

EPA-650/2-74-111

OCTOBER 1974

Environmental Protection Technology Series

PRIMARY COPPER
SMELTING 7.3
AP-42 Section 7.3
Reference Number
#12

pg 41 & 22

AP 42
5th ed.
Section 12.3
#12

Note: This is a reference cited in AP 42, *Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources*. AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/
The file name refers to the reference number, the AP42 chapter and section. The file name "ref02_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

MEASUREMENT OF SULFUR DIOXIDE, PARTICULATE, AND TRACE ELEMENTS IN COPPER SMELTER CONVERTER AND ROASTER/REVERBERATORY GAS STREAMS



Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

EPA-650/2-74-111

**MEASUREMENT OF SULFUR DIOXIDE,
PARTICULATE, AND TRACE ELEMENTS
IN COPPER SMELTER CONVERTER
AND ROASTER/REVERBERATORY
GAS STREAMS**

by

Robert M. Statnick

Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

ROAP No. 21ADM-012
Program Element No. 1AB012

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N. C. 27711

October 1974

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

CONTENTS

	<u>Page</u>
List of Figures	v
List of Tables	vii
Acknowledgments	viii
<u>Sections</u>	
I Introduction	1
Background	1
Conclusions	4
Recommendations	5
Conversion Factors	6
References	7
II Plant Operating Data	8
Converter Operations	8
Roaster and Reverberatory Furnace Operation	10
III Sulfur Oxide Tests	15
Experimental	15
Results	17
Discussion	20
References	24
IV Particulate Tests	25
Experimental--Particulate Mass	25
Particulate Control Equipment	25
Sampling Port Locations	25
Sampling Methods	32
Analytical Procedures	37

Contents (Cont.)

	<u>Page</u>
Sampling Approach	38
Results--Particulate Mass	38
Converter ESP Inlet	38
Converter ESP Outlet	42
Experimental--Particulate Size	43
Results--Particulate Size	48
Discussion	48
Converter ESP Tests	48
R&R ESP Tests	60
References	64
V Elemental Composition	65
Experimental	65
Results	66
Discussion	69
References	71
Appendix A--Sampling and Analysis of Mercury Vapor in Industrial Streams Containing Sulfur Dioxide	A-1
Introduction	A-2
Experimental Methods	A-3
Field Sampling	A-10
Results	A-13
Conclusions and Summary	A-13

FIGURES

<u>No.</u>		<u>Page</u>
1	Schematic of Tacoma Smelter	9
2	Sampling Log for Converter Runs 1A (Inlet) and 1B (Outlet)	11
3	Sampling Log for Converter Runs 2A (Inlet) and 2B (Outlet)	12
4	Sampling Log for R&R Runs 3 and 4	13
5	SO ₃ /SO ₂ Sampling Apparatus	16
6	Sampling Location at Water Spray Chamber Inlet	18
7	Particulate Sampling Sites	26
8	Sampling Point Diagram--R&R Furnace ESP Outlet	28
9	Sampling Point Diagram--Converter ESP Outlet	30
10	Sampling Point Diagram--Converter ESP Inlet	33
11	Brink Sampling Train	44
12	Andersen Sampling Train	46
13	Cumulative Percent of Particles Less than Given Size--Converter Inlet	49
14	Cumulative Percent of Particles Less than Given Size--Converter Outlet	50
15	Cumulative Percent of Particles Less than Given Size--R&R Inlet	51
16	Cumulative Percent of Particles Less than Given Size--R&R Outlet	52
17	Differential Size Distribution--Converter ESP Inlet	53
18	Differential Size Distribution--Converter ESP Outlet	53

Figures (Cont.)

<u>No.</u>		<u>Page</u>
19	Differential Size Distribution--Converter ESP Inlet and Outlet	55
20	Converter ESP Efficiency as a Function of Particle Geometric Diameter	55
21	Differential Size Distribution--R&R ESP Inlet	59
22	Differential Size Distribution--R&R ESP Outlet	59
23	Fractional Collection Efficiency of R&R ESP's	60

TABLES

<u>No.</u>		<u>Page</u>
1	Log of Samples Acquired	3
2	Average Converter ESP Operating Variables	14
3	Average R&R ESP Operating Variables	14
4	Measured Concentrations of SO _x at Standard Conditions	19
5	SO ₂ Emission Levels	22
6	Effect of Acid Plant on SO _x Emission Concentrations	22
7	Summary of ASARCO Particulate Mass Measurements	31
8	ASARCO Particulate Mass Data	39
9	Brink Impactor Operating Conditions--ESP Inlet	47
10	Andersen Mark III Operating Conditions--ESP Outlet	47
11	Converter Particulate Mass Collection Efficiency	57
12	Representative Precipitation Rates	57
13	Chemical Composition of Solids and Residues from the Particulate Mass Sampling Train, % by Weight	64
14	ASARCO Concentration of Vapor-Phase Mercury in Flue Gas	65
15	Elemental Collection Efficiencies of Converter ESP	67
16	Mass Emission Rate of Selected Elements	67

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Messrs. R. Steiber, W. Fowler, and R. Ogan for assisting in the performance of the measurements; and to Monsanto Research Corporation and Research Triangle Institute for performing several of the sampling and analysis tasks.

The author is especially indebted to Mr. J. A. Dorsey who encouraged and supported this effort; and a special thank you to Miss C. Atkinson for tolerating many rewritings.

SECTION I

INTRODUCTION

BACKGROUND

The primary non-ferrous smelting industry is a significant source of sulfur oxides, particulate, and chemical species which could be classified as hazardous (for example, Pb, Zn, or As emissions). Smelters in the continental United States emit 1,920,000¹ short tons* of sulfur to the atmosphere annually. Over 97 percent of the sulfur oxide emissions are due to smelting operations west of the Mississippi River. The primary non-ferrous smelting industry emits an estimated 243,000 tons² of particulate/year. (It is the ninth major source of particulate pollution.) Due to a paucity of data, no reliable estimates of the yearly fine particulate emissions can be made.³ An EPA sponsored program to determine the elemental distribution of ores (or concentrates) smelted in the United States reveals⁴ a wide distribution of abundances of the analyzed elements. As in the case of fine particulates, very sketchy data exists on the elemental abundances in the emitted particulate.

To acquire data useful for developing a viable control program, the Control Systems Laboratory (CSL) sought access to American smelters. In June 1973, EPA Region X's OR&D** office sought the

*Although EPA's policy is to use the metric system in all its documentation, certain non-metric units are used in this report both for convenience and to reflect actual test conditions. Readers more familiar with metric units may use the conversion factors provided on page 6.

**Office of Research and Development.

assistance of CSL's Process Measurements Section to obtain data on emissions and control efficiencies from the American Smelting and Refining Company's (ASARCO) Tacoma, Washington, smelter.

A program to evaluate the efficacy of the existing control equipment--both particulate and sulfur oxides--was developed. The test program was conducted September 25-27, 1973, by personnel from the Process Measurements Section and Monsanto Research Corporation.

A log of the samples acquired, date of acquisition, frequency of acquisition, and sampling location is given in Table 1.

The particulate data presented in this report is based on the dry filterable solids. Previous studies⁵ have shown that when SO₂ is present in the gas stream sampled, the Greenburg-Smith impinger catch is principally (> 90 percent) sulfuric acid. However, the analysis for the elemental abundances in the emitted stream included both the dry filterable solids and the impinger catch. As will be shown later in the report, the observed control efficiencies for the dry filterable solids and the observed control efficiency of the specific elements are nearly identical, which supports the concept of using only the cyclone-filter catch in assessing the particulate mass emission rate.

The data presented in this report is of significant value for assessing the control efficiencies and the emission levels of

Table 1. LOG OF SAMPLES ACQUIRED

Date	Frequency	Type of sample	Location
9/25/73	3	SO ₂	Converter ESP inlet
	3	Hg (vapor)	Converter ESP outlet
	3	Brink impactor	Converter ESP inlet
	3	Andersen impactor	Converter ESP outlet
9/26/73	2	Particle mass loading	Converter ESP inlet
	2	Particle mass loading	Converter ESP outlet
	3	Brink impactor	R&R inlet
	3	Andersen impactor	R&R outlet
	3	SO ₂	R&R ESP outlet
	3	Hg (vapor)	R&R ESP outlet
	3	SO ₂	Acid plant inlet
9/27/73	3	SO ₂	Acid plant outlet
	2	Particle mass loading	R&R outlet

the processes sampled. The data is technically valid and may be used for this purpose. At times, strict adherence to the varied technicalities of compliance testing was not possible; at other times, it was neglected because of the limited resources and the goals of the project. The data should be considered carefully and utilized within the above mentioned limitations.

CONCLUSIONS

Based on the data collected, the mass emission rates of sulfur dioxide, particulate, and selected elements were determined. The size distribution data was used to determine the fractional size collection efficiency of the particulate control equipment. The analysis of these results led to the following conclusions:

1. The sulfur dioxide emission rates from the R&R and converter effluent streams are 518 lb/min and 587 lb/min, respectively. The R&R flue represents 47 percent of the total sulfur dioxide mass emission rate.
2. The efficiency of the acid plant for the control of sulfur dioxide was 96.8 percent which is comparable to the efficiency of other acid plants tested in the same application.
3. The mass collection efficiency of the converter electrostatic precipitator (ESP) for dry filterable solids was 95 percent.
4. The ESP's appear to have a minimum collection efficiency for dry filterable solids between 0.8 and 1.2 μm . Negative collection efficiencies below 0.8 μm were noted on both streams and

could arise from condensation, non-representative sampling locations, or ESP operations. Insufficient data is available to differentiate between these possibilities.

5. Analyses of the emitted particulate for selected elements gave mass emission rates (lb/hr) of: arsenic (58.05); lead (24.65); cadmium (1.32); zinc (15.7); chromium (0.065); and copper (4.825). The control efficiency for the elements analyzed ranged between 90 and 98 percent which is comparable to the overall mass collection efficiency.

RECOMMENDATIONS

Two basic recommendations resulted from the studies conducted during this program.

1. It is recommended that quantitative information be developed for fugitive emissions from the smelting process. These low-level, low-velocity emissions could contribute significantly to As and Pb concentrations in local ambient air. Several attempts have been made, but each was unsuccessful.

2. A program of abatement is recommended based on sulfur oxides and particulate control for the roaster/reverberatory flue. Such a program would achieve a large reduction in emissions from these smelting process operations, because the R&R flue represents approximately 50 percent of the sulfur dioxide emissions and about 75 percent of the analyzed elemental emissions.

CONVERSION FACTORS

Although it is EPA's policy to use metric units for all quantitative descriptions, certain non-metric units are used in this report for convenience. Readers more familiar with the metric system, may use the following factors to convert to that system.

<u>Multiply non-metric</u>	<u>By</u>	<u>To convert to metric</u>
cu ft	28.32	liter
°F	$5/9 (\text{°F}-32)$	°C
ft	30.48	cm
gr	0.06	g
in.	2.54	cm
lb	0.45	kg
sq ft	0.09	sq m
sq in.	6.45	sq cm
ton (short)	0.91	ton
	907.18	kg

REFERENCES

1. Systems Study for Control of Emissions, Primary Nonferrous Smelting Industry, Vol. I, Arthur G. McKee & Company, NTIS No. PB184-884. June 1969. p. II-1.
2. Particulate Pollutant System Study, Vol. I, Mass Emission, Midwest Research Institute, NTIS No. PB 203-128. May 1971. pp. 5, 133.
3. Particulate Pollutant System Study, Vol. II, Fine Particle Emissions, Midwest Research Institute, NTIS No. PB 203-521. August 1971. p. 113.
4. vonLehmden, D. Private communication. September 1972.
5. GASP-Tacoma Area. Newsletter. February 1973. Dr. S. Milhan, State of Washington Health Services Department.

SECTION II

PLANT OPERATING DATA

A solids and effluent flow diagram of the Tacoma Smelter is given in Figure 1. The major gas effluent streams are depicted by the solid lines and the flow of the copper-containing mineral is shown by the dashed lines. The emission streams indicated in the diagram are those which vent into either of two effluent ducts which feed into the 535-foot-tall brick stack. Two oil burners are constantly firing into the base of the stack to raise the effluent gas temperature.

The converters and roaster/reverberatory furnaces at the ASARCO plant were in operation only during the evening and night hours. Careful attention was paid to the meteorological conditions: smelting would begin only when the emissions from the stack would rise and not settle over populated areas.

CONVERTER OPERATIONS

The emissions from the four converters at the plant are controlled by an electrostatic precipitator (ESP). The ESP had 159,450 square feet of surface area and processed approximately 130,000 scfm of flue gas. The ESP parameters are given in Table 2.

A series of four lights on the roof of the building housing the inlet to the ESP and another group of lights on the building over the breeching indicated which units were in operation.

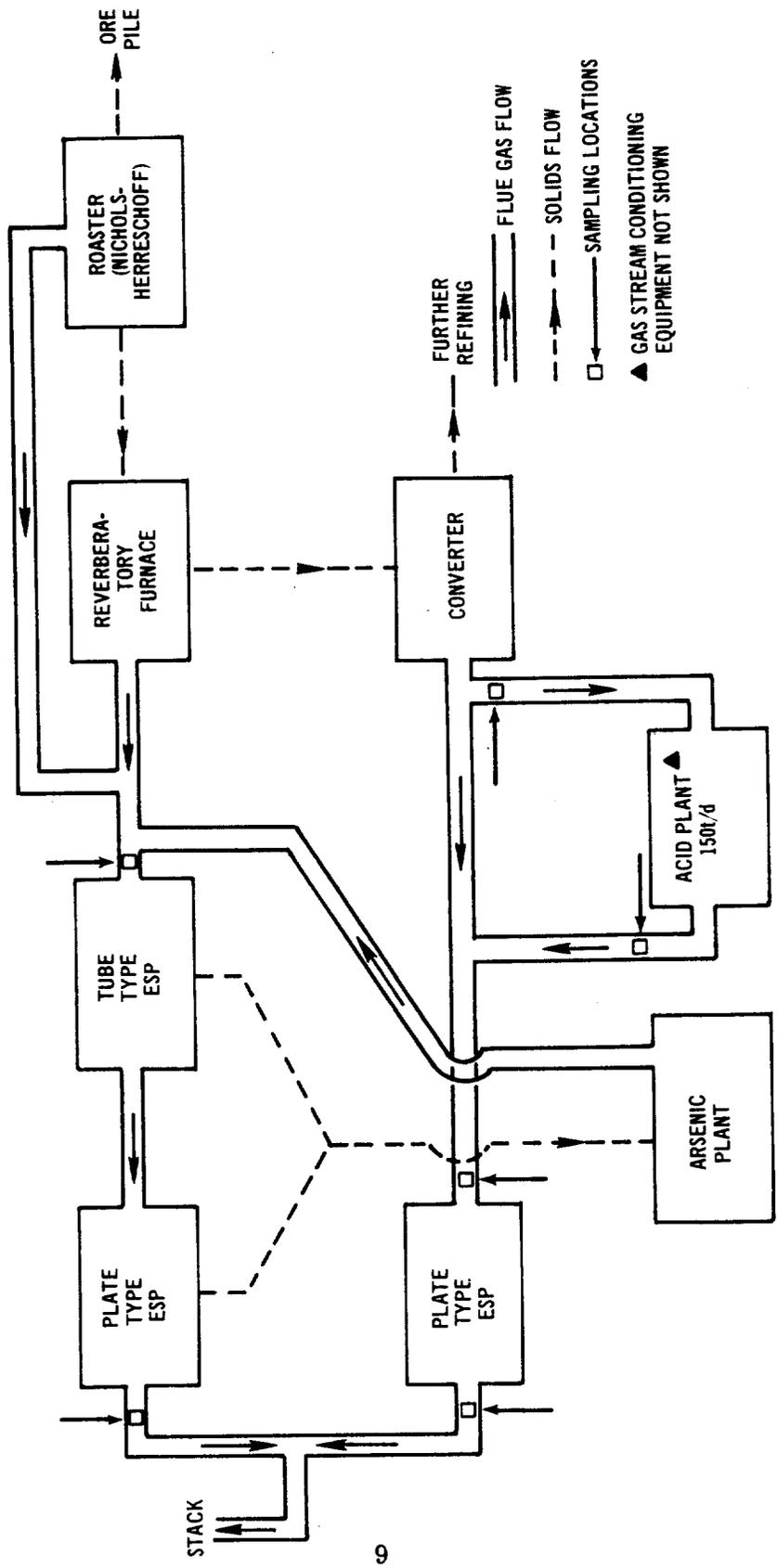


Figure 1. Schematic of Tacoma smelter.

During each of the sampling periods, the information as to whether finish or slagging operations were being conducted was supplied by plant personnel. In general, only two of the four converters operated at any given time.

Once the sampling run began, a notation was made of how long each lamp was lit. Sampling would continue as long as at least one lamp remained illuminated. Sampling was stopped when all lamps were extinguished. Figure 2 is the sampling log of runs 1A and 1B, showing the sampling times and which converters were in operation during the sampling run. Figure 3 is the same type of sampling log for runs 2A and 2B. As can be noted on the sampling logs, sampling was stopped about 1 minute after the lamps were turned off. This delay was caused by the distance from the sampling sites to the lamp observation location.

ROASTER AND REVERBERATORY FURNACE OPERATION

The R&R flue gas was treated by dry pipe type ESP and then by parallel type ESP's. The ESP's treat a nominal 475,000 scfm flue gas. The pipe ESP's had 57,500 sq ft of surface area and the plant ESP's had 174,240 sq ft. The ESP parameters are shown in Table 3.

Under normal conditions at least six of the plant's eight roasters would be in operation at any given time. Sampling was therefore started as soon as word was received from the plant personnel that at least six of the units were on stream. Figure 4 is a log of R&R operations during sampling runs 3 and 4.

