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INDUSTRIAL HYGIENE SURVEY

OF

THE WHITE PINE COPPER COMPANY

White Pine, Michigan

DATES OF SURVEY:
November 27 - December 1, 1972

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16. Abstract (Limit: 200 words)

Air samples were collected to determine worker exposure to lead (7439921) (Pb), cadmium (7440439) (Cd), copper (7440508) (Cu), zinc (7440666) (zn), arsenic (7440382) (As) and sulfur-dioxide (7446095) (S02) at the White Pine Copper Company (SIC-3325) in White Pine, Michigan. None of the samples were in excess of the then existing OSHA standards. The concentrations for Pb, zinc-oxide fumes, Cd dust, Cd fume and arsenic were 0.2, 5, 0.2, 0.1 and 0.5 milligrams per cubic meter (mg/cu m), respectively. Samples for Cu dust taken above the reverberatory furnaces were in excess of the OSHA standard of 0.1 and 1mg/cu m. The estimated time weight average exposure for S02 was less than 1 part per million (ppm). The authors recommend urine sampling to ascertain Cu, Pb, Cd, Zn, and As concentrations. They recommend improved cleaning and better handling of materials, extending the length of the hood over the converter in the smelting building and the use of appropriate hearing protection against high noise levels.

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PLACE VISITED : White Pine Copper Company
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Patrick Harris, *Industrial Hygiene Technician*

UNION : United Steel Workers Local 5024

PURPOSE OF VISIT : To conduct a sampling survey to establish worker exposure to sulfur dioxide, copper, arsenic and other trace metals in the smelting and casting operations.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is responsible for criteria development and epidemiological research of occupational exposures to materials which may produce disease or disability in the working population. Due to a higher suspected incidence of lung cancer in copper smelter workers, a study initiated by the Division of Technical Services, NIOSH, is underway to determine worker exposure to materials such as sulfur dioxide, arsenic, copper dust and fume and other metals in several copper smelters in the West.

The White Pine Copper Company in White Pine, Michigan, works an ore body low in both arsenic and sulfur. This particular smelter was surveyed since this facility has a working population which might act as an epidemiological control group for other copper smelter populations that are exposed to relatively high concentrations of arsenic and sulfur dioxide. This survey also provided an opportunity to compare various sulfur dioxide sampling techniques.

In this survey, the NIOSH personnel of the Division of Field Studies and Clinical Investigations from Cincinnati, Ohio were responsible mainly for the sampling of copper, arsenic, and other trace metals. Since the Division of Technical Services in Salt Lake City, Utah, had already completed a number of copper smelter surveys and has considerable experience in sampling for sulfur dioxide, personnel from this Division were present to take samples for this gas.

NIOSH personnel (Division of Field Studies and Clinical Investigations) conducted a preliminary walk-through survey of the smelter operation on October 11, 1972 and prepared a report that was distributed to the plant, the NIOSH Region V Program Director, and the State Health Department on October 26, 1972. The reader is refered to this earlier report for information concerning the plant layout, medical, safety and industrial hygiene programs, and the process operations.

SAMPLING PROCEDURE

Lead, Cadmium, Copper, Zinc and Arsenic

To sample for the above indicated particulates, total airborne samples (general area and personal) were collected on 0.8µ pore size Millipore AA filters drawn at a flow rate of 1.9 l/min. by a MSA battery powered pump. The samples were collected for approximately a six-hour time period in order to collect enough particulates for accurate chemical analysis and to obtain a representative sample for an entire work shift for a particular location or worker.

The amount of the trace metals (lead, cadmium, copper, and zinc) were determined simultaneously on the same filters by atomic absorption.[1] Separate filters were used for the determination of arsenic. The arsenic samples were wet-ashed with a 1:1 sulfuric-nitric acid mixture and then analyzed by an atomic absorption spectrophotometer-trace metal accessory combination.[2] Both the trace metal and arsenic analyses were performed by the Physical and Chemical Analysis Branch, Division of Laboratories and Criteria Development, Cincinnati, Ohio.

Sulfur Dioxide (SO_2)

Individual air samples (one-half to one hour duration) were collected by midget impingers and analyzed at the plant site using the West-Gaeke Method. (Figure 1) Samples also were taken over a longer time period using the hydrogen peroxide method.[3] These samples were collected in midget impingers filled with a hydrogen peroxide solution and attached to sequential samplers that were left in fixed locations. The sequential samplers were adjusted to give a continuous series of individual impinger samples of one or two hours duration for a total of about 24 hours. These SO_2 samples were analyzed by NIOSH at the Western Area Occupational Health Laboratory, Salt Lake City, Utah.

