

Air



Arsenic Non-Ferrous Smelters

Emission Test Report Phelps-Dodge Copper Smelter Playas, New Mexico

EMISSION TESTING OF PHELPS-DODGE COPPER SMELTER
PLAYAS, NEW MEXICO

TO

ENVIRONMENTAL PROTECTION AGENCY

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SECTION 1

INTRODUCTION

In conjunction with the Environmental Protection Agency's Program for developing new source performance standards, TRW performed fugitive emission tests at the Phelps-Dodge Cooper Smelter located in Playas, New Mexico. The test was conducted July 24-27, 1978.

The process tested was secondary converter hooding system which removed fugitive emissions from the converter during the slag and copper blow cycles.

The testing consisted of three arsenic/sulfur dioxide tests and three particle sizing tests which were performed during the copper and slag blow cycles. The testing location was a seven foot duct located between the hooding system and the stack. These tests were coordinated with a process engineer from the Environmental Protection Agency.

This report presents the results of the testing program. The following sections of the report contain a summary of the results, description of sampling points, description of the process, and the sampling procedure with the laboratory procedure. The appendices contain field data, laboratory data, sample calculations, and the daily activity log.

SECTION 2

SUMMARY AND DISCUSSION OF RESULTS

The results of converter hooding fugitive emission system tests are summarized in Table 1 and Table 2. Table 1 consists of Field, Laboratory and Emission Data. Table 2 contains particle sizing data from the three tests.

During the testing program the following observations and problems were noted.

For the first test, twenty-five minutes per sampling point was used to assure that sampling was done through a complete production cycle. For the second and the third test, twenty minutes per sampling point and a smaller nozzle size was utilized. After 155 minutes of the third test, TRW personnel noticed that the ΔP readings were abnormally low. After checking equipment, the process engineer discovered that the plant operators inadvertently left the dampers on the system in the open position. When the problem was corrected, the Δp reading increased to the appropriate reading. Thus, during 80 minutes of the sampling period of the third test, dilution air entered the duct which resulted in a non-representative sample.

During the Data Reduction, the meter volume was back calculated to account for sulfur dioxide that was removed by the three 10% hydrogen peroxide impingers. The back calculation for sulfur dioxide was accomplished in the following order. First, parts per million sulfur dioxide at standard conditions was calculated. Then parts per million was converted to a fraction by dividing by 10^6 . This number was added to one and the result multiplied by the volume of gas collected through the dry gas meter at standard conditions. The result of multiplication yielded the true gas volume collected at standard conditions. Since SO_2 removal by the peroxide impingers does not reach the dry gas meter, corrected values for dry gas meter volumes (at meter conditions) found on the summary sheets will be slightly higher than those obtained from the field data sheets.