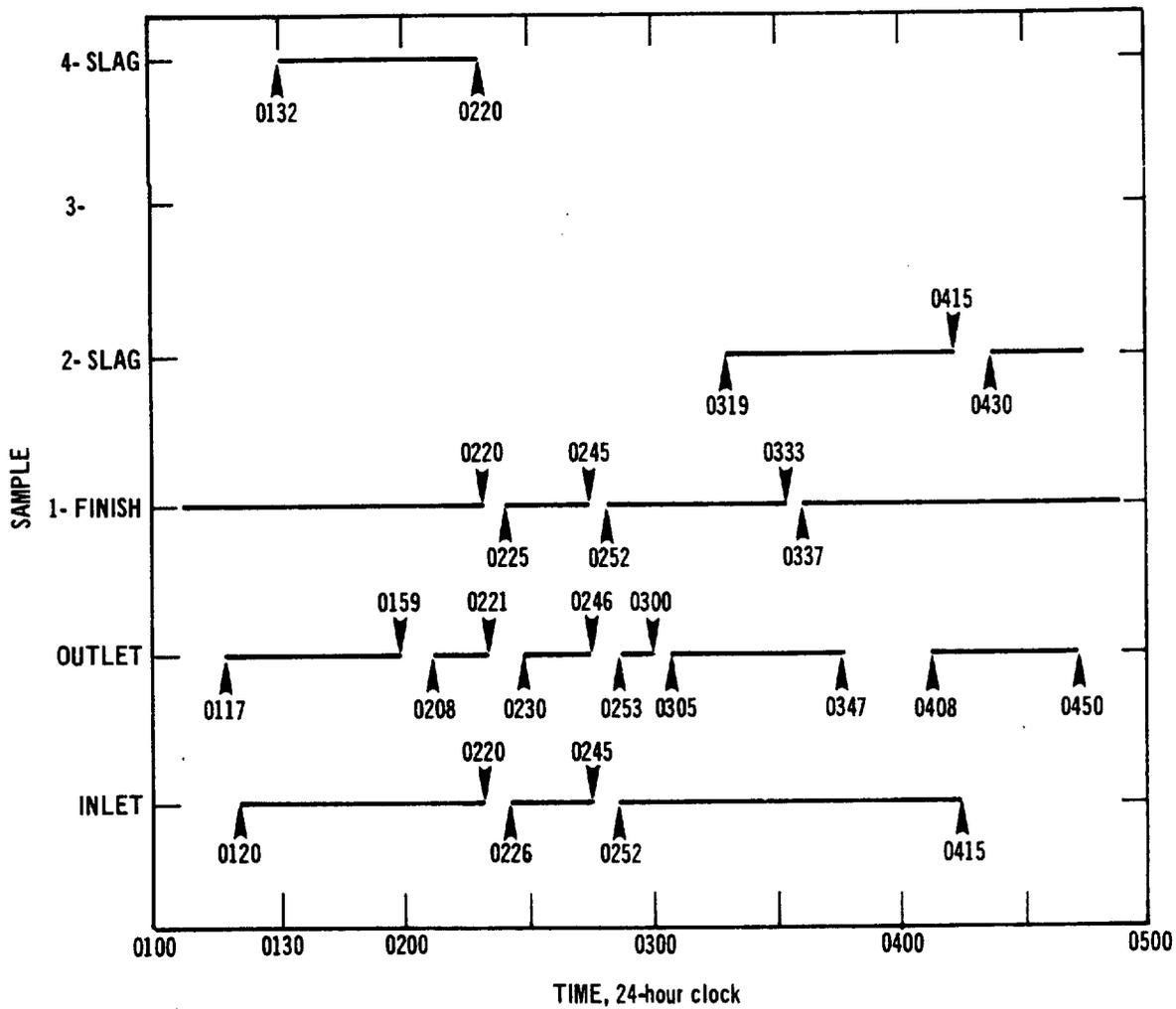


Figure 2. Sampling log for runs 1A (inlet) and 1B (outlet).

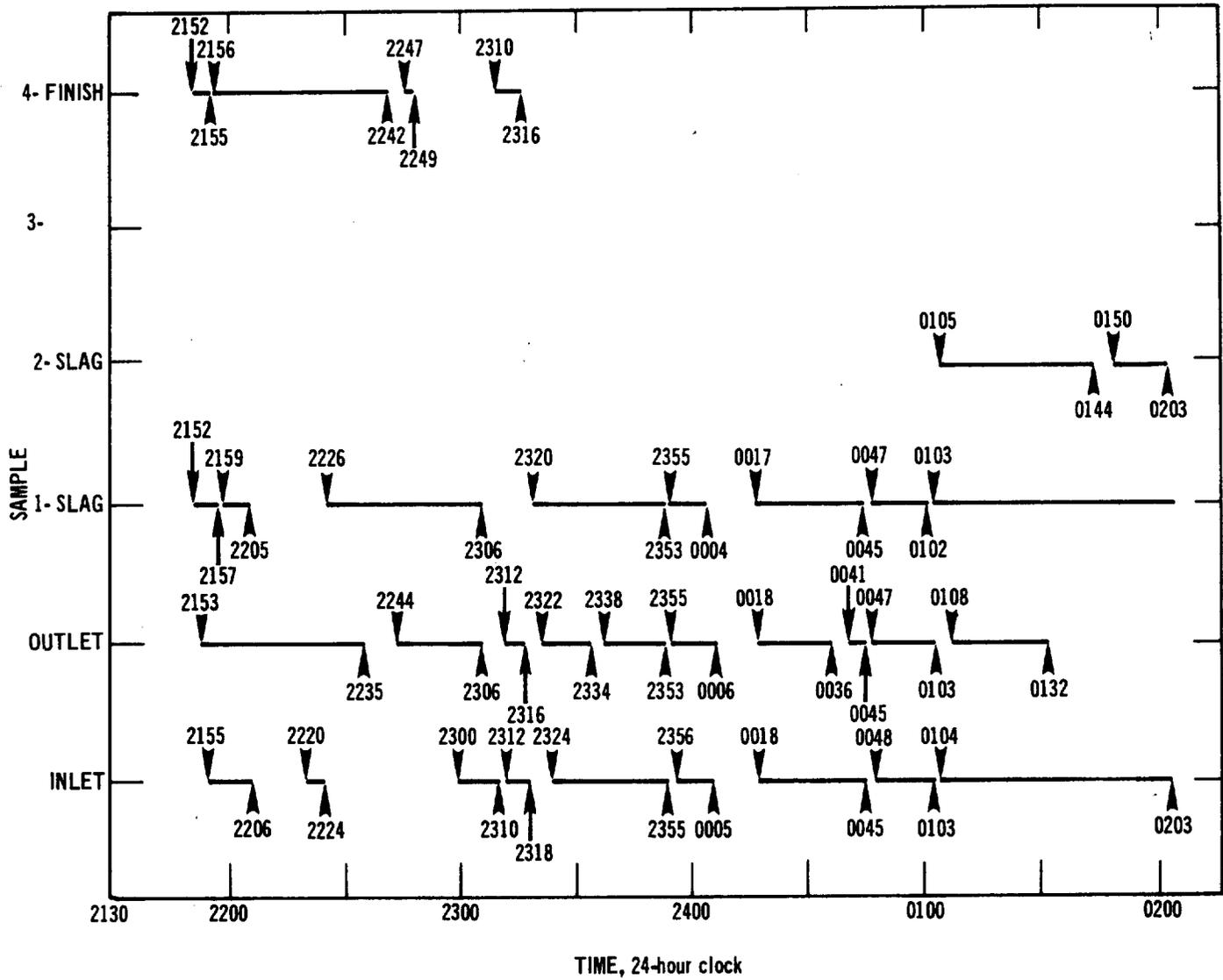


Figure 3. Sampling log for runs 2A (inlet) and 2B (outlet).

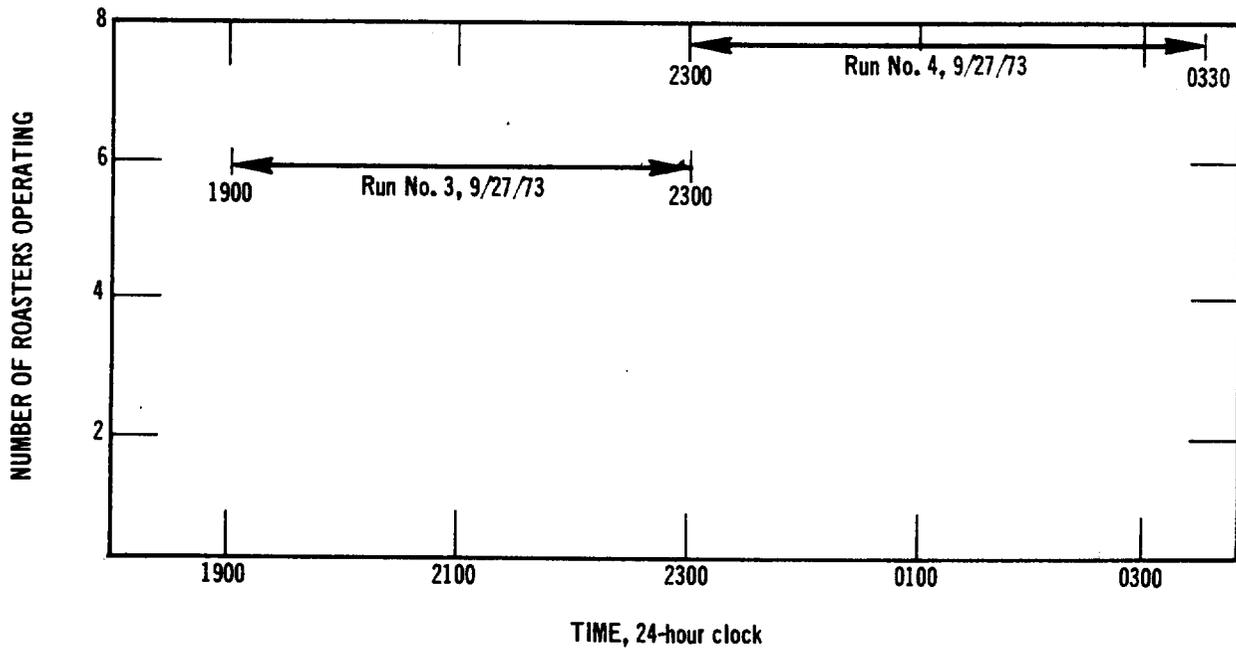


Figure 4. Sampling log for R & R runs 3 and 4.

Table 2. AVERAGE CONVERTER ESP OPERATING VARIABLES

Variable, cfm/sq ft	0.81
Variable, μ a/sq ft	7.8
Variable, spark rate/minute	110
Temperature, ° F	
Inlet	253
Outlet	245.5

Table 3. AVERAGE R&R ESP OPERATING VARIABLES

	Pipe	Plate
Variable, cfm/sq ft	8.25	2.72
Variable, μ a/sq ft	12.5	8.2
Variable, spark rate	0	14.3
Temperature, ° F		
Inlet	NA	--
Outlet	--	178.5

SECTION III
SULFUR OXIDE TESTS

EXPERIMENTAL

The primary concern of EPA Region X centered upon the emission of sulfur dioxide. It was decided to utilize a slightly modified Shell procedure because the sampling team had extensive experience with this method. Since the method requires that the first absorber be filled with 80 percent isopropanol (IPA), it was decided to analyze the IPA solution for sulfate rather than discard it although this analysis would provide an estimate of the acid mist emission since isokinetic sampling was not employed. Identical sulfur oxide sampling procedures were employed at all sampling locations.

The sampling apparatus, shown in Figure 5, differs from that used in the Shell procedure primarily in that a fine frit was not used between the first and second absorbers. Data submitted in the Walden Research Corp. report¹ point out the equivalency, if not superiority, of Lamp Sulfur Absorbers² to midget impingers as gas contactors over a wide range of sampling rates.

The collection media used are identical to those in the Shell method and in the Federal Register³ (80 percent IPA for SO₃ and 3 percent H₂O₂ for SO₂). Further details of the sampling apparatus are obtainable from various other sources.¹

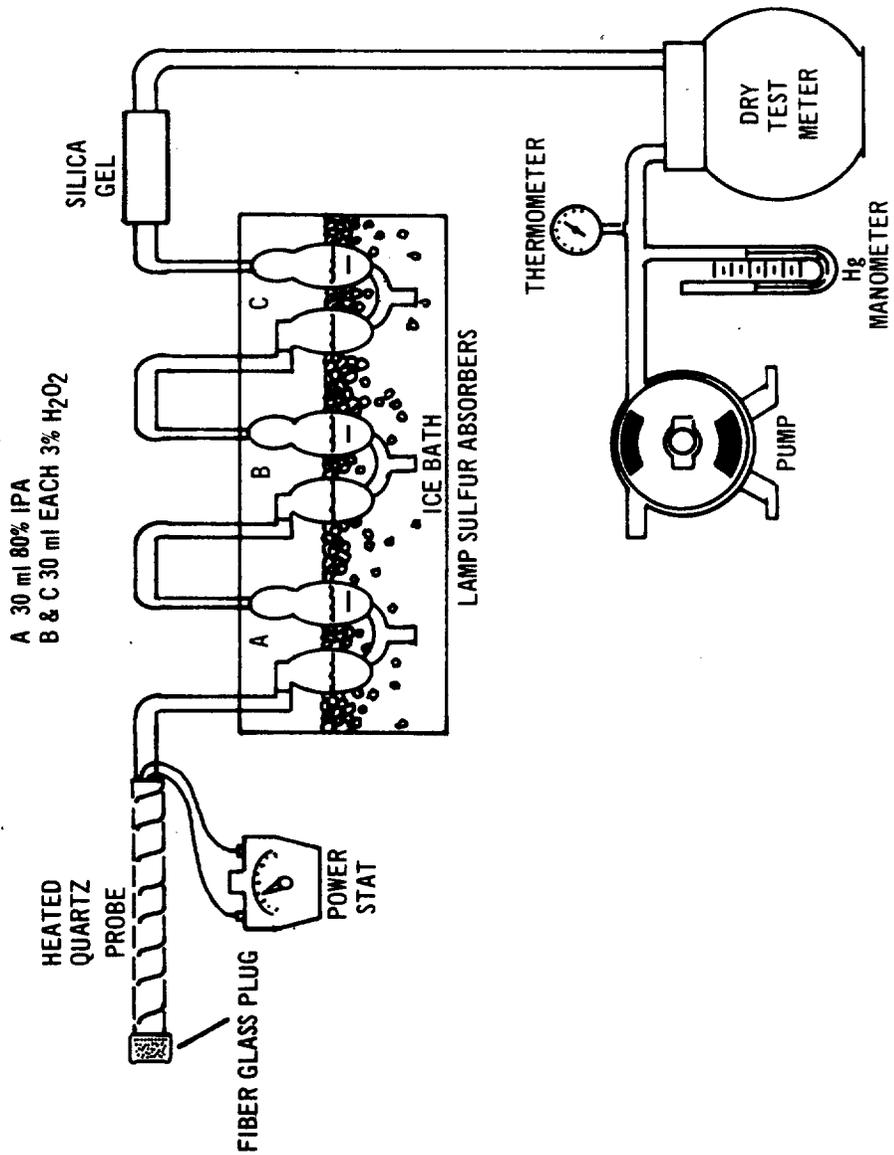


Figure 5. SO₃/SO₂ sampling apparatus.

The sampling location selected on the converter flue duct was preceded by a 200-300 foot run of brick/concrete duct. A single-point sample was acquired from a depth of 6 feet from the top of the duct (11.5 feet high x 24 feet wide), at the inlet to the electrostatic precipitator.

The sulfur dioxide sample from the roaster/reverberatory (R&R) flue was acquired after the electrostatic precipitator and the sample was again acquired at a depth of 6 feet from the top of the duct (16 feet high x 20 feet wide). The sampling location for the R&R flue was preceded by a straight run of about 100 feet of duct work.

Sulfur oxide samples were also acquired from the inlet and outlet of a 150-ton/day Monsanto-designed H₂SO₄ acid plant. The inlet sample was acquired just prior to the acid plant water-conditioning sprays. The spray chamber was about 12 feet wide x 16 feet high, with the sampling point approximately 2-1/2 feet from the top of the duct. (See Figure 6.) The acid plant outlet sample was acquired from the midpoint of a 36-inch diameter fiberglass-reinforced plastic (FRP) duct.

The samples collected were transferred to Teflon bottles for shipment to NERC-RTP. The samples were titrated using barium perchlorate ion to the Thorin endpoint per Federal Register Method 6.³

RESULTS

The results of the SO₂ tests are given in Table 4. The wide range of observed converter SO₂ values can be ascribed to

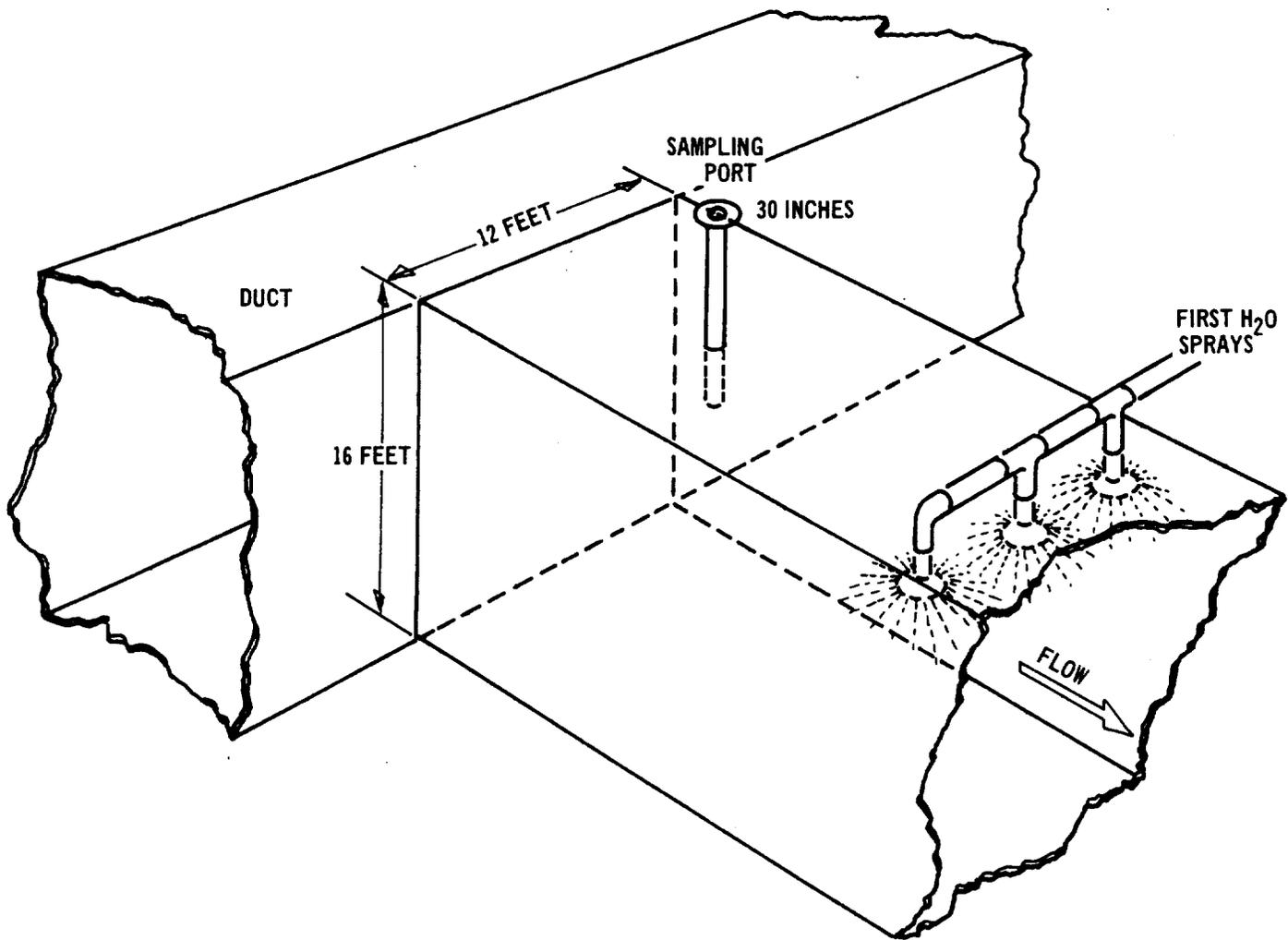


Figure 6. Sampling location at water spray chamber inlet.