Grab samples and instantaneous measurements of SO_2 also were taken using Drager-type sulfur dioxide indicator tubes and an instrument manufactured by Combustion Equipment Association. The Drager tube operates on the principle that a reaction takes place between the SO_2 and the indicator tube packing which results in a color change, with the length of stain being proportional to the SO_2 concentration. The Combustion Equipment instrument requires one minute to draw a known volume of air into a hydrogen peroxide solution which reacts with any SO_2 present to form sulfuric acid and produce a change in conductivity proportional to the concentration of SO_2. This change in conductivity of the solution is measured by the instrument and is converted to the airborne concentration of

SO_2 on a previously calibrated indicating dial.

RESULTS AND DISCUSSION

Lead, Cadmium, Copper, Zinc and Arsenic

The airborne concentrations of lead, cadmium, copper and zinc found in the personal and general air samples in the reverberatory, converter, fire refining, and casting furnace areas (smelter building) are listed in Table 1 while those for arsenic are presented in Table 2. The present Occupational Safety and Health Administration (OSHA) standards for lead, zinc oxide fume, cadmium dust (as Cd), cadmium fume (as Cd) and arsenic (as As) are 0.2, 5, 0.2, 0.1, and 0.5 mg/m^3 respectively. It does not appear that airborne levels of lead, zinc, cadmium or arsenic are excessive in the smelter building since not one of the samples showed a result over the OSHA standards for any of these four contaminants. This is not surprising since these metals are present in the powdered feed (concentrate) of the reverberatory furnaces in very small percentages, (see assay done by plant, Figure 2) and the source of most dust exposure for the job-types sampled was the concentrate.

The OSHA standard for copper is 0.1 mg/m^3 and 1 mg/m^3 if it is an airborne dust or mist. Unfortunately the analytical method can not differentiate between copper dust and fume. One can only assume from the nature of the smelting operations and where the man works whether copper is most likely to be present as a dust or as a fume. Some of the samples of copper dust taken above the reverberatory furnaces appear to be in excess of the dust standard. As a group, the brick masons were exposed to the highest concentrations of copper dust. The workers in the converter and fire-refining areas are subjected to not only copper dust in the concentrate, but also perhaps copper fumes from these furnaces. If the OSHA standard for copper fume is applied, then some of the results from these areas are relatively high. These present OSHA standards, however, are based on irritation which is predominantly caused by exposure to soluble copper compounds. Exposure to insoluble copper compounds <u>may</u> not be a serious a health hazard.

Since the OSHA standards for these contaminants are based on 8-hour time weighted average (TWA) exposures, an estimate was made of the TWA exposure for each job-type sampled. (Table 3) This gives values which may be compared to the standards directly. These estimates were arrived at by first determining the approximate airborne concentration of the contaminant at each area of the smelter from the individual general air sample results. From information provided by the company and the survey team observations, a rough time study was done for each job-type. The average time spent by the job-type in each area was multiplied by the airborne concentration of the contaminant found there, and to determine the TWA exposure for a given job-type from the area samples, these products were added up and divided by the 8-hour time of exposure.

The personal sample results for the trace metals were taken to represent an average exposure for that shift for that given job-type. Any applicable personal sample results were averaged in with the TWA exposure obtained from the general air sample results to give the estimates shown in Table 3.

The TWA estimates for lead, cadmium, zinc, and arsenic reflect the very low individual sample results. Some of the job-types are estimated to have a TWA exposure to copper above the OSHA standards, but lower than what might be implied by only looking at the individual sample results. The tripper man probably would be exposed to lower concentrations of trace metals than the values given in Table 3 since they usually wear a respirator while charging the reverberatory furnace but this personal protection was not taken into account when arriving at the TWA estimates. No other workers in the smelter building were observed wearing a respirator for any operation.

Sulfur Dioxide (SO_2)

The determination of SO_2 by the Drager tubes are presented in Table 4. Table 5 contains the SO_2 determinations by the hydrogen peroxide method for four different locations in the smelter. Results of the midget impinger samples analyzed for sulfur dioxide by the West-Gaeke method are presented in Table 6. Results are not available for the Combustion Equipment instrument because of its mechanical failure.

A direct comparison between the West-Gaeke and hydrogen peroxide methods can not be made since the impinger samples analyzed by the West-Gaeke method were for a different length of time than those used for the peroxide method.