TABLE 1 CONVERTER FUGITIVE EMISSIONS ARSENIC/SO₂ RESULTS

RUN NUMBER	1		2		3		AVERAGE	
	ENGLISH UNITS	METRIC UNITS	ENGLISH UNITS	METRIC UNITS	ENGLISH UNITS	METRIC UNITS	ENGLISH UNITS	METRIC UNITS
I DATE	7/25/78	7/25/78	7/26/78	7/26/78	7/26/78	7/26/78	7/26/78	7/26/78
II STACK PARAMETERS								
Pst - Static Pressure, "Hg (mmHg)	.24	-6.10	.24	-6.10	.24	-6.10	.24	-6.10
Ps - Stack Gas Pressure, "Hg Absolute (mmHg)	25.60	650.24	25.55	648.97	25.55	648.97	25.57	649.39
% CO ₂ - Volume % Dry	.2	.2	.2	.2	.2	.2	.2	.2
% O ₂ - Volume % Dry	20.2	20.2	20.2	20.2	20.2	20.2	20.2	20.2
SO ₂ - Volume % Dry	.38	.38	.48	.48	1.10	1.10	.65	.65
% N ₂ - Volume % Dry	79.22	79.22	79.12	79.12	78.50	78.50	78.95	78.95
Ts - Average Stack Temperature OF (°C)	216.7	102.6	207.5	97.5	216.1	102.3	213.4	100.8
% H ₂ O - % Moisture in Stack Gas, By Volume	1.5	1.5	2.2	2.2	2.2	2.2	2.0	2.0
As - Stack Area, FT ² (M ²)	35.34	3.28	35.34	3.28	35.34	3.28	35.34	3.28
Md - Molecular Weight of Stack Gas, Dry Basis	28.97	28.97	29.01	29.01	29.23	29.23	29.07	29.07
Ms - Molecular Weight of Stack Gas, Wet Basis	28.95	28.95	28.77	28.77	28.98	28.98	28.90	28.90
Vs - Stack Gas Velocity, FT/SEC, (M/SEC)	49.29	15.02	59.49	18.14	40.54	12.36	49.77	15.17
QA - Stack Gas Volumetric Flow at Stack Conditions, ACFM (Nm ³ /min)	104514.5	2960.8	126163.4	3574.0	85957.9	2435.1	105545.3	2989.95
QS - Stack Gas Volumetric Flow at Standard Conditions, DSCFM (Nm ³ /min)	69076.1	1956.8	83345.9	2361.1	56063.1	1588.2	69495.0	1968.7
% EA - Percent Excess Air	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
III TEST CONDITIONS								
Pb - Barometric Pressure, "Hg (mmHg)	25.84	656.34	25.79	655.07	25.79	655.07	25.81	655.49
DN - Sampling Nozzle Diameter, IN. (MM)	.250	6.35	.185	4.70	.185	4.70	.207	5.25
T - Sampling Time, MIN	300.	300.	240.	240.	240.	240.	260.	260.
Vm - Sample Volume, ACF (M ³)	221.95	6.29	131.19	3.72	90.36	2.56	147.83	4.19
Np - Net Sampling Points	12.	12.	12.	12.	12.	12.	12.	12.
Cp - Pitot Tube Coefficient	.84	.84	.84	.84	.84	.84	.84	.84
Tm - Average Meter Temperature OF (°C)	137.9	58.8	104.4	40.2	114.0	45.6	118.8	48.2
Pm - Average Orifice Pressure Drop, "H ₂ O (mmH ₂ O)	1.59	40.39	.78	19.81	.38	9.65	.92	23.28
VLC - Condensate Collected (Impingers and Gel), MLS	-	12.	-	51.7	-	-	36.7	33.5
ΔP - Stack Velocity Head "H ₂ O (mmH ₂ O)	.516	13.11	.756	19.20	.349	8.86	.540	13.72
IV TEST CALCULATIONS								
Vm - Condensed Water Vapor, DSCF (Nm ³)	2.65	.08	2.43	.07	1.63	.05	2.24	.07
Vh - Volume of Gas Sampled at Standard Conditions, DSCF (Nm ³)	169.97	4.82	105.98	3.00	71.69	2.03	115.88	3.28
% H ₂ O - Percent Moisture, By Volume	1.5	1.5	2.2	2.2	2.2	2.2	2.0	2.0
Ms - Molecular Weight of Stack Gas, Wet Basis	28.95	28.95	28.83	28.83	29.05	29.05	28.94	28.94
Vs - Stack Velocity, FT/SEC (M/SEC)	49.29	15.02	59.44	18.12	40.49	12.34	29.74	15.16
% I - Percent Isokinetic	85.3	85.3	98.6	98.6	99.1	99.1	94.3	94.3
V ANALYTICAL DATA								
A) ARSENIC FRONT HALF								
Probe (MG)	-	.71	-	.09	-	.03	-	.28
Cyclone (MG)	-	-	-	-	-	-	-	-
Filter (MG)	-	1.20	-	.60	-	.75	-	.85
Arsenic Front Half Total (MG)	-	1.91	-	.69	-	.78	-	1.1267
PPM, (MG/M ³)	.1272	.3967	.0737	.2298	.1231	.3841	.1080	.3369
#/HR, (KG/HR)	.1026	.0466	.0718	.0326	.0807	.0366	.0850	.0386
B) ARSENIC - IMPINGER COLLECTION								
Impinger #1, 2 (MG)	-	3.577	-	.058	-	.153	-	1.2627
PPM, (MG/M ³)	.2832	.7429	.0062	.0193	.0242	.0753	.0895	.2792
#/HR, (KG/HR)	.1921	.0872	.0060	.0027	.0158	.0072	.0713	.0324
Impinger #3, 4, 5 (MG)	-	-	-	-	-	-	-	-
PPM, (MG/M ³)	-	-	-	-	-	-	-	-
#/HR, (KG/HR)	-	-	-	-	-	-	-	-
C) ARSENIC - IMPINGER TOTAL (MG)	-	3.577	-	.058	-	.153	-	1.2627
PPM, (MG/M ³)	.2832	.7429	.0062	.0193	.0242	.0753	.0895	.2792
#/HR, (KG/HR)	.1921	.0872	.0060	.0027	.0158	.0072	.0713	.0324
D) TOTAL ARSENIC (MG)	-	5.4870	-	.7480	-	.9330	-	2.3894
PPM, (MG/M ³)	.3654	1.1396	.0799	.2491	.1473	.4594	.1975	.6160
#/HR, (KG/HR)	.2947	.1338	.0778	.0353	.0965	.0438	.1563	.0710
E) TOTAL SO ₂ (MG)	-	49329.6	-	38570.4	-	60003.6	-	49301.2
PPM	-	3845.4857	-	4822.2099	-	11090.078	-	6585.9245
(MG/M ³)	-	10244.954	-	12847.0950	-	29545.642	-	17545.897
#/HR, (KG/HR)	2649.4671	1202.6632	4012.9187	1821.5700	6206.6644	2817.3692	4289.6334	1947.2008