Table 4. MEASURED CONCENTRATIONS OF SO_x AT STANDARD CONDITIONS

Location	Date	Time (p.m.)	SO ₂ ppm	SO ₃ ^a ppm	Comments
Converter stream	9/25/73	8:25	13,856	66.3	Taken prior to ESP
		8:50	37,871	36.7	Taken prior to ESP
		9:15	25,766	14.4	Taken prior to ESP
	9/27/73	6:50	35,909	83.2	Smell of SO ₂ when bottle opened; taken at acid plant inlet
		7:08	<u>40,295</u>	67.5	Smell of SO ₂ when bottle opened; taken at acid plant
		7:25	<u>27,720</u>	<u>108.7</u>	Smell of SO ₂ when bottle opened; taken at acid plant inlet
Average		30,236	62.8		
Reverberatory stream	9/26/73	8:40	5,170.9	11.9	Taken after ESP
		9:10	5,609.0	20.6	Taken after ESP
		9:25	<u>5,740.0</u>	<u>4.1</u>	Taken after ESP
	Average		5,506.6	12.2	
Acid plant outlet	9/27/73	7:45	1,849.7	12.8	
		8:00	677.9	8.4	
		8:10	<u>794.6</u>	<u>6.5</u>	
Average		1,107.4	9.2		

^aEstimated gaseous SO₃.

the cyclic nature of the operations of the converter pot line. The cyclic nature of the blowing operation leads to highly variable SO₂ levels which are evident in the short sampling duration manual test results. These data are consistent with reported typical converter acid plant inlet SO₂ values which range between 1.2 and 4.5 percent SO₂, v/v.⁴

The results of the analysis of the 80 percent IPA solution are also given in Table 4. This information is given as an estimate of the magnitude of the gaseous SO₃ concentration.

Particulate control on the converter and R&R flues is achieved by the use of electrostatic precipitators. The high resistivity of the metal oxide fume requires the conditioning of the particulates with H₂SO₄. This acid addition contributes to the SO₃ level as well as direct reaction with particulate to form sulfates.⁵ (PbSO₄ was identified in the dust collected by the converter ESP.) The SO₃ values determined during testing may be higher than in other locations.

DISCUSSION

SO_x associated with the R&R streams are emitted directly to the atmosphere. At the present time, no SO_x control technology is being utilized to abate the "weak" SO_x streams. (Interrupted plant operations are used to achieve ambient air standards.) The mass emission rate at typical flow rates (approximately 480,000 scfm for the R&R stream) is given in Table 5.

The Tacoma smelter converter duct is equipped with an acid plant which has a throughput capacity equivalent to 18 percent of

the total converter flue gas rate (approximately 23,000 scfm). The efficiency of the Monsanto acid plant for SO₂ is given in Table 6. The effluent values are similar to those observed at National Zinc (Bartlesville, Oklahoma)⁶ and Kennecott Copper (Garfield, Utah).⁶

The impact of operation of the acid plant on the SO_x mass emission rate is given in Table 5. The overall emissions associated with the smelting operation are almost evenly split between the R&R stream (518 lb/min) and the converter stream (587 lb/min). It is to be noted that ASARCO is currently installing the dimethylaniline process to handle the remainder of the converter effluent. The concentrated SO₂ stream will be sent to a liquid SO₂ plant. SO₂ removal efficiencies of 95-98.75 percent have been reported.⁷

During the author's field visit, the acid plant experienced an "upset condition" (acid plant taken off-line). During the upset, gas samples were acquired at the converter ESP inlet. The converter emissions, at a nominal flow rate of 130,000 scfm and with the acid plant off-line, are given in Table 5. Since no information could be obtained on the frequency of upsets, the real impact of the acid plant's being off-line on an annual basis cannot be evaluated.

The requirement for adequate SO₂ control technology applicable to a reverberatory or an R&R stream is seen if overall removal of SO_x associated with copper smelter operations is to

Table 5. SO₂ EMISSION LEVELS

Source	SO ₂ lb/min.
Roaster/reverberatory flue	518.01
Converter flue, acid plant on-line	587 ^a
Converter flue, acid plant off-line	715.97

^aEstimated

Table 6. EFFECT OF ACID PLANT ON SO_x EMISSION CONCENTRATIONS

Inlet SO _x , %	Outlet SO _x , %	Average ^a % removal
3.59	0.18	
4.03	0.07	
<u>2.77</u>	<u>0.08</u>	
Avg. 3.46	0.11	96.7

^aThe inlet and the outlet samples were not taken simultaneously. Therefore, only an average removal efficiency is reported.

achieve a level >80 percent. A comparison of the distribution of the SO_x contained in the converter stream and in the R&R stream shows that at normal flow rates the R&R stream contains 47 percent of all SO_x released by the two processes. In practical terms then, SO_x emissions associated with the smelting process cannot be reduced by more than approximately 60 percent unless control is utilized on both effluent streams.

An additional requirement associated with this control technology is the need for separation of entrained dust; for example, the Tacoma smelter processes the collected particulate to produce As₂O₃ as a recoverable by-product. Other smelters process collected particulate matter to yield such valuable metals as cadmium, lead, and indium. The cost of employing such processes as wet limestone scrubbing would have to include additional costs for processing large amounts of unreactive solids or penalties for not processing collected particulate for by-product values.

REFERENCES

1. Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels, Vol. I, Walden Research Corp., NTIS No. PB 209-267, June 1971.
2. Purchased from Ace Glass, Inc., 1430 N.W. Boulevard, Vineland, N. J. 08360.
3. Federal Register, 36, 247, Method 6 (p. 24893-95). December 23, 1971.
4. Godsey, E., ASARCO. Personal communication.
5. Wyatt, S. Miss, ESED, U.S. Environmental Protection Agency, Research Triangle Park, N. C. Personal communication.
6. Ajax, R. J., ESED/ETB, U.S. Environmental Protection Agency, Research Triangle Park, N. C. Personal communication. October 3, 1972.
7. Henderson, J. M., ASARCO. Response to Questionnaire Regarding DMA Scrubbing System. March 15, 1973.

SECTION IV
PARTICULATE TESTS

EXPERIMENTAL--PARTICULATE MASS

Particulate Control Equipment

The ducted emissions from the copper smelter are controlled by two ESP systems: one, a parallel plate ESP, controls the emissions from the converter pot line; the other, consisting of dry tube and parallel plate ESP's with effluent gas flowing through them in series, controls the emissions from the R&R furnaces. The ESP's are connected by individual breechings to a single brick stack, 535 feet tall. A diagram of the ducts sampled for particulate matter is shown in Figure 7.

Sampling Port Locations

All sampling at this plant employed existing sampling ports. In all cases the ports were not located to meet Method 1 criteria. However, no ideal alternate locations for sampling ports were available consistent with program goals and resources. The duct and port locations at each site are described below.

Roaster and Reverberatory ESP Outlet. This outlet was sampled from a series of ten sampling ports installed in the top of the duct. The ports were located about 100 feet from the exit end of the ESP and 3-4 feet before a bend in the breeching to the stack. The duct at this point was 20 feet wide and 16 feet high. The sampling port location, while not meeting Method 1 criteria, was the only site available with existing ports. The

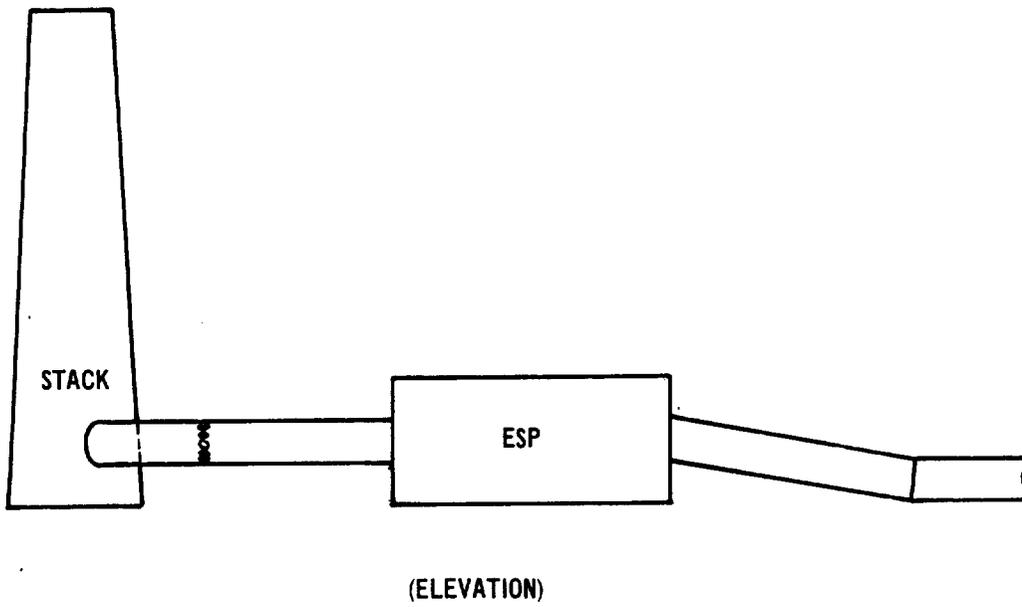
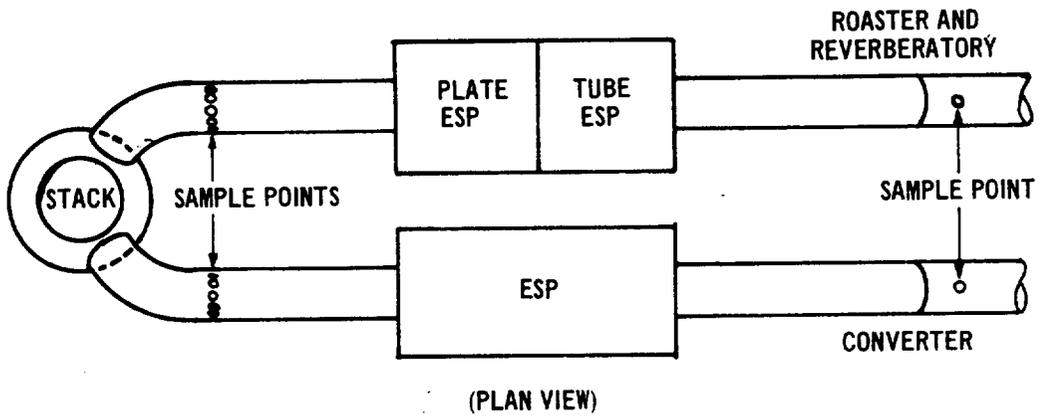


Figure 7. Particulate sampling sites.

sample ports were 3-3/4 x 2-1/2 inches and consisted of pipe sections that extended 17 inches above the roof of the breeching.

Considerable dust had collected on the bottom of the duct, reducing the area of air flow. Soundings of the height of the dust build-up were made by ASARCO personnel. Figure 8, a diagram of the cross-section of the duct at the sampling points, gives the measurements of free area from the dust pile at each port to the roof of the breeching.

As the sampling ports are 2 feet apart, the duct was divided into 2-foot square areas, with the traverse point chosen to be at the center of each area. Thus, the first point was 1 foot inside the duct; the second point, 2 feet deeper, etc. No point was selected that would be very close to the layer of particulate in the duct. The location of each of the 56 sampling points is shown by a circle in Figure 8.

The area of the duct was calculated by multiplying the free air depth of each port in the duct by 2 feet, and then adding the segments together. The resulting area was 289.2 square feet, instead of the 320 square feet indicated by the entire duct dimensions.

Roaster and Reverberatory ESP Inlet. This location was provided with 3/4-inch ID ports and the headroom from the top of the port to the underside of the building roof was about 6 feet. The small port diameter prevented the use of available sampling equipment; therefore, particulate mass was not sampled at this location.

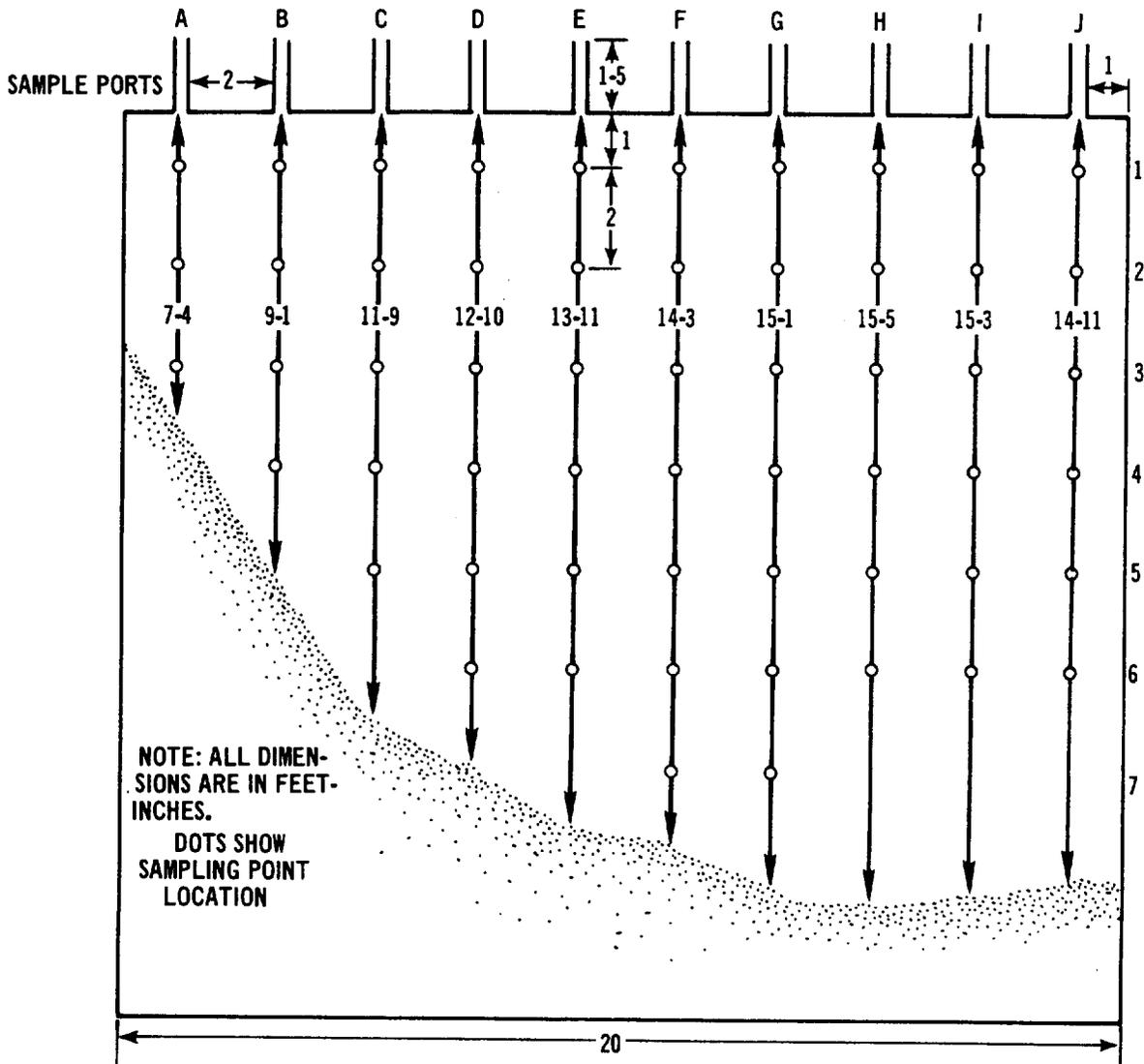


Figure 8. Sampling point diagram--R&R furnace ESP outlet.

Converter ESP Outlet. This outlet duct was provided with a series of ten sampling ports 2 feet apart, beginning 1 foot from the side wall of the duct. These ports were approximately 2 inches ID and extended 30 inches above the roof of the duct. The ports were located about 100 feet from the ESP and 3-4 feet from a bend in the breeching. This site was used for sampling, although Method 1 criteria could not be met at this location.

An initial traverse taken at the location indicated that little or no flow, or in some cases slightly negative flow, could be detected at the seven traverse points on ports B through G, Figure 9. As a result, the ports labeled A, H, I, and J were employed for sampling, each with seven traverse points, for a total of 28 points tested. The duct dimensions at this location were 20 feet wide by 15 feet high for an overall duct area of 300 square feet. The area of gas flow was calculated from the seven 2 x 2 foot traverse areas in the duct for those ports indicating positive flow. The resulting area was 112 square feet instead of the 300 square feet indicated by the entire duct dimensions. The effective area utilized in the calculations given in Tables 7 and 8 is equivalent to a 14 x 8 foot duct. Since the duct had large areas of negative flow, the error introduced by not including the remaining 1 foot of duct height (4.5 percent of the total area) is probably small when compared to the uncertainty in establishing the point of demarkation of the positive and negative flows.

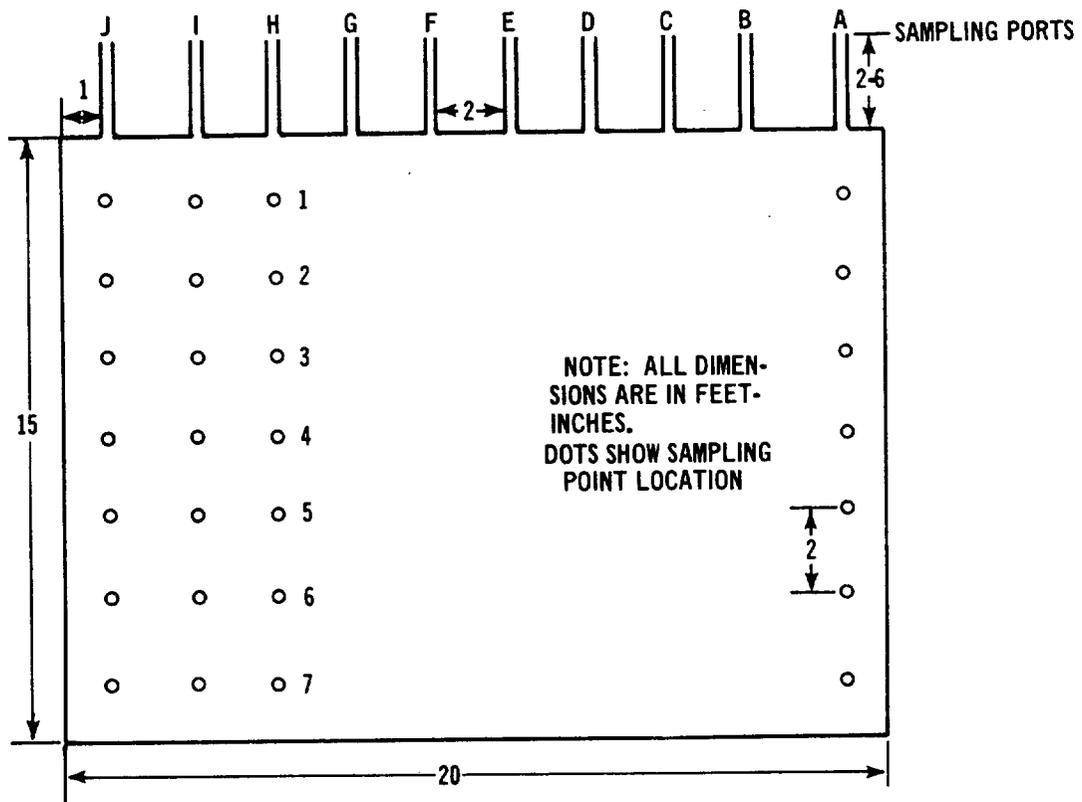


Figure 9. Sampling point diagram-converter ESP outlet.