The highest concentrations of SO_2 were detected in the area of the reverberatory furnaces, especially above these furnaces on the charging floor. However, these concentrations reached peak values for only short periods of time. The results presented in Table 5 show there was a similar pattern of periodic peaks of SO_2 on the operator's floor by the reverberatory furnaces, but the concentration of SO_2 were generally lower than above the furnaces. All of the samples taken by the converting, fire refining, and casting operations showed very low levels of sulfur dioxide to be present.

As was done with the results for arsenic and the trace metals, calculations have been made to provide an estimate of the TWA exposure to SO_2 for certain job-types in the smelting operation (Table 3). This gives a value which may be compared to the OSHA standard of an average exposure of 5ppm for an 8-hour workday. These estimates were arrived at by using the method of combining information from the general area sample results with the work routine of the employee, as described in the preceding section.

It appears that only those workers who are routinely above the reverberatory furnaces on the charging floor, e.g., the trippers, are subjected to any substantial level of SO_2. Laborers and maintenance personnel who periodically work here might also receive a significant exposure. Those workers in the converter, fire refining and casting areas are estimated to be exposed to a TWA exposure of less than 1 ppm SO_2.

It should be noted that even though there is no ceiling value included in the OSHA standard for sulfur dioxide, various studies indicate that high enough concentrations of SO_2 for even a short period of time can be harmful. A concentration of 20 ppm is the least concentration causing coughing or eye irritation. It is recommended that an exposure to 50 ppm SO_2 not be permitted for more than one hour, and concentrations of 400-500 ppm are considered dangerous to life for even short exposures.[4]

RECOMMENDATIONS AND CONCLUSIONS

Based on information and observations of the walk-through survey and the results of this sampling survey, the following recommendations and conclusions are made:

1. The worker exposure to lead, cadmium, zinc, and arsenic is quite low. There does not appear to be any potentially hazardous exposures to these substances in the smelter building. This is largely due to these elements being in the concentrate in only minute quantities. Urine samples could be obtained from personnel in the smelter area to ascertain if levels of these metals are within normal limits.[5] [6]

2.. The levels of copper dust and fumes to which workers in the smelter are subjected exceed the present OSHA standards in some cases, particularly in the area of the reverberatory furnaces. Since the copper in the concentrate is present mostly as insoluble compounds, the potential health hazard is probably less than the results indicate. The urine of those workers who are exposed to the highest airborne concentration of the concentrate could be periodically monitored for copper as a test for the amount of the metal which is actually metabolized.[7]

Exposure to total airborne dust and copper could be lowered by improving housekeeping and handling of the concentrate material, especially on the charging floor above the reverberatory furnace. The reverberatory furnaces now operated under a neutral pressure, rather than positive pressure, to lessen the amount of the concentrate being blown back into the operating room. This source of "spillage" would be reduced even more if these reverberatory furnaces could be operated under slight negative pressure. Another approach to improve housekeeping would be to enclose the conveyor system on the charge floor.

3. It should be noted that since the OSHA standards for arsenic and the trace metals are all based on the total airborne fraction, only gross dust samples were taken. Some thought should be given to sampling and developing standards for these contaminants for the respirable ariborne fraction since this might result in a better index of the worker's actual exposure.

4. Worker exposure to sulfur dioxide in the smelter building is generally below the present OSHA standard of 5 ppm for an 8-hour workday. The highest concentrations of sulfur dioxide occurred near the reverberatory furnaces, predominantly on the charging floor.

Perhaps the area where it would be easiest to reduce the level of sulfur dioxide would be at the tapping stations at the reverberatory furnaces. Extending the length of the hoods would increase the effectiveness of the ventilation and reduce sulfur dioxide exposure to other workers in the reverberatory furnace area as well as the tappers. It also should be relatively simple to lower the amount of sulfur dioxide discharged from the converter furnaces into the smelter building. When these furnaces are rotated, the opening on the top of the converter goes away from the overhead hooding which allows gases to escape into the building. The hooding over the converter could be enlarged or the method of operation could somehow be changed so that the furnaces would not have to be rotated as frequently.

5. A noise measurement taken by the company gave a result of 120 dBA for punching the convertor tuyeres, which is above the OSHA ceiling value for noise of 115 dBA. Even though this job only requires a short period of exposure to this high level of noise, the company should require and furnish appropriate hearing protection to the punchers until such time as this noise problem can be alleviated.