TABLE 2. PARTICLE SIZING SUMMARY

(LOCATION-PHELPS DODGE-PLAYAS, N. MEXICO)

LOCATION	TEST	PARTICLE SIZE DISTRIBUTION %			
		>5 μ	3-5 μ	1-3 μ	< 1 μ
CONVERTER	ONE	24.0	8.0	19.0	49.0
CONVERTER	TWO	19.0	13.0	32.0	36.0
CONVERTER	THREE	38.0	6.0	14.0	42.0

TABLE 3.
PROCESS SAMPLE ANALYSIS

SAMPLE	DATE SAMPLED	AS
Flash Furnace Feed	7/26/78 - 7/27/78	.0132%
Flash Furnace Slag	7/26/78 - 7/27/78	.0032%
Flash Furnace Matte	7/26/78 - 7/27/78	.0051%
Electric Furnace Matte	7/26/78 - 7/27/78	.0088%
Electric Furnace Slag	7/27/78 - 7/27/78	.0120%
Converter Slag	7/27/78 - 7/28/78	.0072%
Converter Blister	7/27/78 - 7/28/78	.0139%

SECTION 3

PROCESS DESCRIPTION

SECTION 4

LOCATION OF SAMPLING POINT

Outlet from Converter Hooding System

Samples from converter hooding system were taken from a seven foot diameter horizontal duct located approximately 70 feet above the ground. The sampling ports on the top and side of the duct allowed for vertical and horizontal traverses during sampling. The nearest upstream flow disturbance was 7 duct diameters from the sampling location. The nearest downstream flow disturbance was greater than ten duct diameters from the sampling location, where there was a 90° bend. Twelve traverse points, six on each traverse, were used. Sampling was done for twenty minutes per point to provide sampling through a complete slag and copper blow cycle. Figure 1 illustrates the cross-sectional view.

Traverse point locations

Tra- verse Point Loca- tions	Fraction of Stack I.D.	Distance From Inside Wall (in)
1	.044	3.66
2	.146	12.30
3	.296	24.85
4	.704	59.15
5	.854	71.70
6	.956	80.34