Table 7. SUMMARY OF ASARCO PARTICULATE MASS MEASUREMENTS

Date 1973	Test	Test site	Average velocity ft/sec	Avg. temp. °F	%O ₂	%CO ₂	%CO	%N ₂	Particulate emission rate Tb/hr	%H ₂ O
9/26	1-A	Inlet to converter ESP	7.95	256	20.2	0.4	0.0	79.4	1040	4.82
9/26	1-B	Outlet to converter ESP	30.3	214					107	3.44
9/26	2-A	Inlet to converter ESP	11.1	250	19.5	0.7	0.0	79.7	810	6.85
9/26	2-B	Outlet to converter ESP	30.0	277					55.9	3.87
9/27	3	Outlet to reverberatory ESP	35.2	176	20.0	0.4	0.0	79.6	18	5.92
9/27	4	Outlet to reverberatory ESP	36.0	181	19.4	0.8	0.0	79.8	268	5.92

Converter ESP Inlet. As shown in Figure 10, the sampling location for the inlet to the converter ESP was in an 11-1/2 foot high x 24 foot wide horizontal duct. About 3-4 feet beyond the sampling ports, this duct was connected to a long inclined duct that led to the electrostatic precipitator. This location, while not meeting Method 1 criteria, was the best available site for sampling.

The three sampling ports, 6 inches ID and 2 feet long, provided at this site were 6, 12, and 18 feet from the side of the duct. These ports were located in a covered area with 6-foot 1-inch headroom. As a result, it would be necessary to have a sectional probe for complete traversing. As only one sectional probe was available, the duct was sampled with a 6-foot probe. Further, since a preliminary velocity traverse indicated uniform velocity and temperature across the measurable portions of the duct, it was decided to sample at only one point because of manpower and time limitations. The point chosen was from the center port and at the maximum depth possible with the available probes. As the overall length of a 6-foot probe when removed from the sample box is 7 feet, the sampling nozzle was located 5 feet below the top of the port.

Sampling Methods

Particulate mass sampling at the ASARCO plant generally followed the procedures outlined in the Federal Register.¹

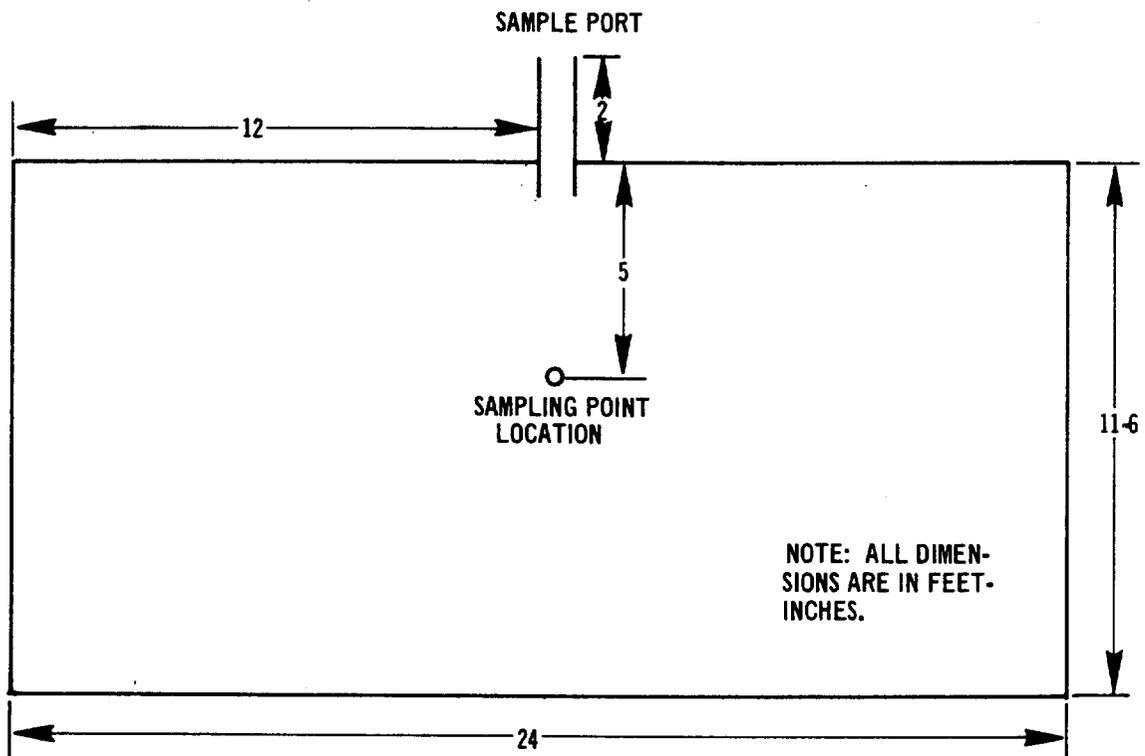


Figure. 10. Sampling point diagram--converter ESP inlet.

Method 2 "Determination of Stack Gas Velocity and Volumetric Flow Rate," was employed by EPA personnel prior to the sampling program to obtain preliminary velocity data. During each particulate sampling run, integrated gas samples were collected in Tedlar bags following the procedures outlined in Method 3 "Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight." The collected gas sampled was analyzed for O₂, CO, CO₂, and N₂ at the site by the Orsat technique. Approximate determination of the moisture in the stack gases for the purpose of defining the nomograph parameters (for Method 5) was completed at the outlet of both ESP's following Method 4 "Determination of Moisture in Stack Gases."

The particulate emissions were determined using a modification of Method 5 "Determination of Particulate Emissions from Stationary Sources." The deviations from the method were specifically in the probe, probe connectors, traversing point location, and number of runs; otherwise, the equipment and techniques used followed Method 5 procedures exactly.

At the outlets of the ESP's, a Process Measurements Section (EPA/CSL) designed probe was used for all sample runs. This probe consisted of electrically heated 1/2-inch OD Teflon tubing² wrapped with foam insulation and a polyvinyl chloride outer protective coating. The tubing was heated by a variable transformer and the temperature was monitored by a Type K thermocouple. As the tubing material is quite flexible, it was encased

in sections of aluminum conduit 2 feet long and fastened together with conduit coupling to provide a 16-foot-long probe. The original intent was to add sections of conduit to the probe as the traverse proceeded; however, this was inconvenient and the probe was left assembled in the desired length.

Two 1/4-inch OD Teflon pitot tube lines were taped to the Dekron tubing and placed in the aluminum conduit. At the stack end of the probe, the Teflon pitot tube lines were connected to a 0.250-inch probe tip. Each section of the conduit was marked to allow alignment of the probe tip into the air flow. At the sample box end of the probe, the pitot line connectors were provided with quick connectors to match the normal sample box lines. A special adapter (consisting of a Swagelok tube unit and a stainless steel female ball joint) connected the sample line to the sample box. With the flexible probe it was possible to traverse downward and leave the sample box in a normal position with respect to the impingers and ice bath.

At the inlet to the converter ESP, the standard heated Pyrex-lined stainless steel probe, stainless steel probe tips, and stainless steel pitot tubes were used. However, as the sample traverse was in a vertically downward direction, the probe could not be connected to the sample box in the normal

manner. Monsanto Research Corporation (MRC) had previously designed and constructed a flexible line to connect the probe to the sample box. This connector consisted of 1/2-inch OD wire-braid-covered Teflon tubing, wrapped with heating tape, and overlaid with pressure-sensitive Teflon tape. At each end, special adapters were made to join Swagelok tube fittings to stainless steel ball joints: a male on one end (for the probe) and a female on the other (for the sample box). A Type K thermocouple was used to monitor the temperature of the connector, the heating of which was controlled by a variable transformer. Other than this flexible connector, all train components were as specified by Method 5 procedures.¹ A digital thermometer and Type K thermocouple were used to monitor stack temperature. Sampling trains designed and built by MRC were also employed at the outlet sampling sites. All temperature readings on these trains are obtained from thermocouples and a digital thermometer.

All thermocouple and thermistor read-out devices and the dry test meters were calibrated prior to the beginning of the program. The orifice plate condition factor was determined and noted on each instrument at calibration time. The pitot tube used for the inlet sampling was calibrated (coefficients of 0.85 were used in all calculations) and found to meet Federal Register specifications.¹

Analytical Procedures

Samples from the Method 5 sampling trains were recovered as outlined in the Federal Register.¹ After removal of the filter, all exposed surfaces of the sample were washed with reagent grade acetone or distilled water as specified. In addition, impinger solutions were retained for analysis. All sample bottles and the petri dishes for sample filters were previously acid-soaked with 1:1 HNO₃ for 1 day, rinsed with distilled water, and soaked with distilled water for 1 day.

Subsequent handling of the Method 5 samples also followed the Federal Register,¹ with one exception: water from both the impingers and washing of the glassware of the train was extracted with chloroform and ether, and then the extracted portion was dried to constant weight. In addition, the water remaining after extraction was evaporated to dryness at 212° F to constant weight.

Sample weights from the Method 5 samplers were reported as "front half" (probe washings and filter collection weights) and "total" (front half plus water, chloroform/ether extract, and impinger acetone washing weights). Only "front half" values have been used in the reporting of results in the following sections on particulate mass and efficiency.

All particulate mass analyses were performed at Monsanto Research Corporation, Dayton Laboratory.

Sampling Approach

Both the inlet and outlet of the converter ESP were sampled simultaneously to determine the efficiency of the devices. Due to time limitations, two runs (Runs 1 and 2) were made at each site. Runs 1A and 2A were at the inlet; and Runs 1B and 2B, at the outlet of the ESP. Sampling was continued as long as at least one converter was in operation. A series of lights near the sampling location indicated how many and which of the four converters were being used. Outlet sampling was completed by traversing all points showing a positive flow, but only one traverse point was sampled at the inlet.

The outlet of the R&R ESP was sampled by traversing all points in the moving air stream. Since this duct contained a considerable amount of settled dust, sampling points were chosen to avoid this material. The inlet to this ESP could not be sampled due to inadequate overhead clearance for the sampling probe at the port location.

RESULTS--PARTICULATE MASS

A summary of the test sites and emission data is given in Table 7. Additional data is presented in Table 8, based on the computer printout of the Method 5 calculations.

Converter ESP Inlet

The inlet data from the converter ESP (Runs 1A and 2A) was obtained by sampling at one point in the 11.5 x 24 foot

Table 8. ASARCO PARTICULATE MASS DATA

Description	1-A	1-B	2-A	2-B	3	4
Duration of run, min.	162.0	162.0	176.0	168.0	168.0	140.0
Barometric pressure, in. Hg	30.33	30.38	30.38	30.41	30.30	30.30
Avg. orifice press. drop, in. H ₂ O	0.703	0.849	0.417	1.100	1.060	1.100
Vol. dry gas (meter con.), dcf	77.335	76.423	65.893	76.468	97.628	82.202
Avg. gas meter temp., °F	83.7	77.4	85.4	63.3	84.5	75.4
Vol. dry gas (std. cond.), dscf	76.50	76.60	65.00	78.90	96.40	82.60
Total H ₂ O collected, ml	81.7	57.7	100.9	67.0	128.0	109.8
Vol. H ₂ O vapor (std. con.), scf	3.870	2.730	4.780	3.180	6.070	5.200
Moisture by vol., %	4.82	3.44	6.85	3.87	5.92	5.92
Mole fraction dry gas	0.952			0.941	0.941	0.941
CO ₂ , %	0.4			0.4	0.4	0.8
O ₂ , %	20.2			20.0	20.0	19.4
N ₂ , %	79.4			79.6	79.6	79.8

Table 8. ASARCO PARTICULATE MASS DATA (Cont.)

Description	1-A	1-B	2-A	2-B	3	4
Mol. wt. of dry gas	28.9	28.9	28.9	28.9	28.9	28.9
Mol. wt. of stack gas	28.4	28.5	28.1	28.5	28.3	28.3
Avg. stack velocity head, in. H ₂ O	0.015	0.286	0.029	0.355	0.324	0.346
Stack temperature, °F	256.0	214.0	250.0	277.0	176.0	181.0
Stack pressure (static), in. H ₂ O	-0.12	-0.10	-0.12	-0.10	-2.70	-2.70
Stack pressure (ABS), in. Hg	30.32	30.37	30.37	30.40	30.10	30.10
Avg. stack gas velocity, fpm	477.0	1820.0	664.0	1800.0	2110.0	2160.0
Stack diameter, in.	225.00	143.30	225.00	143.30	230.26	230.26
Stack area, sq in.	39800.0	16100.0	39800.0	16100.0	41600.0	41600.0
Stack flow rate (dry std.), dscfm	94100.0	157000.0	129000.0	141000.0	481000.0	488000.0
Stack flow rate (actual), acfm	132000.0	204000.0	183000.0	201000.0	610000.0	623000.0

Table 8. ASARCO PARTICULATE MASS DATA (Cont.)

Description	1-A	1-B	2-A	2-B	3	4
Probe tip diameter, in.	0.482	0.250	0.384	0.250	0.250	0.250
Percent isokinetic	109.5	99.0	98.1	109.0	101.2	102.4
Particulate (front), mg	6428.7	395.3	6913.9	237.2	482.7	343.3
Particulate (total), mg	7138.9	1281.6	7539.6	762.8	587.5	683.6
Particulate (front), gr/dscf	1.2900	0.0795	1.6400	0.0463	0.0771	0.0640
Particulate (total), gr/dscf	1.4400	0.2580	1.7900	0.1490	0.0939	0.1270
Particulate (front), gr/acf	0.9200	0.0612	1.1600	0.0325	0.0608	0.0501
Particulate (total), gr/acf	1.0300	0.1990	1.2600	0.1050	0.0740	0.0993
Particulate (front), lb/hr	1040.000	107.000	1810.000	55.900	318.000	268.000
Particulate (total), lb/hr	1160.000	347.000	1980.000	180.000	387.000	531.000

duct. An initial velocity traverse at depths of 3 and 5 feet at each of the three ports indicated a pitot reading of 0.02 inches of water at each point and an average temperature of 129° F. As shown in Table 8, the pitot tube readings during Runs 1A and 2A were 0.015 and 0.029 inches of water, and the temperature averaged 256 and 250° F, respectively. These results yield quite different values for the velocity, causing differences to appear in the gas flow and particulate emission rates. The results can be considered approximate: only one location was sampled in a large duct, and the velocities were quite low.

Converter ESP Outlet

Data from the outlet of the converter ESP (Runs 1B and 2B) was consistent, except for stack temperature: 214° F in Run 1B and 277° F in Run 2B. The average temperature from Run 2B was rather unexpected: it was higher than the inlet average temperature during the same time period. A possible explanation is that heat from the burner at the base of the stack which was used to create draft in the stack increased the temperature in the outlet breeching. As quite a large portion of the duct showed essentially a zero flow, this heat could be carried back into the sampling area. Unfortunately, no data was recorded on the operation of this burner.

The stack flow rate from Runs 1B and 2B, in terms of both the dry standard conditions and the actual cubic feet/minute,

agree quite well; however, the particulate weights from these two runs are not very similar. Review of the production data does not indicate any apparent reason for the difference in weight of material collected. However, the ratio of the front half mass loadings to front half plus back half mass loadings is quite close, indicating that the same type of particulate was emitted during both runs.

EXPERIMENTAL--PARTICULATE SIZE

The size distribution of the fine particulates, $\leq 5 \mu\text{m}$, was experimentally determined at the inlet and outlet of both ESP systems, using aerodynamic sizing techniques. Particle size was measured with inertial classifiers manufactured by Monsanto (Brink Model B) and by 2000 Inc. (Andersen Stack Sampler, Mark III).

Due to the high particulate concentration ($> 1 \text{ grain/scf}$) reported prior to the control device, the Brink impactor was used to determine the particle size distribution of the inlet streams. Figure 11 shows the sampling arrangement used at the ASARCO smelter. All Brink impactor measurements were made with the impactor in the duct and vertical. Prior sampling at non-ferrous smelters³ had established that the size distribution of metal condensate fumes tended to be what is classified as fine particles; therefore, pre-scalping cyclones were not used at this smelter.

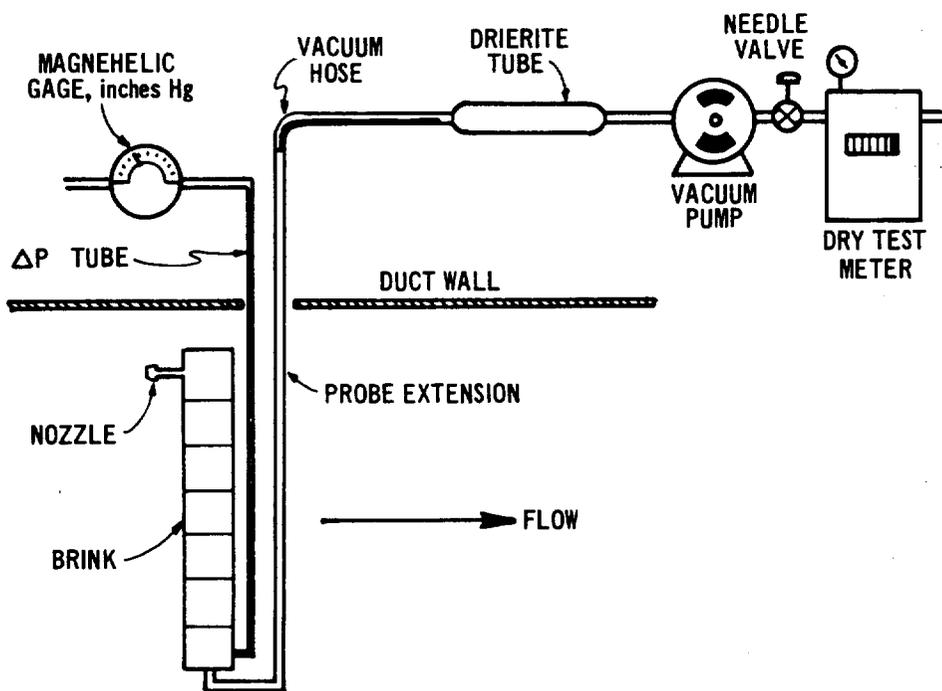


Figure 11. Brink sampling train.