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APPENDIX

TABLE	DESCRIPTION
1	Gross Particulate Concentrations of Trace Metals
2	Gross Airborne Concentration of Arsenic
3	Estimated 8-Hour Time Weighted Average Exposure to Trace Metals, Arsenic, and Sulfur Dioxide
4	Drager Tube Sample Results for Sulfur Dioxide
5	Hydrogen Peroxide Results for Sulfur Dioxide
6	West Gaeke Results for Sulfur Dioxide

FIGURE	DESCRIPTION
1	West-Gaeke Method
2	Typical Analysis White Pine Concentrate
3	Hydrogen Peroxide Method for Sulfur Dioxide

TABLE 1

GROSS PARTICULATE CONCENTRATIONS OF TRACE METALS

WHITE PINE COPPER COMPANY

November 27 - December 1, 1972

JOB OR LOCATION	*SAMPLE #*	*DATE TAKEN*	*COPPER*	*LEAD*	*ZINC*	*CADMIUM*
			CONCENTRATION - (mg/m³)			
Reverberatory Furnace Area - Personal Samples						
Reverberatory Furnace Operator	1	11-27-72	0.762	0.005	0.010	0.005
Reverberatory Furnace Operator	20	11-28-72	0.765	N.D.*	0.010	0.003
Tripper Man	6	11-27-72	0.628	0.002	0.004	0.005
Tripper Man	10	11-27-72	0.301	N.D.	0.005	0.011
Flue Duct Man	5	11-27-72	0.131	N.D.	0.004	0.004
Conveyor Belt Operator	7	11-27-72	0.722	0.004	0.009	0.012
Laborer	8	11-27-72	0.492	0.002	0.004	0.004
Laborer	9	11-27-72	0.462	N.D.	0.015	0.005
Laborer *(cleaning the conveyor belts)*	26	11-28-72	3.171	0.006	0.018	0.004
Tapper	4	11-27-72	0.336	0.003	0.014	0.019
Tapper Helper	28	11-28-72	0.378	N.D.	0.017	0.012
Brick Mason	15	11-28-72	0.630	0.004	0.007	0.006
Brick Mason	16	11-28-72	2.902	0.010	0.021	0.042
Brick Mason	19	11-28-72	4.563	0.008	0.025	0.045
Brick Mason	21	11-28-72	13.673	N.D.	0.005	0.004
Research Technician	22	11-28-72	0.165	N.D.	0.008	0.009
Reverberatory Furnace Area - General Air Samples - Operating Floor Level						
By control room near Reverb. #1	36	11-29-72	0.087	0.005	0.020	0.014
By control room near Reverb. #1	47	11-29-72	0.413	0.005	0.013	0.016
By tapping station, Reverb. #1	45	11-29-72	0.359	0.003	0.006	0.006

Table 1 (continued)

JOB OR LOCATION	*SAMPLE #*	*DATE TAKEN*	*COPPER*	*LEAD*	*ZINC*	*CADMIUM*
			CONCENTRATION - (mg/m³)			
Between #1 & #2 Reverbs.	33	11-28-72	0.165	N.D.	N.D.	0.001
Between #1 & #2 Reverbs.	53	11-29-72	0.350	0.002	0.006	0.004
In front of Reverb #2	31	11-28-72	0.067	N.D.	0.006	N.D.
In front of Reverb #2	49	11-29-72	0.160	0.005	0.031	0.022
<u>Reverberatory Furnace Area - Upstairs above Furnaces - General Air Samples</u>						
Between Reverb. #1 & Waste Heat Boiler	59	11-30-72	0.400	0.004	0.010	0.012
Above Reverb. #1	38	11-29-72	0.394	0.005	0.012	0.020
On Conveyor for Reverb. #1	57	11-30-72	2.375	0.013	0.021	0.053
Catwalk Between Reverb. #1 & #2	40	11-29-72	0.762	0.005	0.020	0.019
Above Reverb #2	27	11-28-72	2.336	0.008	0.016	0.052
Above Reverb #2	55	11-30-72	0.274	0.002	0.005	0.003
Above and towards front of Reverb #2	61	11-30-72	0.480	0.006	0.004	0.004
<u>Converter Furnace Area - Personal Samples</u>						
Puncher	24	11-28-72	0.075	N.D.	0.002	0.002
Puncher - Conv. #1	2	11-27-72	0.213	N.D.	0.003	0.005
<u>Converter Furance Area - General Air Samples</u>						
On platform by converter #1	67	11-30-72	0.390	0.004	0.005	0.005
By control panel for #2 furnace	69	11-30-72	0.051	N.D.	0.005	0.002
By control panel for converter #2	63	11-30-72	0.110	N.D.	0.003	0.002
Rear deck by converter #2	35	11-29-72	0.143	0.003	0.016	0.012
Platform in front of converter #2	65	11-30-72	0.111	N.D.	0.003	0.003
<u>Fire Refining Area - Personal Samples</u>						
Furnace Operator	14	11-27-72	0.059	N.D.	0.001	N.D.
Rappler	13	11-27-72	0.104	N.D.	0.002	0.001