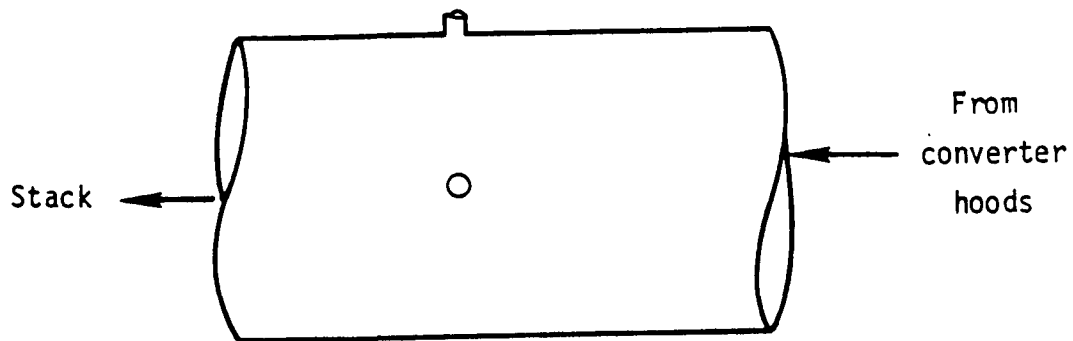
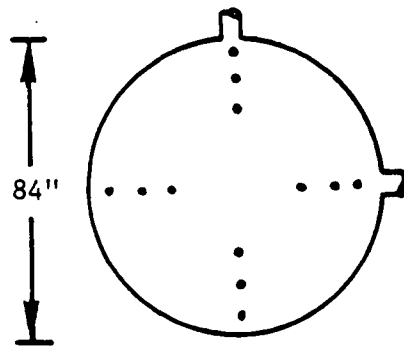


Figure 1. Converter fugitive emission duct

SECTION 5

SAMPLING AND ANALYTICAL PROCEDURE

A. Arsenic/Sulfur Dioxide Sampling

The sampling train used for arsenic/sulfur dioxide collection consists of an EPA method 5 train modified by adding two additional impingers in series to the four used in the method 5 train. The first two impingers contained 150 milliliters of distilled water each, the third impinger was empty, the fourth, fifth and sixth impingers contained 150 milliliters of 10% hydrogen peroxide each. The seventh impinger contained 250 grams of silica gel. Sampling train schematic is presented in figure 2.

Before each test a velocity traverse of the stack was done to determine the average stack temperature and velocity pressure. The velocity traverse was done according to EPA Methods 1 and 2. A grab sample of the stack gas was taken and analyzed with a Fryite apparatus for CO₂. Before the first test at each location the moisture content of the gas stream was estimated by either condensation in impingers as in EPA Method 4, or by wet and dry bulb thermometer if the stack gas temperature was below 120°F.

The arsenic/sulfur dioxide samples were taken at traverse points at the center of equal areas within the stack. The number of traverse points was determined by the number of duct diameters upstream and downstream from the nearest flow disturbances. The sampling rate was adjusted to isokinetic conditions using a nomograph which had been set based on the preliminary velocity traverse data, and moisture estimate.

The sampling time per traverse point was 20-25 minutes, to assure sampling during the whole process cycle.

Leak checks of the sampling train were done at the beginning of each test, just before the sampling port change, and at the end of the test. At the end of each test the sampling train was inspected for cracked or broken glassware, and to assure that the filter remained intact.

Sample Recovery

The sampling nozzle and probe liner were rinsed with 0.1N NaOH and brushed out with a nylon bristle brush with a teflon tubing handle. The remainder of the sampling train was removed to the mobile laboratory. The front half of the filter and connecting glassware were rinsed with 0.1N NaOH and this rinse was added to the nozzle and probe rinse. The filter was removed from the filter holder and placed in a polyethylene container, which was labeled and sealed. The first three impinger solutions were measured and placed in a glass sample container along with a 0.1N NaOH rinse of the impingers. The contents of the fourth, fifth, and sixth impingers were measured and placed in a separate glass sample container along with a distilled water rinse of the impingers. The silica gel in the seventh impinger was weighed to the nearest 0.5 grams, and regenerated.