After preparation of the impactor, an appropriate nozzle and sampling probe were selected to provide isokinetic rates at the nozzle inlet. The inlet duct to the converter and to the R&R ESP were both 16 x 24 feet with the air flow wing horizontal. With the in-stack sampler, probes were used that placed the inlet to the impactor 4 feet from the top of the duct. The impactor operating conditions are given in Table 9.

The Andersen Mark III impactor was used at the ESP outlets. The anticipated low grain loading (< 0.1 gr/scf) made the selection of a high-sampling-rate inertial sizing device mandatory. The sampling arrangement used is shown in Figure 12. As required by the impactor inlet design, all Andersen Mark III measurements were made with the impactor horizontal. Extreme care was used in removing the impactor from the duct so that collected particulates would not be jarred loose from the collection stage. (The smelter dust has a tendency to coke and optical measurements of the impactor stages following the sampling period revealed no evidence of jarring.)

After preparation of the impactor, an appropriate nozzle and sample probe were selected to provide isokinetic rates at the nozzle inlet. With in-stack sampling, the probes used placed the inlet to the impactor 4 feet from the top of the duct. The Andersen impactor operating conditions are given in Table 10.

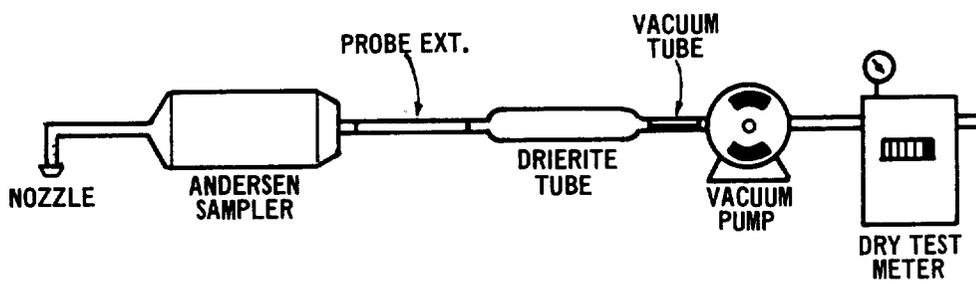


Figure 12. Andersen sampling train.

Table 9. BRINK IMPACTOR OPERATING CONDITIONS--ESP INLET

	Converter Flue	R&R Flue
Temperature, ° F	220	170
Warm-up time, min.	30	30
Sampling time, min.	15	15
ΔP across impactor, in. Hg	1 ^a	1 ^a
Position	Vertical	Vertical

^aCorresponds to flow rate of approximately 0.1 acfm.

Table 10. ANDERSEN MARK III OPERATING CONDITIONS--ESP OUTLET

	Converter Flue	R&R Flue
Temperature, ° F	220	170
Warm-up time, min.	30	30
Sampling time, min. (approx.)	50	50
Sampling rate, acfm	0.75-0.93	0.9
Position	Horizontal	Horizontal

In all cases, the samples (Brink stages or Andersen filters) were weighed at NERC-RTP. The samples were dried for 3 hours at 80° C, desiccated for about 2 hours, and weighed on a Mettler H20T balance.

RESULTS--PARTICULATE SIZE

The raw weights combined with impactor operating parameters were numerically manipulated using a computer program.⁴ The cumulative size distributions from the data reducing program are given in Figures 13, 14, 15, and 16: Figures 13 and 14 represent the inlet and outlet cumulative size data for the converter ESP; and Figures 15 and 16 are the inlet and outlet cumulative size data of the R&R flue. The observed experimental scatter is not a typical of impactor data.⁵

DISCUSSION

Converter ESP Tests

Based on the data obtained from the front half of the particulate mass loading tests, the estimated particulate mass removal efficiencies are given in Table 11.

Differential size distributions for each run were obtained by differentiation of the cumulative size distributions. The $dM/(d \log D)$ values which are the result of this step are in $gr/ft^3/\mu m$. The shape of the differential distributions, plotted in Figures 17 and 18, is of significant interest. The numerical values, used to determine size collection efficiency, are established by the following procedure:

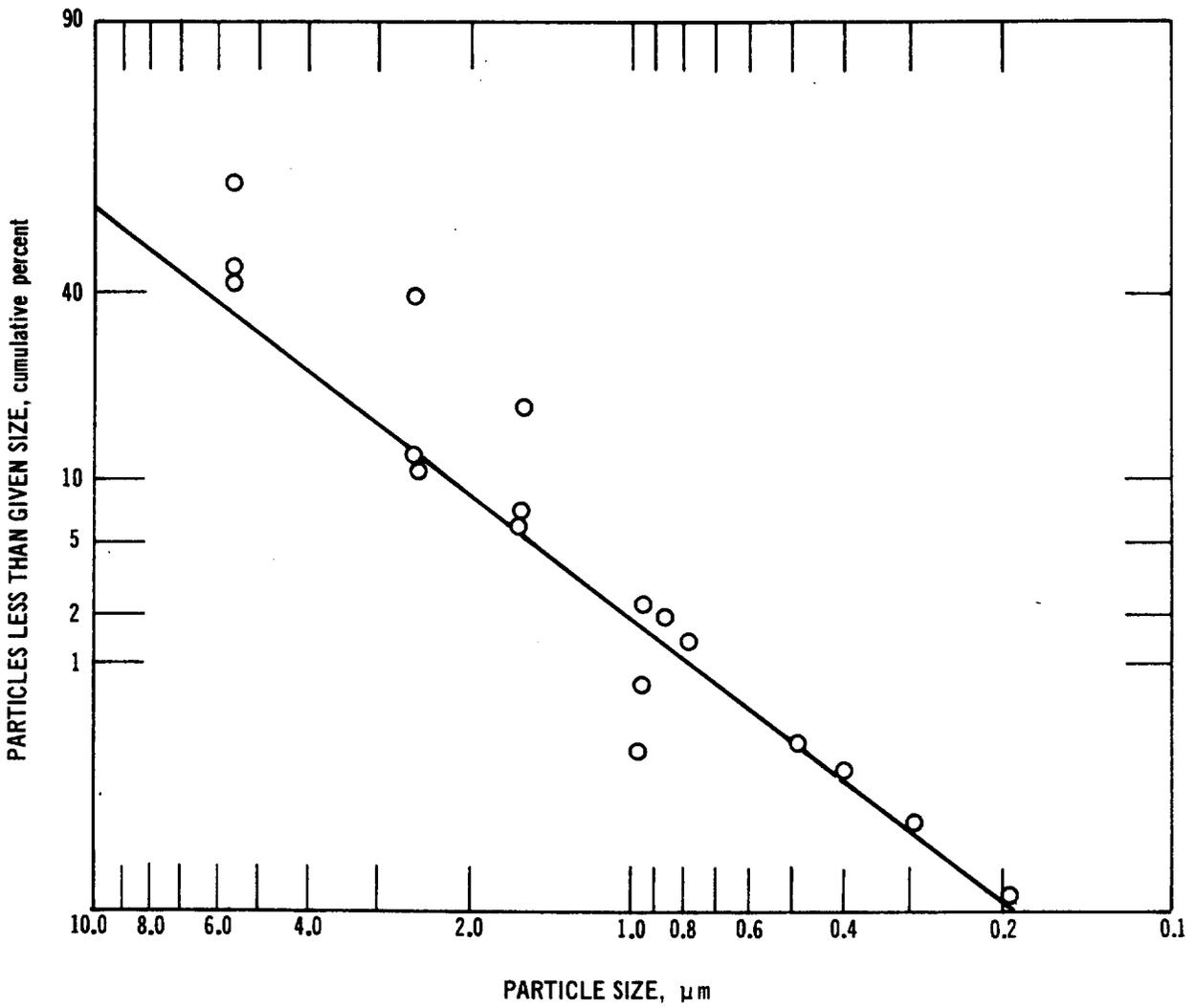


Figure 13. Cumulative percent of particles less than given size--converter inlet.

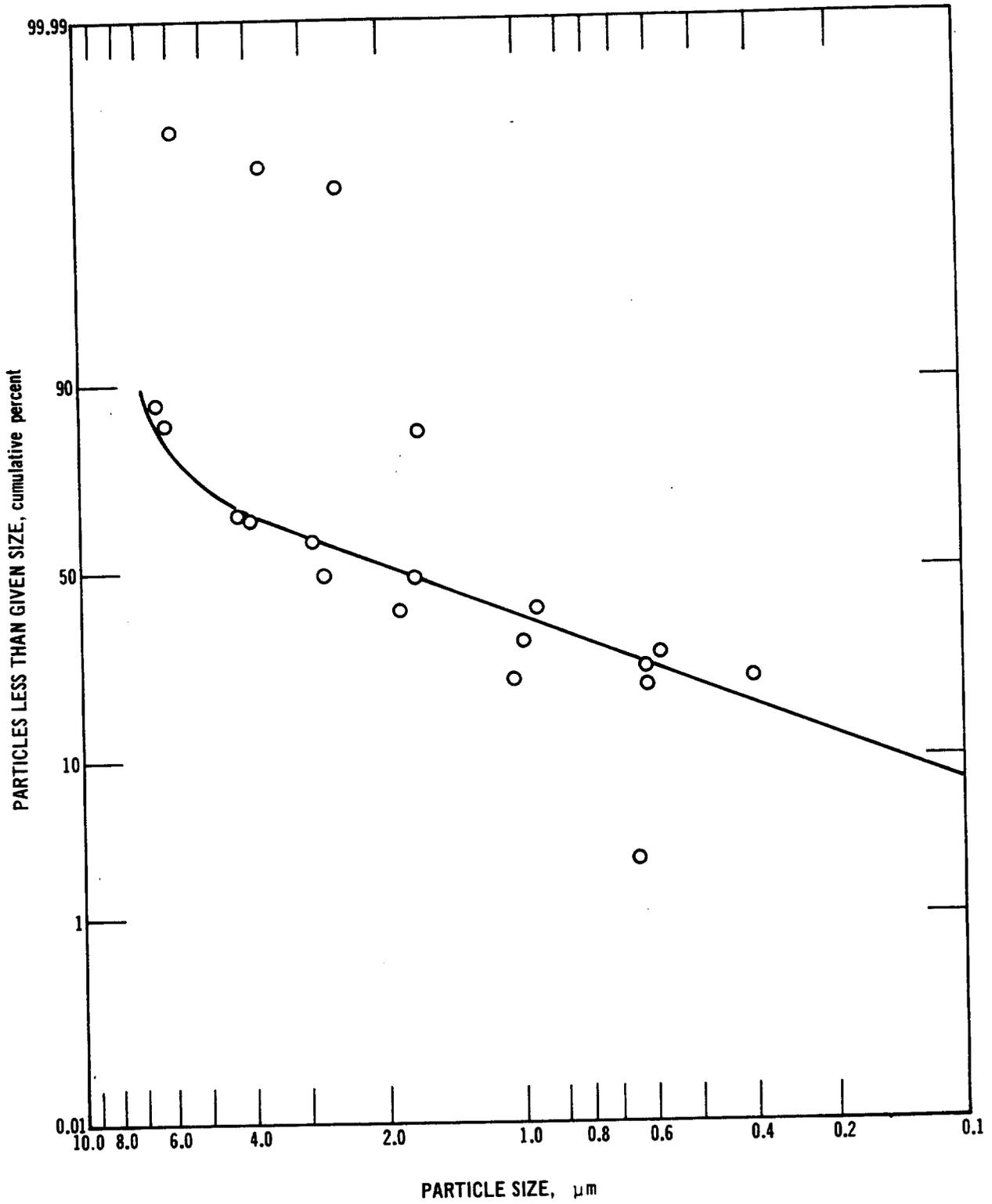


Figure 14. Cumulative percent of particles less than given size--converter outlet.

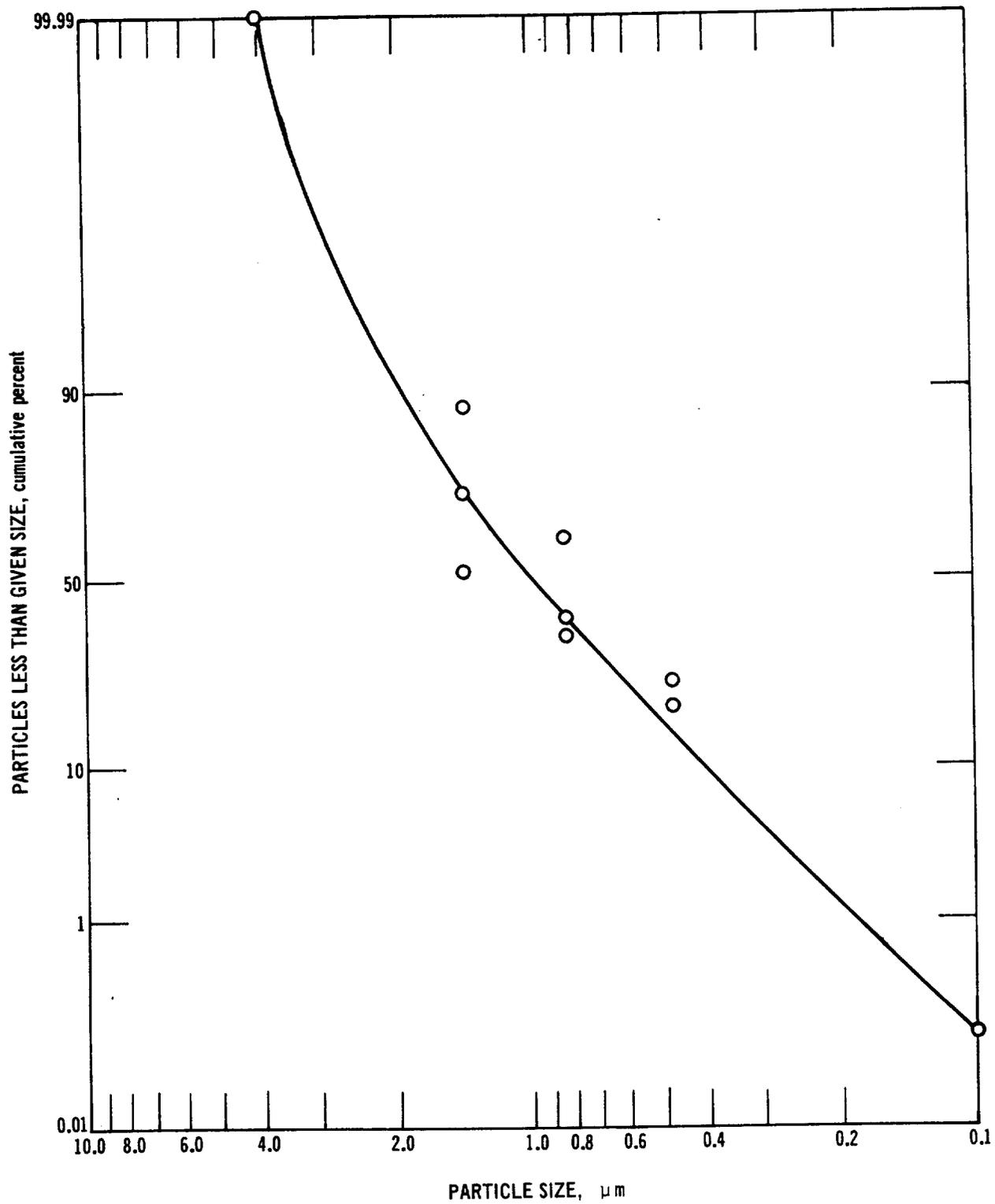


Figure 15. Cumulative percent of particles less than given size-- R&R inlet.

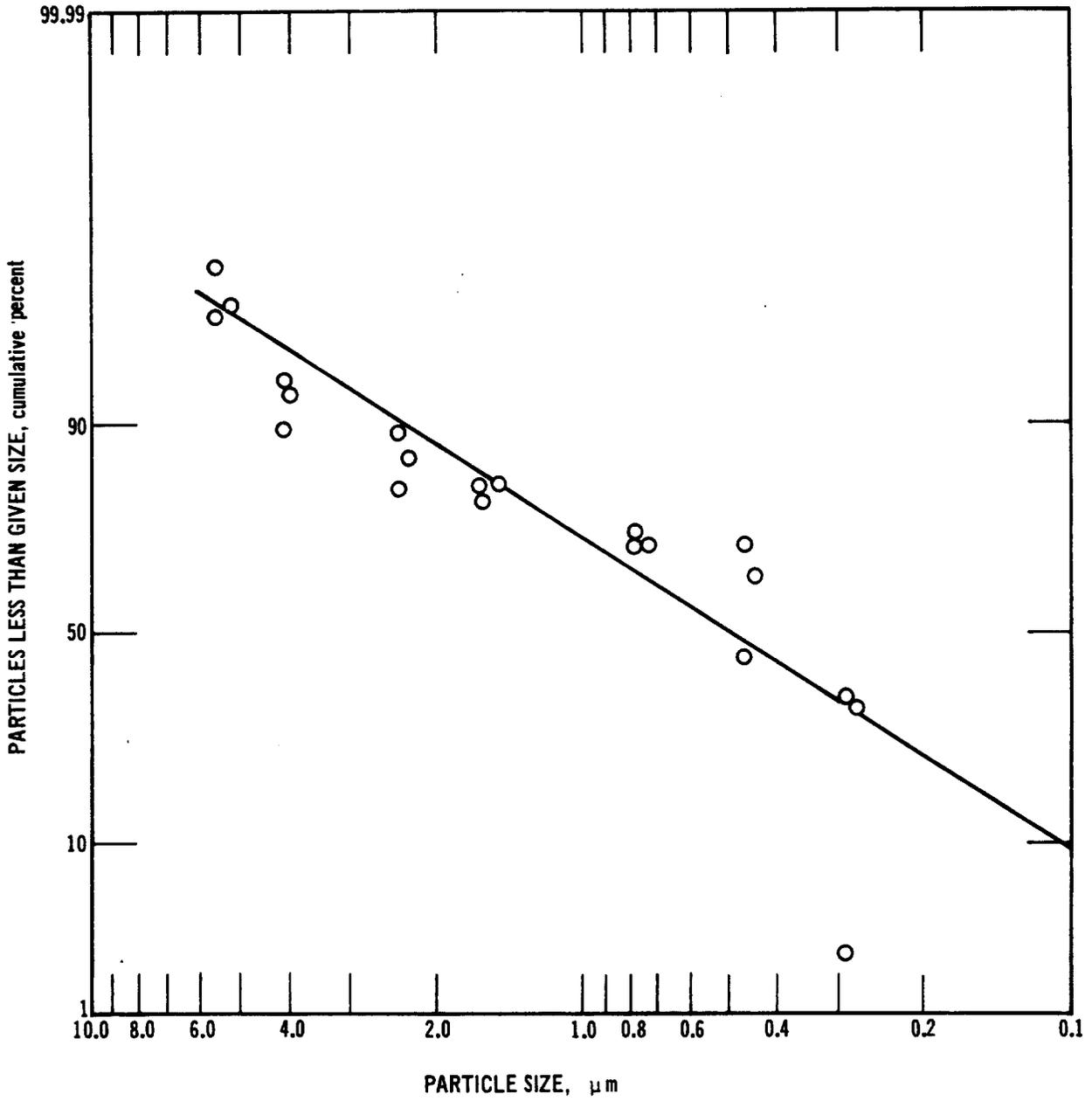


Figure 16. Cumulative percent of particles less than given size-- R&R outlet.