Table 1 (continued)

JOB OR LOCATION	SAMPLE #	DATE TAKEN	COPPER	LEAD	ZINC	CADMIUM
			CONCENTRATION - (mg/m^3)			
<u>Fire Refining Area - General Air Samples</u>						
In front of fire refining furnaces	29	11-28-72	0.081	0.003	0.001	N.D.
In front of fire refining furnaces	43	11-29-72	0.154	0.006	0.009	0.007
By discharge spout where pour furnace	77	11-30-72	0.145	0.003	0.003	N.D.
Beside furnace where are skimming	79	11-30-72	0.367	0.003	N.D.	N.D.
<u>Casting Area - General Air Samples</u>						
In control booth where operate saw for rods	73	11-30-72	0.025	N.D.	0.002	N.D.
By casting furnace	75	11-30-72	0.146	0.009	0.003	N.D.
<u>Miscellaneous</u>						
Personal - Craneman	12	11-27-72	0.082	N.D.	0.002	0.001
GA on platform in front of holding furnace	71	11-30-72	0.164	0.002	0.006	0.006
GA operating floor level by waste heat boiler #2	51	11-29-72	0.220	0.002	0.006	0.004

* NONE DETECTED

<u>OSHA STANDARDS</u>

Copper dust or mist	1 mg/m^3
Copper fume	0.1 mg/m^3
Inorganic lead	0.2 mg/m^3
Zinc oxide fume	5 mg/m^3
Cadmium dust (as Cd)	0.2 mg/m^3
Cadmium fume (as Cd)	0.1 mg/m^3

TABLE 2

GROSS AIRBORNE CONCENTRATION OF ARSENIC

WHITE PINE COPPER COMPANY

November 27 - December 1, 1972

JOB OR LOCATION	*SAMPLE #*	*DATE TAKEN*	*ARSENIC ($\mu g/m^3$)*
<u>Reverberatory Furnace Area - Personal Samples</u>			
Laborer - by conveyor belt above reverb. furnace	11	11-27-72	3.2
Brick Mason - Reverb. furnace	17	11-28-72	13.1
Brick Mason - Reverb. furnace	18	11-28-72	10.5
Tripper Man - Reverb. furnace	25	11-28-72	3.8
<u>Reverberatory Furnace Area - General Air Samples</u>			
By control room near Reverb. #1	37	11-29-72	7.3
By control room near Reverb. #1	48	11-29-72	5.4
By tapping station, Reverb. #1	46	11-29-72	5.4
Between #1 & #2 Reverbs.	34	11-28-72	<0.2
Between #1 & #2 Reverbs.	54	11-29-72	2.8
In front of Reverb. #2	32	11-28-72	1.3
In front of Reverb. #2	50	11-29-72	9.0
<u>Reverberatory Furnace Area - Upstairs above Furnaces - General Air Samples</u>			
Between Reverb. #1 and Waste Heat Boiler	60	11-30-72	3.1
Above Reverb. #1	39	11-29-72	5.5
On conveyor for Reverb. #1	58	11-30-72	14.0
Catwalk between Reverb. #1 & #2	41	11-29-72	11.5
Above Reverb. #2	56	11-30-72	3.8
Above and towards front of #2	62	11-30-72	8.0

Table 2 (continued)

JOB OR LOCATION	*SAMPLE #*	*DATE TAKEN*	*ARSENIC ($\mu g/m^3$)*
Converter Furnace Area - Personal Samples			
Puncher - Converter #1	3	11-27-72	5.2
Brick Mason - Converter	23	11-27-72	14.2
Converter Furnace Area - General Area Samples			
On Platform by converter furnace #1	68	11-30-72	11.3
By control panel by converter furnace #2	70	11-30-72	1.7
By control panel by converter furnace #2	64	11-30-72	3.5
Rear deck by converter #2	42	11-29-72	10.3
Platform in front of converter #2	66	11-30-72	4.2
Fire Refining Area - General Area Samples			
In front of fire refining furnaces	44	11-29-72	8.1
By discharge spout where pour refining furnaces	78	11-30-72	1.0
By side furnace where skimming	80	11-30-72	4.2
Casting Area - General Air Samples			
In control booth where cut copper rods	74	11-30-72	NONE DETECTED
By casting furnace	76	11-30-72	0.9
Miscellaneous			
On platform in front of holding furnace	72	11-30-72	5.1
Operating floor level by waste heat boiler #2	52	11-29-72	2.3