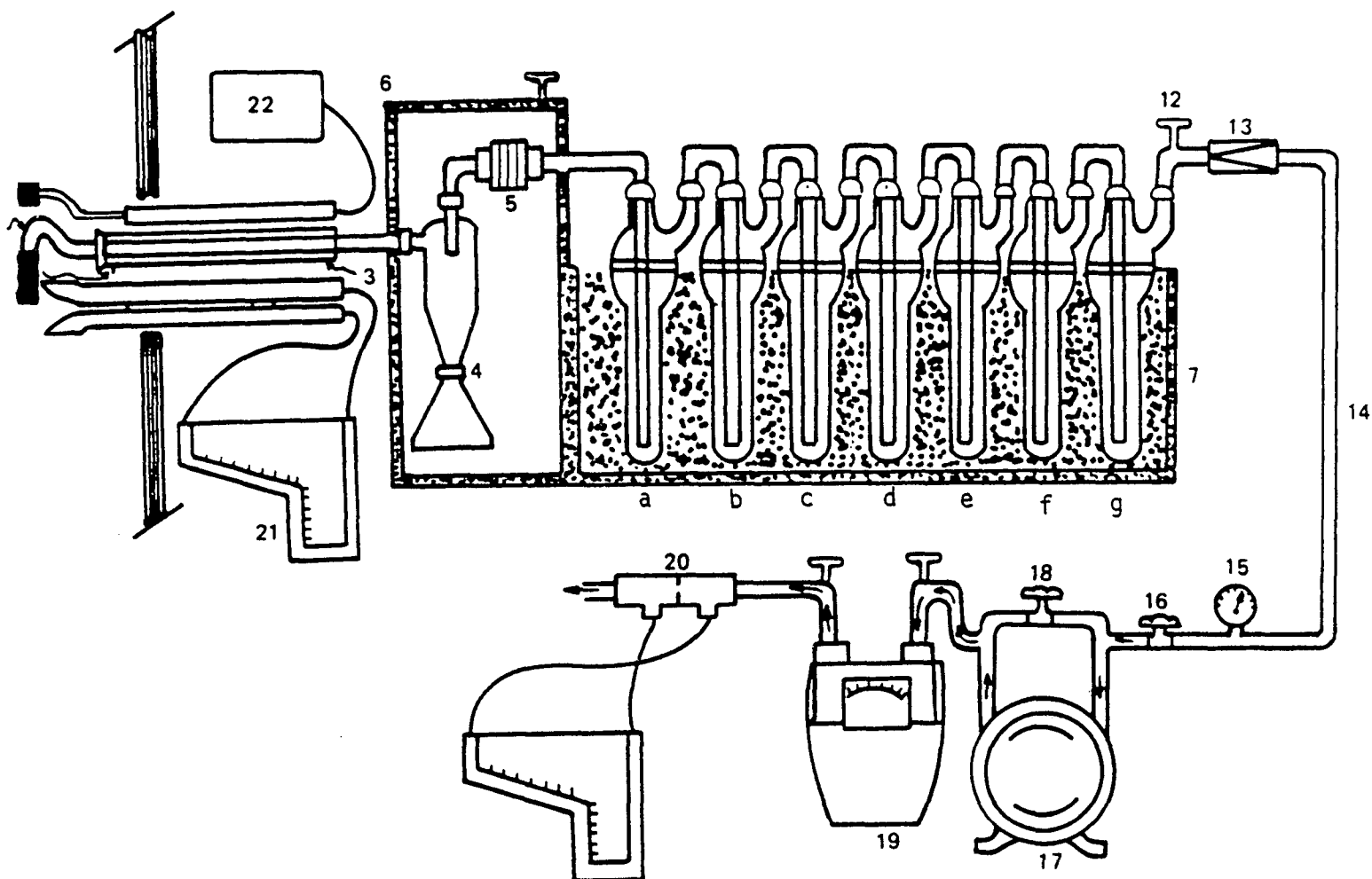


Figure 2. Arsenic sulfur dioxide train

KEY

- | | | |
|----------------------------|-----------------------|---------------------|
| 1. Calibrated Nozzle | c. Empty | 16. Main Valve |
| 2. Heated Probe | d. 150 mls H_2O_2 | 17. Air Tight Pump |
| 3. Type S Pitot | e. 150 mls H_2O_2 | 18. By-Pass Valve |
| 4. Cyclone Assembly | f. 150 mls H_2O_2 | 19. Dry Test Meter |
| 5. Filter Holder | g. 250 gms. Silca Gel | 20. Orifice |
| 6. Heated Box | 12. Thermometer | 21. Pitot Manometer |
| 7. Ice Bath with Impingers | 13. Check Valve | 22. Thermometer |
| a. 150 mls H_2O | 14. Vacuum Line | |
| b. 150 mls H_2O | 15. Vacuum Gauge | |

B. Analysis

The samples were analyzed for sulfur dioxide by taking an aliquot of the hydrogen peroxide impinger solutions and titrating with barium perchlorate solution and thorin indicator as described in EPA Method 6 (Determination of Sulfur Dioxide Emissions from Stationary Sources).