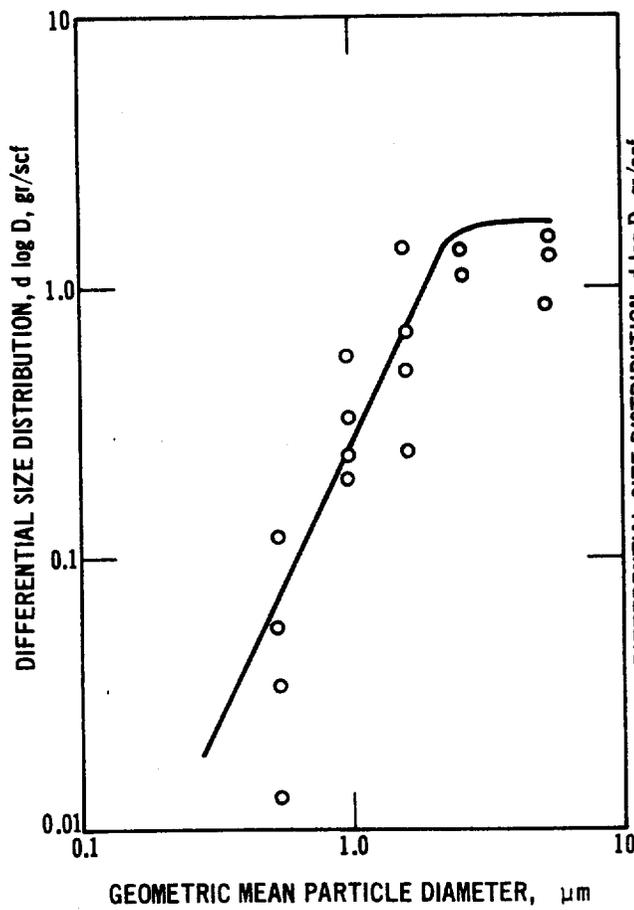


Figure 17. Differential size distribution--converter ESP inlet.

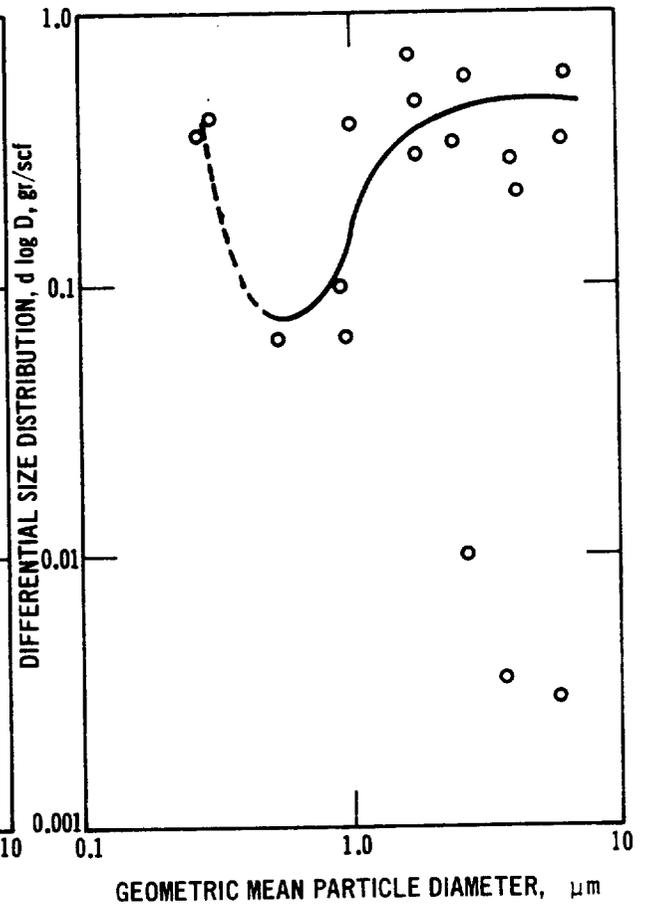


Figure 18. Differential size distribution--converter ESP outlet.

1. The mean value curves in Figures 17 and 18 are transcribed to a single plot (Figure 19).
2. Values of $dM/d \log D$ are interpolated from these curves at preselected geometric mean diameters.
3. The collection efficiency is determined at each diameter by:

$$E = \frac{(dM/d \log D) \text{ in.} - (dM/d \log D) \text{ out.}}{(dM/d \log D) \text{ in.}} \times 100\%$$

The collection efficiencies calculated in step 3 are presented in Figure 20 as a function of geometric mean diameter. Several apparent features of the resultant curve are:

1. The collection efficiency for particles larger than $3 \mu\text{m}$ exceeds 90 percent.
2. A monotonic decrease in the collection efficiency is observed for particulate between $3 \mu\text{m}$ and about $1.2 \mu\text{m}$.
3. A plateau in the collection efficiency occurs in the size range between 0.8 and $1.2 \mu\text{m}$.
4. A strong decrease and negative efficiencies (the effluent from the control device contains a greater mass of particulate in a given size range than the inlet to the control device) occur through the remaining size cuts.

The first two features of this curve have been observed in field studies of very high efficiency ESP performance at coal-fired power plants: an ESP model has been developed for coal

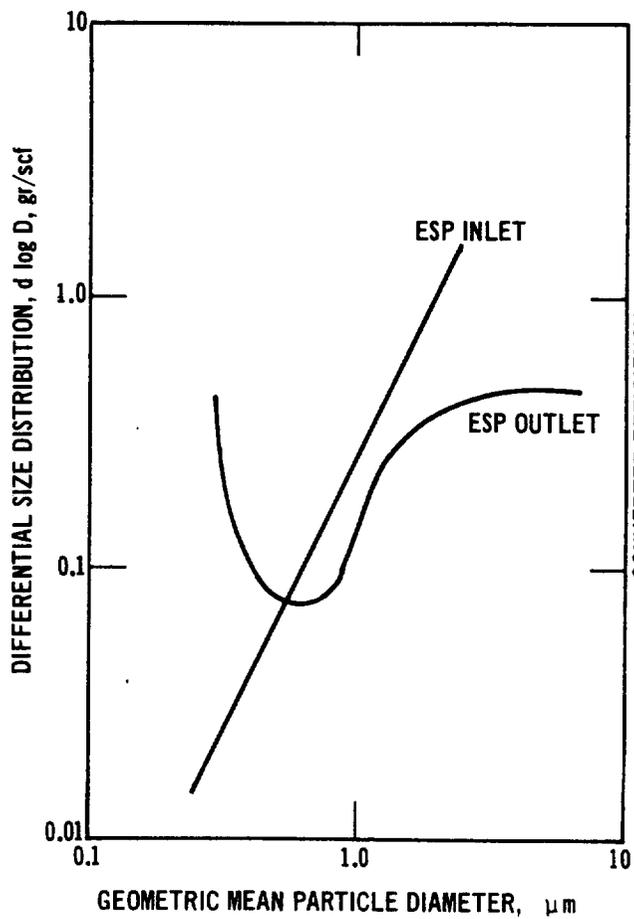


Figure 19. Differential size distribution--converter ESP inlet and outlet.

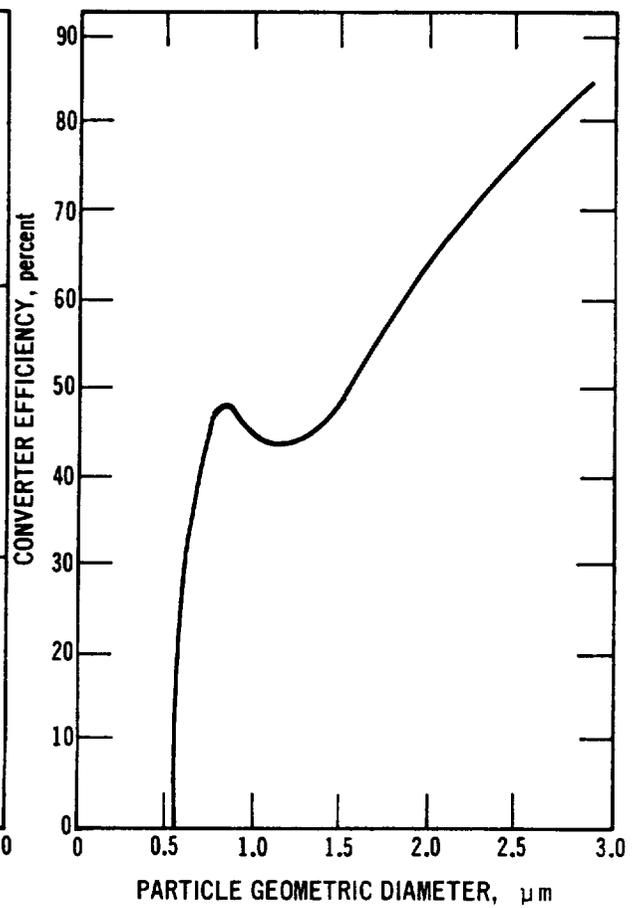


Figure 20. Converter ESP efficiency as a function of particle geometric diameter.

flyash which predicts a shallow minimum between 0.1 and 1 μm . Therefore, the observed decrease in efficiency as a function of size was expected, but the degree of particulate penetration of the control device at the minimum was unexpected. Possible explanations for the depth of the minimum in the fractional efficiency curve are the relatively low overall efficiency of the ESP and the high resistivity of metal oxide fumes which leads to low precipitation rates. Table 12 lists representative precipitation rates for various applications: the smelter dust precipitation rate is about a factor of 7 lower than that for utility flyash. The lowering of the precipitation rate could amplify the magnitude of the minimum in the fractional efficiency curves.

While the preceding explanation would explain a minimum in the fractional efficiency curve, it would not satisfactorily explain the negative efficiencies observed. Probable causes for this feature of the curve include:

1. Sampling locations were not representative of the dust loading distribution.
2. Agglomerated particulate broke up impaction. This would have occurred only at the outlet to produce the results observed.
3. Condensation and/or reaction of a flue gas component with the collection substrate.

Table 11. CONVERTER PARTICULATE MASS COLLECTION EFFICIENCY

Run	Inlet, gr/scf	Outlet, gr/scf	Efficiency, %
1	1.29	0.0795	93.8
2	1.64	0.0463	97.1

Table 12. REPRESENTATIVE PRECIPITATION RATES

Application	Precipitation rate avg ft/sec
Utility flyash	0.43
Pulp and paper	0.25
Sulfuric acid	0.24
Cement (wet)	0.35
Smelter	0.06
Open hearth	0.16
Cupola	0.10
Blast furnace	0.36

4. Re-entrainment and/or evaporation of collected particulates due to electric sparkover.
5. Back corona churning of the collected dust.

Causes 1 and 2 are the least probable for these observations, since they would require that (in 12 tests conducted over a 2-day period) the same errors and/or conditions were encountered and repeatable. There is some credibility to cause 3, based on the other test results observed; however, Southern Research Institute⁴ has reported this same type of efficiency behavior at an ESP installation when the particulate is a dry fluffy material. This observation leaves items 4 and 5 as the most probable causes.

R&R ESP Tests

Since inlet mass data could not be collected, particulate mass removal efficiencies could not be estimated. Emission values were reported earlier in the section, under Results-- Particulate Mass.

The fractional efficiency of the in-series R&R ESP's was determined using the procedures described previously. Figures 21 and 22 represent the results of numerically differentiating the cumulative size distributions; Figure 23 represents the fractional collection efficiency of the two ESP's as a function of size.

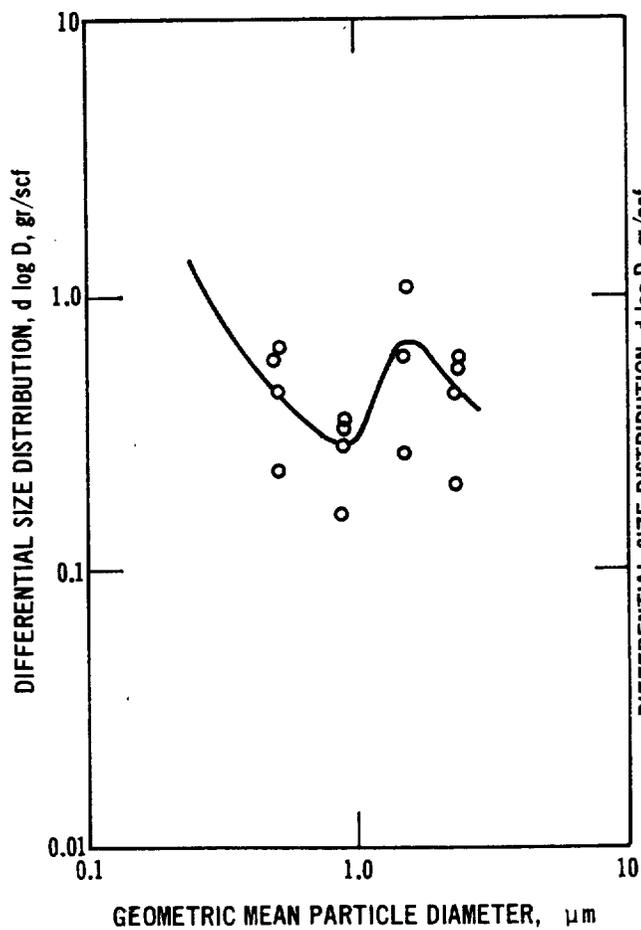


Figure 21. Differential size distribution--R&R ESP inlet.

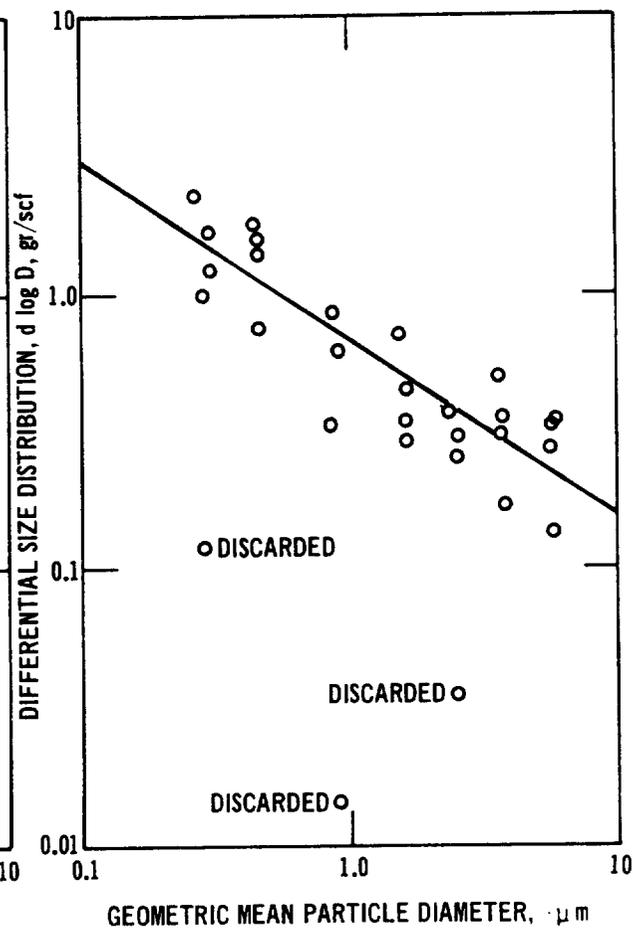


Figure 22. Differential size distribution--R&R ESP outlet.

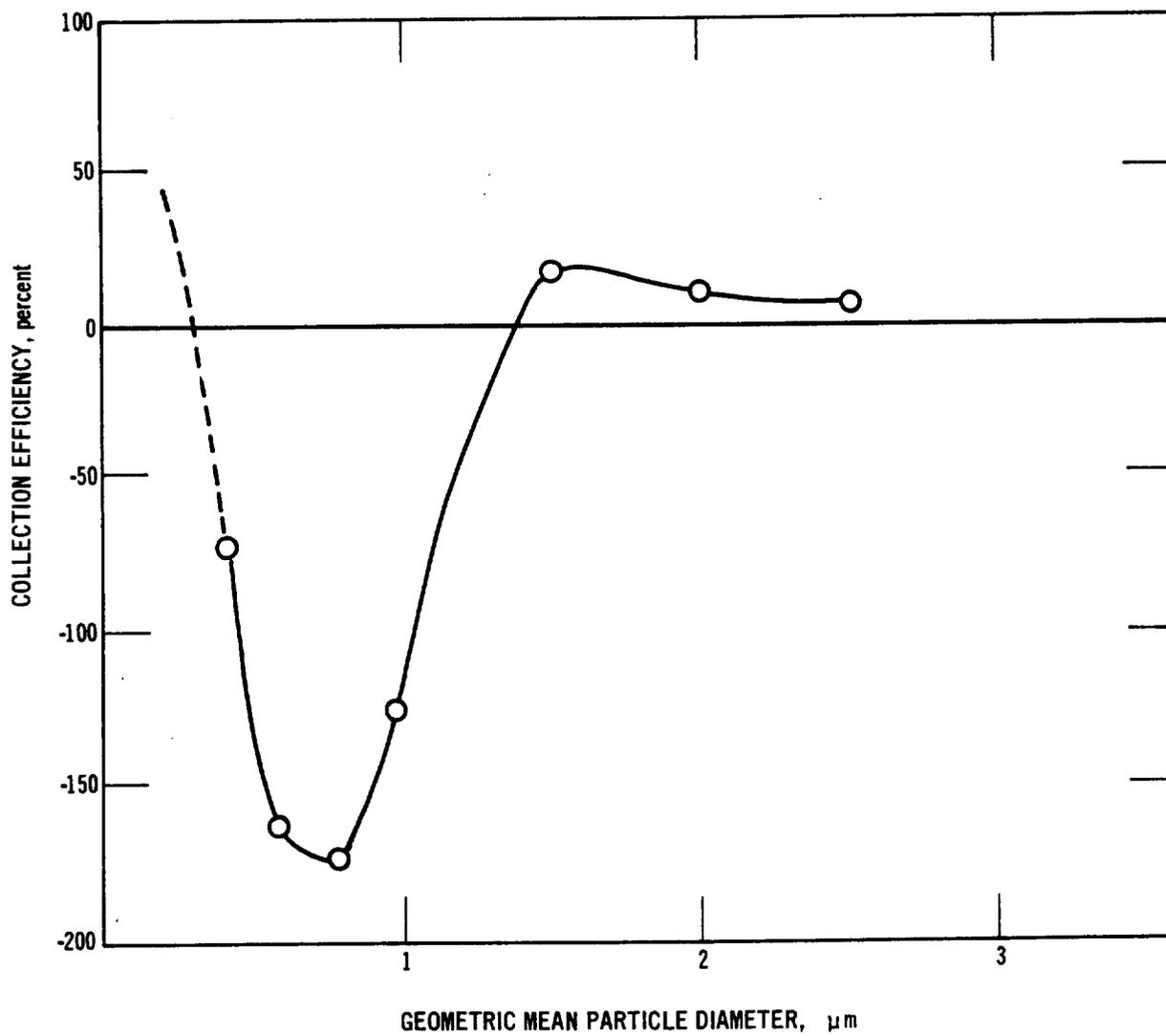


Figure 23. Fractional collection efficiency of R&R ESP's.