OSHA STANDARD

Arsenic and compounds (as As) - 0.5 mg/m^3 or 500 $\mu g/m^3$

TABLE 3

ESTIMATED 8-HOUR TIME WEIGHTED AVERAGE EXPOSURE
TO
TRACE METALS, ARSENIC, AND SULFUR DIOXIDE

WHITE PINE COPPER COMPANY

November 27 - December 1, 1972

JOB	*ESTIMATED TIME WEIGHTED AVERAGE EXPOSURE*					
	Copper *mg/m³*	*Lead* *mg/m³*	*Zinc* *mg/m³*	*Cadmium* *mg/m³*	*Arsenic* *µg/m³*	*Sulfur Dioxide* *ppm*
Tripper Man - charges Reverberatory furnace[1]	0.57	0.002	0.010	0.011	6.1	4-6
Tapper	0.29	0.002	0.013	0.012	4.0	2-4
Reverberatory furnace operator	0.76	0.002	0.010	0.004	5.0	2-4
Brick Mason	5.44	0.006	0.015	0.024	11.6	1-2
Puncher	0.15	N.D.	0.002	0.002	3.0	<1
Converter furnace operator	0.15	N.D.	0.002	0.002	2.5	<1
Fire Refining furnace operator	0.10	N.D.	0.001	N.D.	4.0	<1
Copper Slab Saw operator	0.08	0.05	0.002	N.D.	<1	<1
Casting Furnace operator	0.08	0.05	0.002	N.D.	<1	<1
Craneman	0.08	0.001	0.002	0.001	<1	<1

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[1] *Even though these men occasionally wear respirators, this is not taken into account at arriving at these estimated values.*

OSHA STANDARDS

Copper dust or mist	1 mg/m³	Cadmium Dust-(as Cd)	0.2 mg/m³
Copper fumes	0.1 mg/m³	Cadmium Fume-(as Cd)	0.1 mg/m³
Inorganic lead	0.2 mg/m³	Arsenic and Compounds-(as)As	0.5 mg/r
Zinc Oxide fume	0.1 mg/m³	Sulfur Dioxide-5 ppm	

TABLE 4

DRAGER TUBE SAMPLE RESULTS FOR SULFUR DIOXIDE

WHITE PINE COPPER COMPANY

NOVEMBER 27 - DECEMBER 1, 1972

Date	Time	Conc.	Location
11/29	1430	10	E. side, No. 2 reverb, 10' below charge floor
"	1434	2	N.W. corner, No. 1 reverb, on charge floor
"	1440	5	N.E. corner, No. 1 reverb, on charge floor
"	1445	14	S.E. corner, No. 2 reverb, on charge floor
"	1450	0	N.W. corner, No. 2 reverb, on operator's floor
"	1455	2	Between No. 1 and No. 2 reverbs, on operator's floor
"	1500	<1	E. side, No. 1 reverb, on operator's floor
"	1505	5	S. side, No. 1 reverb, on charge floor
"	1550	0	E. side, No. 1 reverb, on operator's floor
"	1555	6	E. side, No. 2 reverb, on charge floor
"	1600	0	S. side, between reverbs, along deck of crane aisle
"	1730	5	E. side, No. 2 reverb, on charge floor
"	2040	5	E. side, No. 2 reverb, on charge floor
"	2115	5	E. side, No. 2 reverb, on charge floor
11/30	1415	0	Casting room, saw area
"	1430	0	Skim deck, No. 2 convertor

OSHA STANDARD

Sulfur Dioxide 5 ppm

TABLE 5

HYDROGEN PEROXIDE RESULTS FOR SULFUR DIOXIDE

WHITE PINE COPPER COMPANY
NOVEMBER 27 - DECEMBER 1, 1972

Date	Time	Conc. (ppm)	Location
11/29	1233-1400	2.4	Between No. 1 and No. 2 reverbs, on operator's floor
	1400-1600	3.0	
	1600-1800	4.3	
	1800-2000	1.7	
	2000-2200	0.8	
	2200-2400	0.9	
11/30	0000-0200	2.4	
	0200-0400	7.1	
	0400-0600	0.3	
	0600-0800	1.3	
	1141-1200	11.8	
	1200-1300	6.4	
	1300-1400	7.1	
	1400-1500	0.5	
	1500-1538	No data	
11/29	0925-1000	≤0.1	N.W. corner, No. 2 reverb, on operator's floor
	1000-1200	0.5	
	1200-1400	0.6	
	1400-1600	0.8	
	1600-1800	1.0	
	1800-2000	0.9	
	2000-2200	1.5	
	2200-2400	0.8	
11/30	0000-0200	0.6	
	0200-0400	1.2	
	0400-0600	0.5	
	0600-0800	0.6	
11/29	0955-1000	No data	E. side, No. 1 reverb, on operator's floor
	1000-1200	No data	
	1200-1400	4.0	
	1400-1600	1.4	
	1600-1800	6.7	
	1800-2000	4.0	
	2000-2200	2.5	
	2200-2400	1.2	