Arsenic-Analysis

1. Filter - warm filter and loose particulate matter with 50 ml 0.1N NaOH for about 15 minutes. Add 10 ml concentrated HNO_3 and bring to boil for 15 minutes. Filter solution through no. 41 Whatman paper and wash with hot water. Evaporate filtrate, cool, redissolve in 5 ml of 1:1 HNO_3 , transfer to a 50 ml volumetric flask and dilute.

2. Probe Wash and Impinger Solns - These should be combined and a 200 ml sample withdrawn. Add 10 ml concentrated HNO_3 and evaporate to a few milliliters. Redissolve with 5 ml 1:1 HNO_3 and dilute to 50 mls. A reagent blank should be carried through the same procedure. The resulting blank solution should be used in the dilution of standards to matrix match samples and standards.

3. All the samples prepared above should be screened by air/acetylene flame. The filter samples may require dilution with 0.8N HNO_3 . Impinger solutions containing more than 25 mg/l of arsenic should be diluted since linearity decreases dramatically above that level.

Since an entrained hydrogen flame provides about five times as much sensitivity as the air/acetylene flame, a matrix check of a sample in a hydrogen flame should be carried out by the method of standard additions, and compared with a value obtained from matrix matched standards in a hydrogen flame. If values are comparable ($\pm 5\%$) the air entrained hydrogen flame value should be used.

Due to high concentrations of copper on the filter an air/acetylene flame should always be used to dissociate any AsCu compounds stable in the cooler hydrogen flame.

4. For samples below the 1mg/l level, hydride generation is necessary. An appropriate aliquot of digested sample in 0.8N HNO_3 containing less than about 10ug of arsenic is chosen (some screening may be necessary). Five milliliters of concentrated H_2SO_4 is added to the sample which is then placed on a hot plate until SO_3 fumes fill the flask. A reduction in volume to about 5 ml or less may be necessary. This step removes HNO_3 which causes a violent

reaction when the reducing agent is added resulting in poor reproducibility and lowered sensitivity by producing I_2 , NO_2 and possibly other species.

One milliliter of 30% KI and 1 ml of 30% $SnCl_2$ are added to the sample, the former to act as catalyst in hydride formation and the latter to reduce all the arsenic to As^{+3} . The sample is then diluted to about 15 ml, and 15 ml of concentrated HCl is added. Powdered Zn (or $NABH_4$) is then added, the reaction vessel is immediately closed and the nitrogen or argon carrier flow initiated. A peak should be produced within a few seconds.

C. Particle Sizing

The size distribution of the particulates was estimated with a Brinks six stage impactor. Figure 3 is a diagram of the Brinks impactor sampling system used.

Sampling Procedure

The Brinks impactor was introduced into the gas stream through the sampling port with the nozzle facing the flow of gas. The sampling pump was turned on and the pressure drop across the impactor adjusted with the by-pass valve. The pressure drop across the impactor was read from the mercury manometer. The pressure drop is proportional to the flowrate through the impactor, and to the particle sizing cutoffs of each stage.

Sampling time at each location varied according to grain loading in the particular duct being sampled. The impactor plates were inspected after each test and the sampling time altered on the succeeding test to optimize the amount of particulate sampled. Sampling for too long results in carry-over from one stage to the next, while sampling for too short a time can result in insufficient particulate on one or more of the stages for accurate analysis.

Analysis

The impactor plates and filters had been dessicated to a constant weight before the tests, and tare weights taken. After the test the same procedure was used to get the final weights of the impactor plates and filters. The difference between the tare weight and final weight is the weight of particulate collected.

