3 4.3	0.2 2.5	32 71	ND ND	ND ND	
	Eleven	12/17/81	0:100	--- (5.0)	Front-half Back-half	97:03	4.3 21	1.3 5.2	0.2 2.7	25 70	ND ND	ND ND	
	Eight	12/16/81	0:100	--- (6.7)	Front-half Back-half	97:03	3.1 43	2.1 6.5	0.3 2.8	41 62	ND ND	ND ND	
C	Eight	3/4/82	36:54	9.1 (5.4)	Front-half Back-half	88:12	25 4.2	2.3 3.6	0.4 0.1	35 75	ND ND	ND ND	
	Eleven	3/23/82	33:67	10.2 (6.6)	Front-half Back-half	98:02	6.9 27	2.4 5.4	0.2 7.1	26 49	ND ND	ND ND	
	Two	2/18/82	0:100	7.5 (4.0)	Front-half Back-half	95:05	15 21	2.0 3.4	0.2 2.6	60 40	ND ND	ND ND	
	Five	2/22/82	0:100	9.5 (5.4)	Front-half Back-half	80:20	5.0 0.8	2.6 1.2	0.1 0.1	60 83	ND ND	ND ND	

(1) ND = Not Detected (<0.1% by weight).

TABLE 4-17

PERCENT FUEL SULFUR CONVERTED TO PARTICULATE

Refinery/ Source	Fuel Oil Sulfur Content, %	% Oil Fired in Boiler	% O ₂ Exiting Boiler	Sulfate Particulate Emission Rate, as S, lb/hr	Fuel Sulfur Input to Boiler, lb/hr	% Fuel Sulfur Converted to Particulate
A/2	0.22	30	5.1	0.32	7.0	4.6
		26	6.4	0.46	5.6	8.2
		60	5.3	0.57	13	4.5
		60	6.8	0.76	13	5.9
B/2	0.73	67	5.0	2.2	148	1.5
		73	6.7	2.1	151	1.4
		100	5.0	1.9	218	0.9
		100	6.7	3.0	221	1.3
C/1	1.19	54	5.4	2.2	62	3.6
		67	6.6	1.0	64	1.6
		100	4.0	2.7	130	2.0
		100	5.4	4.0	99	4.0



Analytical results (Table 4-18) showed that a greater percentage of solvent extractable material was produced under gas-firing conditions than for oil. Back-half catches contained a higher proportion of solvent extractables than did the front-half samples. Excess air levels had no effect on the solvent extractable content of the particulate.

4.4 NO_x Emissions

The NO_x emission test results are presented in this section. The data are compared to EPA AP-42 emission factors in Tables 4-19 and 4-20. More detailed NO_x information is contained in Appendix A.

4.4.1 Heaters and Boilers

Survey findings for all sources are compared to AP-42 emission factors in Tables 4-19 and 4-20.

TABLE 4-19

COMPARISON OF MEASURED VS. AP-42 NO_x EMISSION FACTORS

Refinery/ Source	Fuel Firing Condition % Gas : % Oil	Percent of Predicted AP-42 Emission Factor ¹
A/1 (Heater)	95:5 53:47	16 35
B/1 (Heater)	100:0	100
A/2 (Boiler)	100:0 72:28 40:60	23 63 80
B/2 (Boiler)	30:70 0:100	31 32
C/1 (Boiler)	40:60 0:100	76 129

¹For mixed-fuel-firing conditions, measured values are compared to prorated AP-42 factors.

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BOILER SOURCES
TABLE 4-18
SOLVENT EXTRACTABLES RESULTS

Refinery	Test Run Number	Test Date	Fuel Firing Ratio % Gas : % Oil	Percent O ₂ Exiting Boiler (at test point)	Particulate Catch Ratio % Front-half:% Back-half	Residue Catch Fraction Analysis	Solvent Extractables, % by Weight ¹
A	Nine	5/9/82	100:0	2.9 (6.6)	35:65	Front-half Back-half	13 32
	Twelve	5/11/82	100:0	4.6 (8.5)	36:64	Front-half Back-half	53 88
	Three	5/5/82	59:41	5.5 (8.9)	55:45	Front-half Back-half	15 56
	Six	5/7/82	58:42	6.8 (10.0)	52:48	Front-half Back-half	12 31
B	Three	12/12/81	33:67	--- (5.1)	82:18	Front-half Back-half	0.8 7.1
	Six	12/14/81	27:73	--- (6.6)	93:07	Front-half Back-half	0.2 73
	Twelve	12/18/81	0:100	--- (4.7)	82:18	Front-half Back-half	0.8 77
	Nine	12/16/81	0:100	--- (6.6)	96:04	Front-half Back-half	0.8 61
C	Nine	3/4/82	48:52	5.4 (9.1)	89:11	Front-half Back-half	2.3 79
	Twelve	3/23/82	37:63	6.5 (9.7)	92:08	Front-half Back-half	0.9 73
	Three	2/19/82	0:100	3.5 (7.2)	71:29	Front-half Back-half	0.05 6.4
	Six	2/23/82	0:100	5.5 (9.6)	90:10	Front-half Back-half	0.09 17

¹Large weighing errors ($\pm 50\%$) may be present in results for those samples containing <10 mg of particulate.