The shape and the level of control achieved by the R&R ESP system in general exhibit the same features as the fractional efficiency curve for the converter ESP: a notable exception is an upturn in the curve at particle diameters less than 0.7 μm . It is felt that the same causes/effect relationships exist for the R&R ESP as for the converter ESP. This feeling is reinforced by the similarity between the two fractional efficiency curves.

REFERENCES

1. Federal Register, 36, 247, December 23, 1971.
2. Tubing is Dekron, Samuel Moore Co., Aurora, Ohio.
3. Harris, D. B., R. M. Statnick, D. C. Drehmel, and D. K. Oestreich. Measurement of Air Pollutants from Selected Non-Ferrous Smelting Processes, unpublished.
4. Southern Research Institute computer program, modified by F. Briden (EPA/CSL/PMS).
5. Field Measurements of Particle Size Distribution with Inertial Sizing Devices, Southern Research Institute, NTIS No. PB 226-292/AS. October 1973.
6. An Electrostatic Precipitator Systems Study; A Manual of of Electrostatic Precipitator Technology: Part I, Fundamentals, Southern Research Institute. NTIS No. PB 196-380, August 1970.

SECTION V
ELEMENTAL COMPOSITION

EXPERIMENTAL

The total particulate train catch (front and back half residues of the EPA particulate mass sampling train) was submitted for chemical analysis of selected elements. The samples were brought into solution by adding 10 ml of aqua regia to each of the following: residue from acetone washings of exposed surfaces of all samples; residue from acetone washing of the Greenburg-Smith impingers; residue from evaporation of the water in the Greenburg-Smith impingers; and residue from the chloroform/ether extract. The fiber glass filters were placed in separate beakers and also treated with 10 ml of aqua regia. All samples were digested at room temperature for 72 hours and the supernate liquors from each test run were combined into a single sample.

Samples 1B, 2B (converter ESP outlets), 3, and 4 (R&R ESP outlets) were free of undissolved solids after the initial treatment with aqua regia. The combined supernate liquors from these samples were evaporated to dryness. The residue was redissolved in 5 ml of aqua regia, transferred to a 25 ml volumetric flask, and diluted to the mark with deionized water.

The samples from Runs 1A and 2A (converter ESP inlets) contained undissolved solids after initial treatment with aqua

regia. The liquors were heated to 90° C for 2 hours and cooled. Any remaining residue was filtered. The filtrate was evaporated to dryness and the residue redissolved in aqua regia. The samples were transferred to 250 ml volumetric flasks and diluted to the mark with deionized water.

All analyses were carried out on a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer, calibrated using commercially available standards. Sample concentrations were derived from calibration data, fitted to a linear regression least squares program. The following wavelengths were used from the appropriate hollow cathode lamp: arsenic (193.7 nm), cadmium (228.8 nm), chromium (357.9 nm), copper (324.7 nm), mercury (253.6 nm), lead (283.3 nm), and zinc (213.9 nm). All analyses, except for mercury, were performed by direct aspiration into an air/acetylene flame. The mercury analyses were performed by flameless atomic absorption procedures.¹

In addition to the analysis of mercury in the particulate samples, gas-phase mercury was determined using acid permanganate absorption preceded by a sodium carbonate prescrubber for SO₂ removal. This procedure, fully described elsewhere,² is given in Appendix A.

RESULTS

The results of the elemental analyses were expressed as weight percent of the total material analyzed and are given in Table 13. The vapor-phase mercury concentrations are given in Table 14.

Table 13. CHEMICAL COMPOSITION OF SOLIDS AND RESIDUES FROM THE PARTICULATE MASS
SAMPLING TRAIN, % BY WEIGHT^a

Element	Run No.			
	1A	2A	1B	2B
				3
				4
As	17.22±0.29	16.16±0.87	3.83±0.27	4.31±0.16
				7.09±1.03
				12.76±0.96
Cd	1.27±0.08	0.96±0.005	0.17±0.003	0.21±0.004
				0.062±0.004
				0.092±0.004
C ^b	81.7±10.0	60.6±9.8	71.5±2.5	65.2±3.5
				228.7±8.4
				73.3±11.8
Cu	0.88±0.009	0.598±0	0.144±0.004	0.15±0
				1.22±0
				0.79±0.007
Hg ^b	23.4±1.28	13.2±4.6	18.6±1.6	5.49±0.35
				--
				--
Pb	8.39±0.21	9.04±0.08	4.73±0.07	6.69±0.1
				1.77±0.09
				2.67±0.05
Zn	7.65±0.13	4.69±0.487	0.883±0.05	0.585±0.03
				4.28±0.25
				2.04±0.45

^aBased on weight of elements in the zero oxidation state, m^o.

^bIn ppm (rather than % by weight).

Table 14. ASARCO CONCENTRATION OF VAPOR-PHASE MERCURY
IN FLUE GAS

Sample No.	Date & location	Volume liters	Total Hg μg	ppm ^a
5	9/25/73 Converter inlet	184.7	2.5	0.0002
6	9/25/73 Converter inlet	103.7	5.0	0.0005
7	9/25/73 Converter inlet	221.2	0.3	0.0000
11	9/26/73 R&R outlet	269.9	4.5	0.0002
12	9/26/73 R&R outlet	285.9	17.5	0.0007
13	9/26/73 R&R outlet	319.4	17.4	0.0007

^aFormulas used for calculations of ppm:

$$\frac{\text{Total } \mu\text{g}}{\text{mol wt}} \times 22.4 = \text{liters of sample}$$

$$\frac{\text{Liters}}{\text{Total liters}/10} = \text{ppm}$$

DISCUSSION

Combining the percent composition data with the particulate loading, a collection efficiency for the converter ESP can be calculated for each element. The results of such a calculation are given in Table 15, where:

$$\text{Efficiency} = \frac{(\text{gr/scf}) \text{ in.} \times \% \text{ comp. in.} - (\text{gr/scf}) \text{ out.} \times \% \text{ comp. out.}}{(\text{gr/scf}) \text{ in.} \times \% \text{ comp. in.}}$$

The collection efficiency of each individual element can be compared with the particulate mass collection efficiency, when this elemental collection efficiency is observed. The implication that the elemental composition of the emitted particulate is homogeneous over all size ranges is supported by the fractional size collection efficiency curves.

The quantity of each element emitted to the atmosphere from the two flues is given in Table 16. All values are expressed as the element in the zero oxidation state.

The total emissions of all elements analyzed, except cadmium and lead, can be reduced significantly by concentrating the control effort on the R&R flue. Reducing the R&R effluent grain loading from 0.055 to 0.0275 gr/scf would reduce arsenic emissions from 58.05 to 34.2 lb/hr (about 40 percent); whereas, the same 50 percent reduction of the converter effluent grain loading would reduce arsenic emissions from 58.05 to only 52.8 lb/hr (about 10 percent). For lead, the same reduction in R&R grain loading would reduce lead emissions from 24.6 to 19.3 lb/hr, or about 25 percent. Complete control of R&R emissions will result in a maximum reduction of 40-50 percent.

Table 15. ELEMENTAL COLLECTION EFFICIENCIES OF
CONVERTER ESP

Element	Collection efficiency, % (average of two runs)
As	96
Pb	90
Cd	97
Zn	98
Cr	95
Cu	97

Table 16. MASS EMISSION RATE OF SELECTED ELEMENTS

Element	Total lb/hr	Converter lb/hr	Percent	R&R lb/hr	Percent
As	58.05	10.5	18	47.55	82
Pb	24.65	14.2	58	10.45	42
Cd	1.34	0.97	72	0.375	28
Zn	15.7	2.05	13	13.65	87
Cr	0.065	0.005	8	0.06	92
Cu	<u>4.825</u>	<u>0.375</u>	<u>8</u>	<u>4.45</u>	<u>92</u>
Total	104.63	28.1	27	76.535	73

REFERENCES

1. Hatch, W. R. and W. L. Ott. Anal. Chem., 40, 2085 (1968).
2. Statnick, R. M., D. K. Oestreich, and R. Steiber. Sampling and Analysis of Mercury Vapor in Industrial Streams Containing Sulfur Dioxide. Presented at ACS annual meeting, Chicago. August 26-31, 1973.

Appendix A
SAMPLING AND ANALYSIS OF MERCURY
VAPOR IN INDUSTRIAL STREAMS CONTAINING SULFUR
DIOXIDE

by

R. M. Statnick
D. K. Oestreich
R. Steiber

Research Branch
Control Systems Laboratory

For Presentation at 1973 ACS Annual Meeting, Chicago, Illinois,
August 26 - 31, 1973

U. S. Environmental Protection Agency
Office of Research and Development
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Introduction

The measurement of the level of mercury contained in off-gases resulting from various high temperature industrial processes often requires the collection of samples from streams high in sulfur dioxide concentration. For example, waste gas streams from non-ferrous smelters and fossil fuel combustion contain sulfur dioxide in concentration ranges several orders of magnitude greater than the concentration of mercury. Mercury most often occurs in these gas streams as elemental mercury vapor because most inorganic mercury compounds are thermodynamically unstable at high temperatures with respect to elemental mercury. At 25°C the relative nobility of mercury metal is indicated by the standard oxidation potentials:



It can be seen from the potentials that elemental mercury is thermodynamically stable with regard to oxidation at lower temperatures.

Even after considerable adiabatic cooling has taken place in the waste gas stream, the mercury formed from high temperature reactions will be present as the vapor since the gas phase concentrations based on equilibrium vapor pressure considerations far exceed concentrations actually found in typical source waste gas streams. The variation of the equilibrium vapor pressure of mercury with temperature is given in

(1) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," 3rd ed, Macmillan Company, New York, N. Y., 1964, p 529.

Figure 1.²

The chemical inertness of mercury vapor, combined with its high vapor pressure, implies that it might best be sampled by collection in a wet scrubber containing an oxidizing medium. Numerous oxidizing substances or mixtures have been used:^{3,4} the most common oxidant is acidic potassium permanganate (Couple $E^\circ = -1.695$)¹, closely followed by iodine-monochloride solution (Couple $E^\circ = -1.19$).

The high chemical reactivity of sulfur dioxide, combined with its presence in industrial gas streams in concentrations which are at least 3 orders of magnitude greater than the mercury concentration, interferes seriously with any oxidizing system for the collection of mercury. In the case of acid permanganate, sulfur dioxide reduces the permanganate ion and precipitates manganese dioxide; in the case of iodine monochloride, elemental iodine is precipitated by sulfur dioxide.

This paper describes the development of a modification to existing mercury sampling procedures which makes it possible to utilize these procedures on sulfur-dioxide-containing waste gas streams.

Experimental Methods

Mercury Collection Efficiency Tests

Of the collection media which have been used for mercury, the nitric

(2) Q. R. Stahl, "Preliminary Air Pollution Survey of Mercury and Its Compounds," NAPCA, NTIS No. PB 188-074, p 74 (1969).

(3) Federal Register, 36, 23245, 1971.

(4) C. E. Billings and W. R. Matson, Science, 176, 1232 (1972).

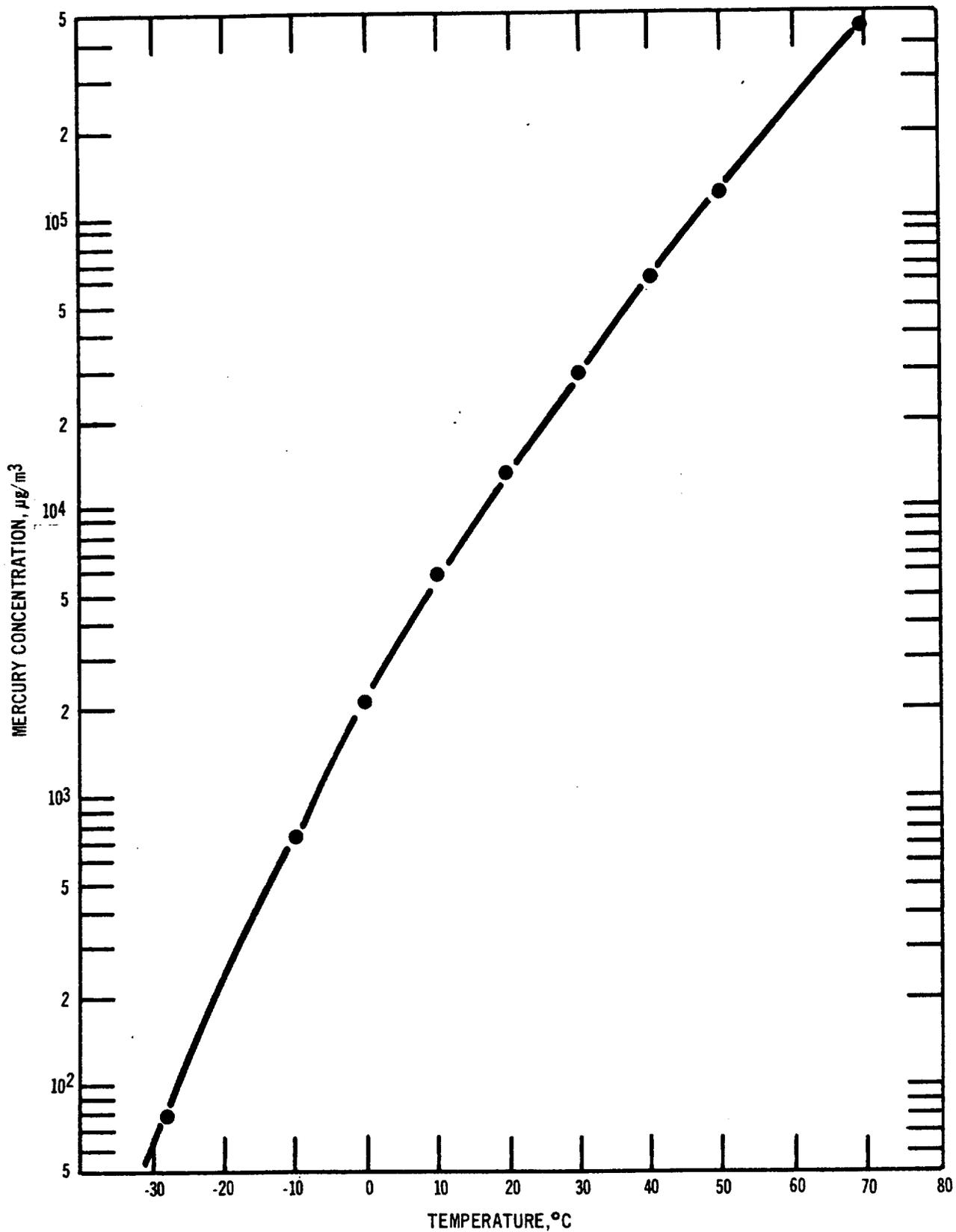


Figure 1. Saturation concentration of mercury in air.

acid/potassium permanganate solution was selected because of ease of preparation in the field and the general availability of reagents. To determine mercury collection efficiency, a series of laboratory tests was conducted with 2.0 μg total mercury present. A standard mercury solution of 1000 μg Hg/ml was purchased from Harleco Division of American Hospital Supply Corp.⁵ and was used as the primary standard for this work. A standard solution of 1 $\mu\text{g}/\text{ml}$ mercury was prepared by appropriate dilution of the primary standard. Two ml aliquots of the 1 $\mu\text{g}/\text{ml}$ stock solution were used to prepare the charges for the mercury reduction-evolution apparatus. The procedure of Hatch and Ott⁶ was used to generate elemental mercury vapor. The experimental apparatus is described in Figure 2.

A 2 ml aliquot of the appropriate stock solution was transferred to the evolution flask and appropriate amounts of nitric acid, stannous chloride, and hydroxyl amine hydrochloride were added. The system was then quickly closed and the bellows pump operated for 10 minutes. Previous tests with this system, operated in an open loop manner, indicated that all the mercury was evolved in 2 to 3 minutes.

The resultant mercury-laden collection media were placed in 100 ml volumetric flasks and diluted with distilled, de-ionized water to the mark. One to four milliliter aliquots of this sample were then analyzed utilizing the atomic absorption procedure of

(5) 1740 Ridge Avenue, Evanston, Ill. 60201

(6) W. R. Hatch and W. L. Ott, Analytical Chemistry, 40, 2085-2087 (1968).