Table 5 (continued)

Date	Time	Conc. (ppm)	Location
11/30	0000-0200	0.6	E. side, No. 1 reverb, on operator's floor
	0200-0400	2.4	
	0400-0600	2.9	
	0600-0800	0.4	
	1131-1200	27.2	
	1200-1300	6.4	
	1300-1400	1.5	
	1400-1500	0.3	
	1500-1533	No data	
11/29	0950-1000	4.0	E. side, No. 2 reverb, on charge floor
	1000-1200	2.7	
	1200-1400	21.7	
	1400-1600	14.1	
	1600-1800	7.0	
	1800-2000	8.8	
	2000-2200	35.6	
	2200-2400	7.8	
11/30	0000-0200	3.1	
	0200-0400	2.9	
	0400-0600	4.4	
	0600-0800	3.3	
	0947-1000	0.8	
	1000-1100	2.5	
	1100-1200	13.7	
	1200-1300	44.3	
	1300-1400	43.7	
	1400-1500	1.7	

TABLE 6

WEST GAEKE RESULTS FOR SULFUR DIOXIDE

WHITE PINE COPPER COMPANY
NOVEMBER 27 - DECEMBER 1, 1972

Date	Time	Conc. (ppm)	Location
11/29	1228-1307	1.7	E. side, No. 1 reverb, operator's floor
	1308-1339	1.6	
	1501-1535	1.5	
	1717-1742	6.0	
	2035-2109	0.2	
11/29	1236-1309	0.3	Between No. 1 and No. 2 reverbs, operator's floor
	1310-1344	0.4	
	1502-1538	0.3	
	1718-1744	0.5	
	2037-2110	2.0	
11/29	1138-1312	0.4	N.W. corner, No. 2 reverb, operator's floor
	1313-1347	0.5	
	1503-1541	0.4	
	1719-1746	0.4	
	2038-2111	0.05	
11/29	1242-1315	4.4	E. side, No. 2 reverb, charge floor
	1316-1353	6.2	
	1505-1545	3.4	
	1722-1749	0.2	
	2039-2113	0.05	
11/29	1245-1318	1.7	E. side, No. 1 reverb, charge floor
	1319-1355	6.8	
	1506-1547	3.4	
	1725-1750	6.7	
	2040-2113	5.7	

Table 6
(continued)

Date	Time	Conc. (ppm)	Location
11/30	0920-1013	0.02	S. of No. 2 converter
	1405-1432	0.09	
	1433-1506	0.04	
11/30	0928-1015	0.02	Rail behind skimmer's control panel, No. 2 conv.
	1407-1434	0.06	
	1435-1506	0.1	
11/30	0934-1017	0.03	S. of No. 2 converter
	1408-1435	0.1	
	1436-1507	0.01	
11/30	1409-1437	0.07	Rail in front of No. 1 converter
	1438-1507	0.1	
11/30	1410-1439	0.01	S. of casting area
	1440-1508	0.04	

OSHA STANDARD

Sulfur Dioxide 5 ppm

FIGURE 1

WEST-GAEKE METHOD

TENTATIVE REFERENCE METHOD FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

(Key Words: Sulfur Dioxide, Ambient Air, Pararosaniline, Tetrachloromercurate)

1. PRINCIPLE AND APPLICABILITY OF METHOD

1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachl mercurate (TCM). A dichlorosulfitomercurate complex, which resists oxidation by oxygen in the air, is formed.[1,2] Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen).

1.2 The complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid.[3] The absorbance of the so tion is measured spectrophotometrically.

2. RANGE AND SENSITIVITY

2.1 Concentrations of sulfur dioxide in the range of 25 to 1000 μg/m^3 (0.01 0.40 ppm) can be measured under the conditions given. One can extrapolate to co centrations below 25 μg/m^3 by sampling larger volumes of air, but only if the absorption efficiency of the particular system is first determined. Higher conce trations can be analyzed by using smaller gas samples, a larger collection volume or a suitable aliquot of the collected sample.