The above data indicate that measured NO_x emissions are usually lower than predicted by AP-42. Data in Table 4-20 show that NO_x emissions increase with rising excess air levels and quantity of oil fired.

The reader is referred to AP-42 for a discussion of emissions dependency on the grade and composition of fuel, the type and size of boiler, the firing and loading practices used, and the level of equipment maintenance. Some of the differences between measured and predicted NO_x emissions shown in the above table are due to the way AP-42 categorizes heaters and boilers. This is especially true for Refinery/Source A/1 and A/2 when firing gas.

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TABLE 4-2.0
SUMMARY OF NO_x EMISSION FACTORS FROM PROCESS HEATERS AND BOILERS

Refinery	Source	Test Run Numbers	Fuel Firing Ratio % Gas : % Oil	Percent O ₂ at Test Location (at Boiler)	Heat Input Rate 10 ⁶ BTU/hr	Fuel Firing Rate		NO _x Emission Factors, as NO ₂			
						Gas	Oil	Measured 1b/10 ⁶ BTU (1b/10 ³ gal oil)	EPA ¹ 1b/10 ⁶ BTU	Measured 1b/10 ⁶ SCF gas (1b/10 ³ gal oil)	EPA ² 1b/10 ⁶ SCF gas (1b/10 ³ gal oil)
						10 ⁶ ft ³ /hr	10 ³ gph				
A	1 (Heater)	1,2,3	97:3	2.0	262	0.212	0.054	0.048	0.42	---	490:105
		4,5,6	93:7	4.0	257	0.200	0.125	0.088	0.42	---	476:105
		7,9,11,5	51:49	4.0	270	0.115	0.914	0.18	0.58	---	532:105
B	1 (Heater)	8,12,13	54:46	5.5	252	0.113	0.802	0.21	0.55	---	473:105
		4,5,6	100:0	4.1	15	0.015	---	0.148	0.117-0.225	151	120-230:---
		1,2,3	100:0	6.0	16	0.016	---	0.149	0.117-0.225	152	120-230:---
A	2 (Boiler)	7,8,9	100:0	6.8 (2.9)	199	0.181	---	0.11	0.55	110	602:---
		10,11,12	100:0	8.6 (4.7)	204	0.185	---	0.18	0.57	180	630:---
		13,14	69:31	8.9 (5.2)	196	0.123	0.411	0.31	0.48	---	576:583
B	2 (Boiler)	15,16	75:25	9.7 (6.5)	194	0.132	0.328	0.29	0.48	---	567:58
		1,2,3	40:60	8.7 (5.5)	182	0.066	0.737	0.33	0.42	---	518:58
		4,5,6	40:60	10.0 (6.8)	187	0.068	0.758	0.35	0.43	---	532:58
C	1 (Boiler)	1,2,3	31:69	5.0	549	0.114	2.53	0.19	0.62	---	630:105
		4,5,6	29:71	6.7	541	0.103	2.59	0.20	0.62	---	609:105
		10,11,12	0:100	4.9	560	---	3.75	0.22	0.70	(33)	---
C	1 (Boiler)	7,8,9	0:100	6.6	567	---	3.80	0.23	0.70	(35)	---
		10,11,12	43:57	9.1 (5.4)	172	0.072	0.653	0.24	0.35	---	525:354
		1,2,3	37:63	10.1 (6.5)	160	0.057	0.674	0.26	0.31	---	469:35
C	1 (Boiler)	4,5,6	0:100	7.3 (3.7)	203	---	1.36	0.27	0.23	(40)	---
		1,2,3	0:100	9.6 (5.4)	155	---	1.04	0.34	0.23	(50)	---
		4,5,6	0:100	9.6 (5.4)	155	---	1.04	0.34	0.23	(50)	---

¹Calculated using the following equation:

$$1b\ NO_x\ 10^6\ BTU = \left(\frac{\text{Gas Emission}}{\text{(Gas Fired Duty)}} (AP-42\ Factor) + \left(\frac{\text{Oil Emission}}{\text{(Oil Fired Duty)}} (AP-42\ Factor) \right) \right)$$

²Values obtained from AP-42 Third Edition, April 1981, assuming all units to be non-tangentially fired. Gas emission factors were calculated by correcting the maximum gross load boiler emission factor for units >100 x 10⁶ BTU/hr (= 700 lb NO₂/10⁶ BTU) with a load reduction coefficient determined from actual load conditions.

³Oil emission factor based on Refinery A, Source 2 fuel composition of N content = 0.30 wt % and 1b NO_x/10³ gal oil = 22 + 400N² = 58

⁴Oil emission factor based on Refinery C, Source 1 fuel composition of N content = 0.18 wt % and 1b NO_x/10³ gal oil = 22 + 400N² = 35

⁵Run 10 was discounted because of process swings during test.

APPENDIX A

DETAILED TEST DATA AND TEST RESULT SUMMARIES



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