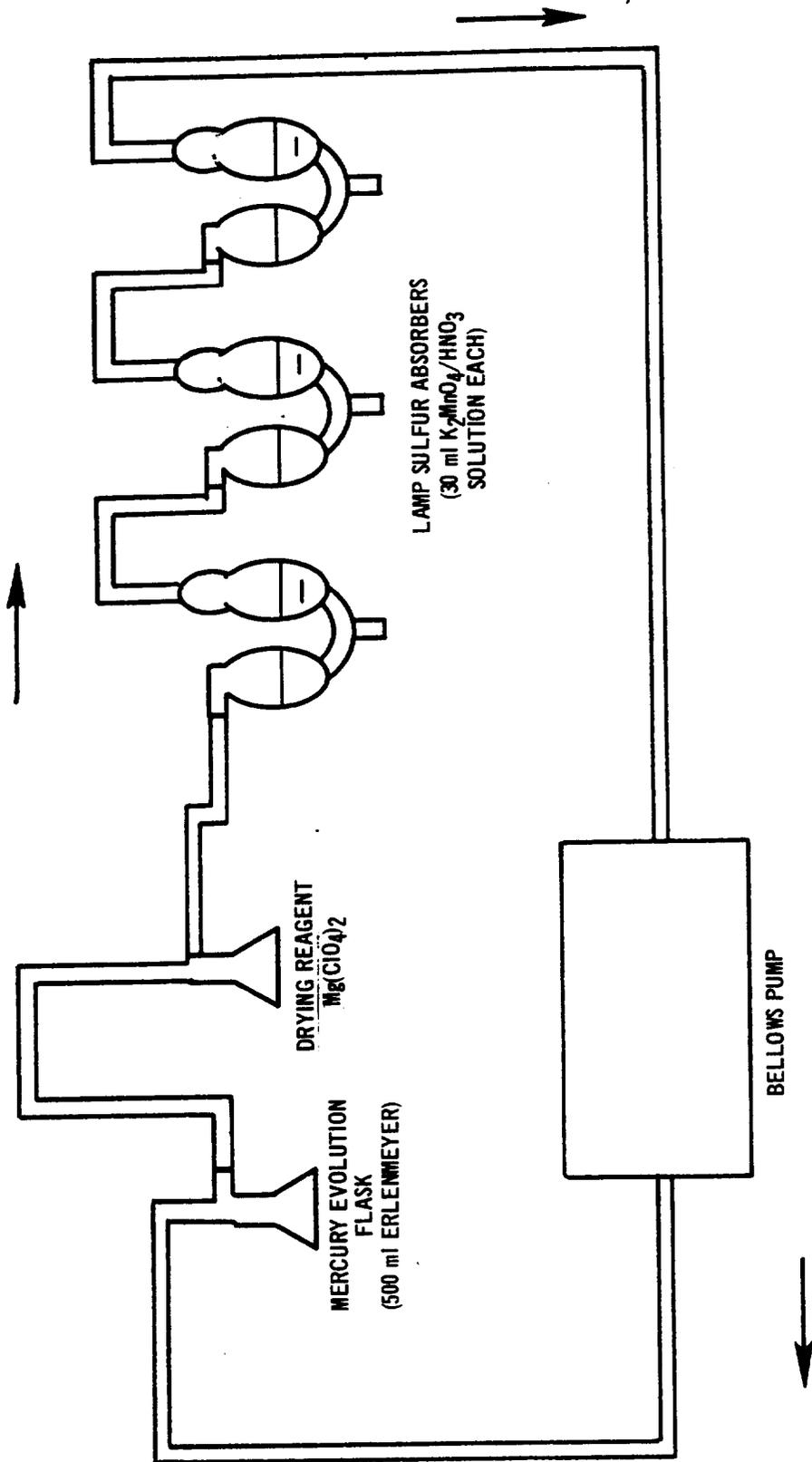


Figure 2. Material recovery test apparatus.

Hatch and Ott.⁶ The results are reported in Table 1. Similar recoveries were observed by the Occupational Safety and Health Administration.⁷

Table 1. MERCURY RECOVERY

(µg mercury found in Lamp Sulfur Absorbers)

Test Run No.	Total µg Hg Present	Absorber No. 1	Absorber No. 2	Absorber No. 3	% Recovery ⁷
1	2.0	1.6	ND	ND	80
2	2.0	1.7	ND	ND	85
3	2.0	1.6	ND	ND	80

ND = not detected

Adaptation of Procedure to Sulfur Dioxide Containing Streams

In order to make the sampling procedure for mercury compatible with streams containing 0.1 to 8% v/v of sulfur dioxide, a procedure was sought for selectively and quantitatively removing all of the sulfur dioxide present. Experience has shown various alkaline scrubbing media to be effective for sulfur dioxide removal. A recent study⁸ has shown sodium carbonate solutions to be an exceedingly effective sulfur dioxide removal medium. Based on this experience, a prescrubber containing saturated sodium carbonate solution was

(7) R. L. Larkin, OSHA, Cincinnati, Ohio, personal communication, 1973.

(8) D. C. Draemel, EPA/OR&M/NERC-RTP/CSL, personal communication, 1973.

prepared and tested for effectiveness in a synthetic flue gas stream. The prescrubber was followed by acid/permanganate scrubbers; after sampling 0.18 m³, no visible deterioration of the acidic permanganate was observed. This was true even at sulfur dioxide levels approaching 90+% v/v.

The question of the possible retention of mercury by the sodium carbonate solution was then addressed. A test stand, shown in Figure 3, was assembled to determine the fate of mercury in sodium carbonate solution.

For these tests, mercury vapor was generated by aspirating air through a midget impinger containing several grams of elemental mercury. The mercury-containing stream was bypassed around the sodium carbonate scrubber until a steady state value was observed with the atomic absorption instrument (Perkin Elmer Model 403) operated in the flameless mode. The stopcock was then turned to direct the flow through the scrubber; when a steady state was again achieved, the recording was noted. Indirect measurements⁹ indicated that the mercury content of the scrubber was less than 20 ppb. A 10% mercury loss into the prescrubber liquor would have resulted in a mercury level of 60 ppb being observed in the scrubber liquor.

(9) These results were also observed by Radian Corporation and TRW Systems Group personnel at a later date.

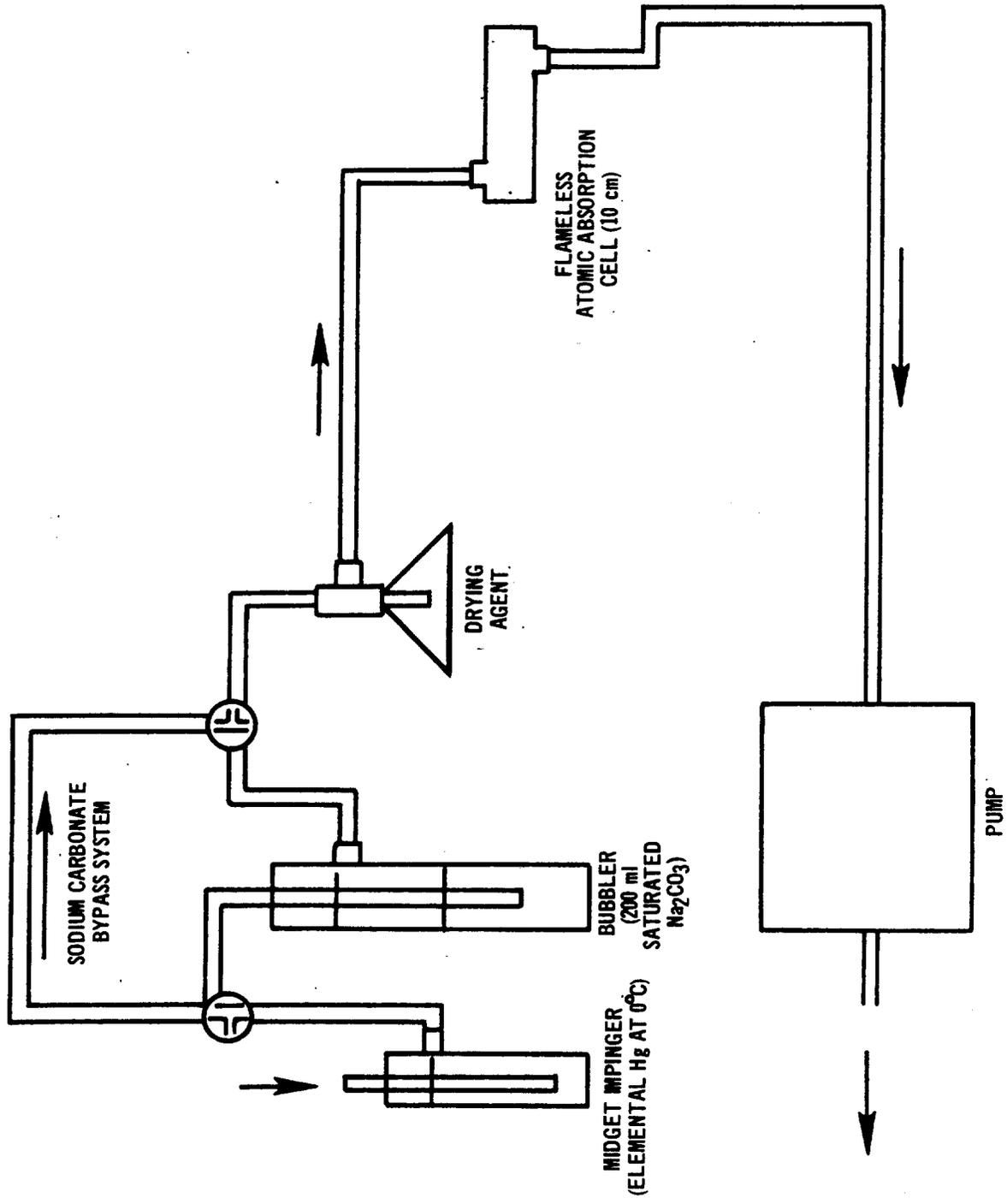


Figure 3. Test stand used to determine fate of mercury.

Sampling Procedure

The apparatus used for sampling various gas streams for mercury is shown in Figure 4. Prior to the taking of a sample, a fresh glass-wool plug was inserted in the borosilicate glass sample probe to act as a particulate filter. The probe was then preheated to 150°C to approximate the temperature of the gas stream sampled and to avoid condensation in the probe. The Lamp Sulfur Absorbers¹⁰ were prepared by charging each with 30 ml of the potassium permanganate/nitric acid solution. The Greenberg-Smith impinger was loaded with 200 ml of saturated sodium carbonate solution.

After assembly of the complete sample train (as shown in Figure 3) and the initial heating of the probe, an initial dry gas meter reading was taken. The pump was then started and the pressure to the dry gas meter noted. After a suitable volume had been sampled, the pump was shut down and the dry gas meter reading again noted. The contents of the Lamp Sulfur Absorbers were then transferred into prewashed (with acid) polyethylene bottles. A sample of fresh acid/permanganate solution was also stored in a polyethylene bottle to serve as a reagent blank. After proper dilution and aliquoting, the samples were analyzed, using the cold atomic absorption method of Hatch and Ott.⁶

Field Sampling

To ascertain the precision of the procedure described above under field sampling conditions, a series of experiments was conducted with a

(10) Purchased from Ace Glass, Inc., 1430 N.W. Boulevard, Vineland, N. J. 08360.

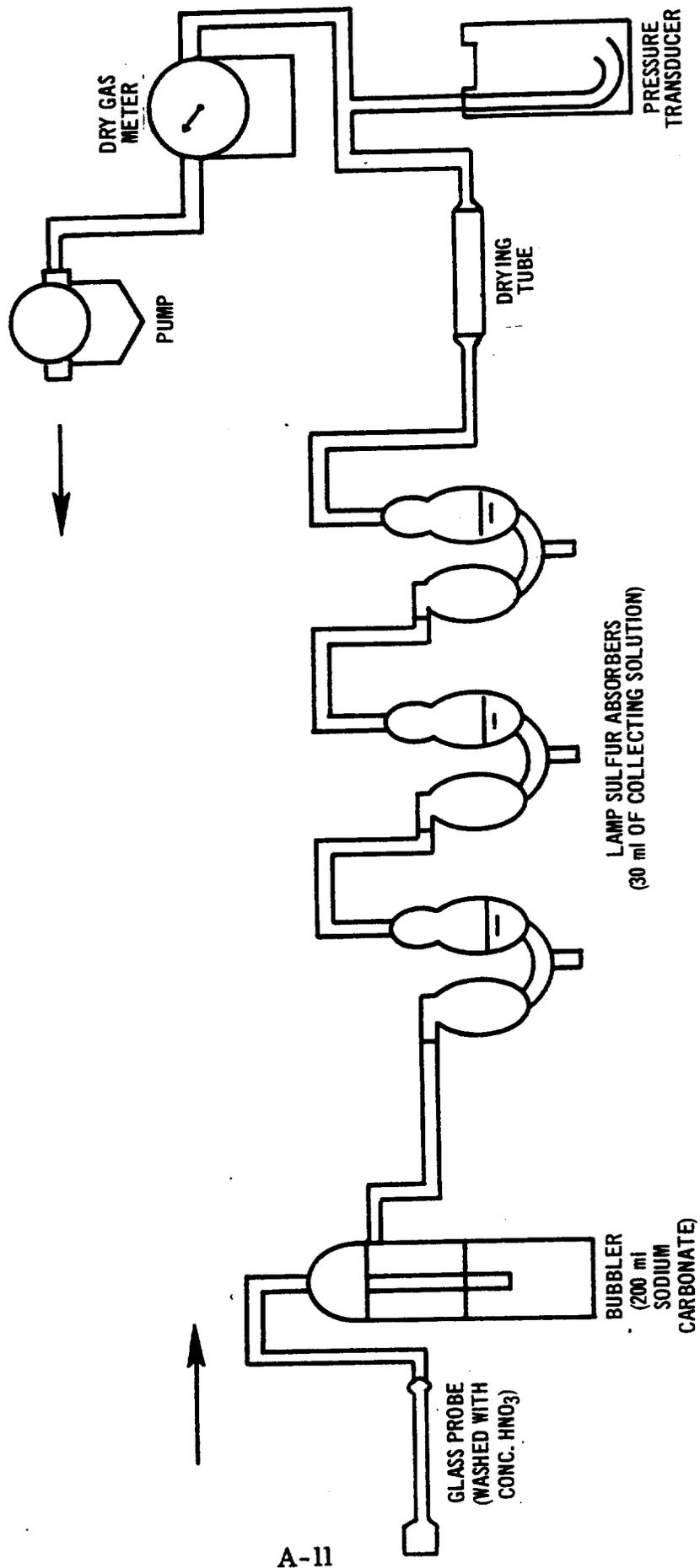


Figure 4. Mercury sampling train.

coal-fired boiler. Two sampling probes, held close to each other, were inserted in the duct. A gas sample was aspirated through both sampling trains simultaneously to determine the sampling-analysis precision.

The results given in Table 2 indicate: a 32% total coefficient of variation; and a 13.7% average dispersion for duplicate analysis.

Table 2. MERCURY FIELD SAMPLING PROCEDURE TEST RESULTS

<u>Test Run No.</u>	<u>Train A μg/m³</u>	<u>Train B μg/m³</u>
1	31	25
2	25	20
3	15	15

Information presented in Table 3 indicates that the precision of the mercury field sampling procedure compares favorably with those of the typical field sampling procedures applied to other types of analyses.

Table 3. COEFFICIENT OF VARIATION FOR VARIOUS FIELD SAMPLING PROCEDURES

<u>Procedure</u>	<u>Coefficient of Variation, %</u>
Mercury	32
Sulfur Dioxide	8-20
Carbon Dioxide	0.97-9.3 ¹¹
Particulate Mass Loading	6-60 ¹²

(11) Walden Research Corp., Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutant from the Combustion of Fossil Fuels.

(12) W. J. Mitchell, EPA Internal Report, A Method to Obtain Replicate Particulate Samples from Stationary Sources.

Much of the lack of precision observed with various procedures is the result of variability in the streams being sampled as a function of time, rather than of the procedures being used.

Results

Field experience using the new mercury sampling procedure was acquired by sampling a number of different industrial processes.

Included in the processes sampled were:

1. A zinc smelter roaster.
2. A lead smelter blast furnace.
3. A coal-fired steam generating station.
4. An experimental coal gasifier.

Chemical analysis of the samples taken using the flameless atomic absorption method gave results as indicated in Table 4.

Conclusions and Summary

A mercury sampling procedure has been developed which is operable in the presence of large concentrations of sulfur dioxide and which is suitable for field use.

The procedure employs a sodium carbonate prescrubber for sulfur dioxide removal, followed by two scrubbers containing nitric acid/potassium permanganate solution for mercury collection. The prescrubber may be operated for 45 minutes at a flow rate of about 2 liters/minute and sulfur dioxide concentration of 80,000 ppm before the solution is exhausted. These figures may be used to predict the useful lifetime of the prescrubber under various conditions.

The long sampling times possible provide greater analytical sensitivity as well as a time-integrated sample which is less subject

Table 4. MERCURY ANALYSIS OF VARIOUS INDUSTRIAL GAS STREAMS

<u>Source</u>	<u>SO_x Level, ppm</u>	<u>Volume Sampled, l</u>	<u>Hg, $\mu\text{g}/\text{m}^3$</u>	<u>Total Stream Flow Rate (Q), $\text{m}^3/\text{min.}$</u>
Experimental Coal Gasifier	30	19.64	484	36
Coal-Fired Boiler, 175-Megawatt	-2500	233.47	91.5	9000
		180.17	73.2	9000
		285.05	11.9	9000
Zinc Smelter Roaster	80,000	93.9	220	1250
		80.1	20	1250
		64.2	970	1250
Lead Smelter Blast Furnace	100-2500 ¹³	170	3380	9000
		283	2590	9000

(13) Estimated from data presented in A. G. McKee report, Systems Study for Control of Emissions: Primary Nonferrous Smelting Industry, NTIS No. PB 184-884, 184-885, and 184-886, June 1969. (Vols. I-III.)

to short-term fluctuations in sample concentration caused by anomalies in process operations than are real time analyses done with instrumental mercury monitors. Instruments which monitor mercury directly are also subject to severe interference from hydrocarbons in that they operate in the ultraviolet spectrum.

While the mercury collection efficiency shown in Table 1 is not 100%, a consistent efficiency of collection was observed; consequently, the low bias may be compensated for with a good degree of confidence.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-650/2-74-111	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Measurement of Sulfur Dioxide, Particulate, and Trace Elements in Copper Smelter Converter and Roaster/Reverberatory Gas Streams	5. REPORT DATE October 1974	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Robert M. Statnick	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS EPA, Office of Research and Development NERC-RTP, Control Systems Laboratory Particulate and Chemical Processes Branch Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO. 1AB012; ROAP 21ADM-012	
	11. CONTRACT/GRANT NO. NA (In-House)	
12. SPONSORING AGENCY NAME AND ADDRESS NA	13. TYPE OF REPORT AND PERIOD COVERED Final: 6/73-4/74	
	14. SPONSORING AGENCY CODE	

15. SUPPLEMENTARY NOTES

16. ABSTRACT The report gives the results of the analysis of data on particulate, sulfur dioxide (SO₂), and trace element emissions and control efficiencies for a copper smelter. The SO₂ emission rates from the roaster/reverberatory and converter effluent streams were 518 and 587 lb/min, respectively. The acid plant's SO₂ control efficiency was 96.8 percent. The mass collection efficiency of the converter's electrostatic precipitator (ESP) for dry filterable solids was 95 percent. The ESPs appear to have a minimum collection efficiency for dry filterable solids of 0.8-1.2 μm. Analyzing emitted particulate gave the following mass emission rates (in lb/hr) for selected elements: arsenic (58.05), lead (24.65), cadmium (1.32), zinc (15.7), chromium (0.065), and copper (4.825). Control efficiency for the analyzed elements was between 90 and 98 percent.

7. KEY WORDS AND DOCUMENT ANALYSIS		
DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Copper Converters Smelters Measurement Sulfur Oxides Trace Elements	Air Pollution Control Stationary Sources Particulates	13B 11F 14B 07B
3. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

ENVIRONMENTAL PROTECTION AGENCY
Technical Publications Branch
Office of Administration
Research Triangle Park, N.C. 27711

OFFICIAL BUSINESS

AN EQUAL OPPORTUNITY EMPLOYER



POSTAGE AND FEES PAID
ENVIRONMENTAL PROTECTION AGENCY
EPA - 335

Return this sheet if you do NOT wish to receive this material ,
or if change of address is needed . (Indicate change, including
ZIP code.)

PUBLICATION NO. EPA-650/2-74-111