The cumulative percentage of the total particulate catch which was collected in each stage was plotted on semi-log graph paper against the size cutoffs for each stage. The resulting best fit straight line is the estimated particle size distribution of the collected particulates.¹

¹ Brink, J.A. "Cascade Impactor for Adiabatic Measurements," Industrial and Engineering Chemistry, Vol. 5, No. 4, April 1958, page 647

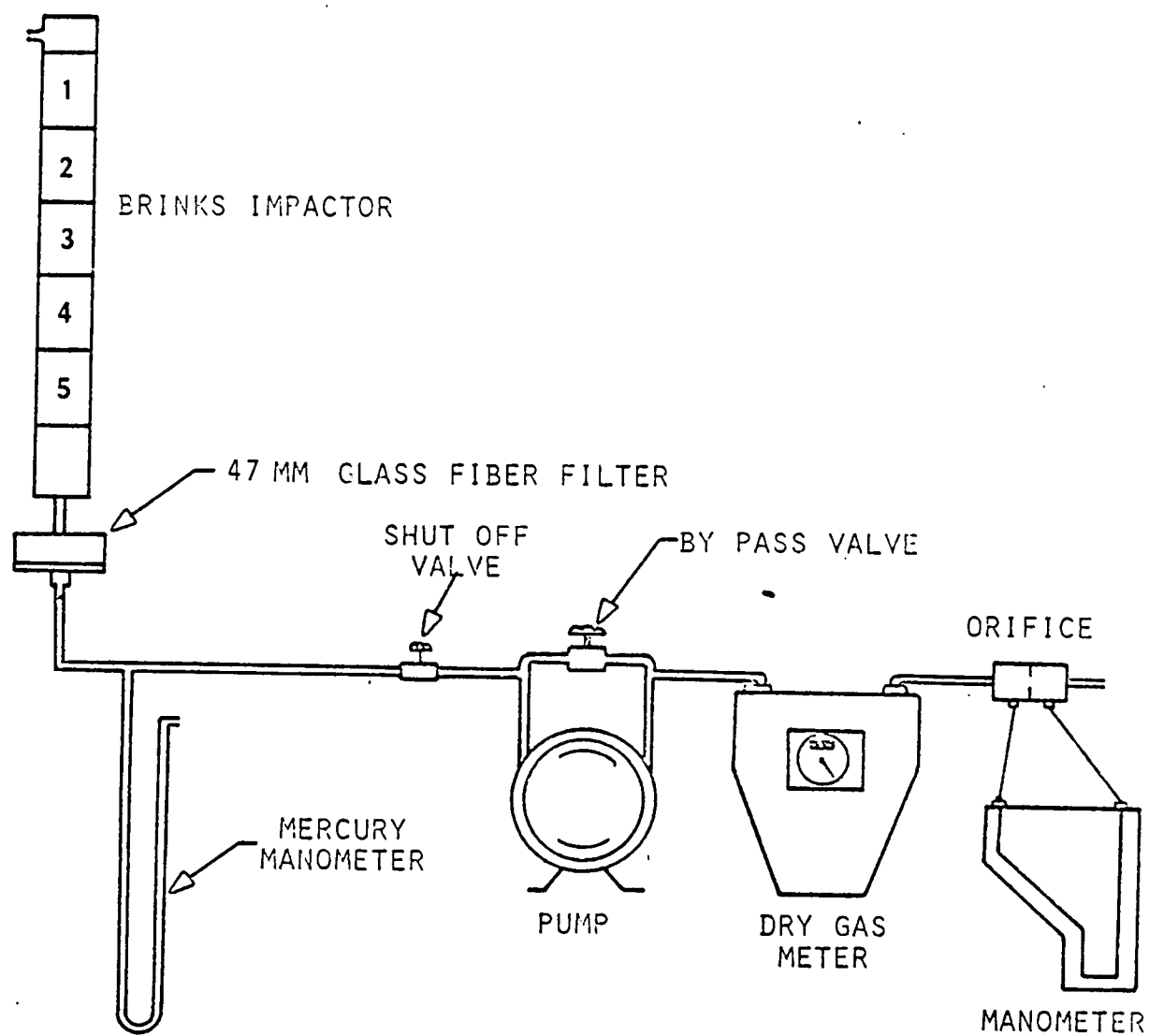


Figure 3. Brinks impactor particle sizing system schematic