2.2 The lower limit of detection of sulfur dioxide in 10 ml TCM is 0.75 μg (based on twice the standard deviation) representing a concentration of 25 μg/m^3 SO_2 (0.01 ppm) in an air sample of 30 liters.

2.3 Beer's Law is followed through the working range from 0.03 to 1.0 absorba units (0.8 to 27 μg of sulfite ion in 25 ml final solution computed as SO_2).

3. INTERFERENCES

3.1 The effects of the principle known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulfamic acid, ozone by time-delay[6], and heavy metals by EDTA (ethylenediaminetetraacetic acid disodium salt) and phosphoric acid.[4,6] At least 60 μg Fe(III), 10 μg Mn(II), and 10 μg Cr(III) in 10 ml absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg Cu(II) and 22 μg V(V).

4. PRECISION, ACCURACY, AND STABILITY

4.1 Relative standard deviation at the 95% confidence level is 4.6% for the analytical procedure using standard samples.[5]

4.2 After sample collection the solutions are relatively stable. At 22°C losses of sulfur dioxide occur at the rate of 1% per day. When samples are stored at 5°C for 30 days, no detectable losses of sulfur dioxide occur. The presence of EDTA enhances the stability of SO_2 in solution, and the rate of decay independent of the concentration of SO_2.[7]

5. APPARATUS

5.1 Sampling

5.1.1 Absorber - Absorbers normally used in air pollution sampling are acceptable for concentrations above 25 $\mu g/m^3$ (0.01 ppm). An all-glass midget impinger, as shown in Figure 1, is recommended for 30-min. samples.

5.1.2 Pump - Capable of maintaining an air pressure differential greater than 0.7 atmosphere at the desired flow rate.

5.1.3 Air Flowmeter or Volume Meter - Capable of measuring air flow within ± 2%. A wet or dry gas meter, with manometer, or a specially calibrated rotameter, is satisfactory. A 22-gauge hypodermic needle 1 in. long may be used as a critical orifice to give a flow of about 1 liter/min. if it has first been calibrated in the system. Use a membrane filter to protect the needle (See insert, Fig. 1).

5.2 Analysis

5.2.1 Spectrophotometer - Suitable for measurement of absorbance at 548 nm with an effective spectral band of less than 15 nm. Reagent blank problems may occur with spectrophotometers having greater spectral band width. The wavelength calibration of the instrument should be verified. If Transmittance is measured, this can be converted to absorbance:

$$A = \log_{10} (1/T)$$

6. REAGENTS

6.1 Sampling

6.1.1 Distilled water - Must be free from oxidants.

6.1.2 Absorbing Reagent [0.04 M Potassium Tetrachloromercurate (TCM)] - Dissolve 10.86 g mercuric chloride, 0.066 g EDTA (Ethylenediaminetetraacetic acid disodium salt), and 6.0 g potassium chloride in water and bring to mark in a 1000-ml volumetric flask. (Caution: highly poisonous. If spilled on skin, flush off with water immediately). The pH of this reagent should be approximately 4.0, but it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3.[7] The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

6.2 Analysis

6.2.1 Sulfamic Acid (0.6%) - Dissolve 0.6 g sulfamic acid in 100 ml distilled water. Prepare fresh daily.

6.2.2 Formaldehyde (0.2%) - Dilute 5 ml formaldehyde solution (36-38%) to 1000 ml with distilled water. Prepare daily.

6.2.3 Stock Iodine Solution (0.1 N) - Place 12.7 g iodine in a 250-ml beaker; add 40 g potassium iodide and 25 ml water. Stir until all is dissolved, then dilute to 1000 ml with distilled water.

6.2.4 Iodine Solution (0.01 N) - Prepare approximately 0.01 N iodine solution by diluting 50 ml of stock solution to 500 ml with distilled water.

6.2.5 Starch Indicator Solution - Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with a little water, and add the paste slowly to 200 ml boiling water. Continue boiling until the solution is clear; cool, and transfer to a glass-stoppered bottle.

6.2.6 Stock Sodium Thiosulfate Solution (0.1 N) - Prepare a stock solution by dissolving 25 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1000 ml freshly boiled, cooled, distilled water and add 0.1 g sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh, to the nearest 0.1 mg, 1.5 g primary standard potassium iodate dried at 180°C and dilute to volume in a 500-ml volumetric flask. To a 500-ml iodine flask, pipet 50 ml of iodate solution. Add 2 g potassium iodide and 10 ml of 1 N hydrochloric acid. Stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml starch indicator solution and complete the titration. Calculate the normality of the stock solution:

$$N = \frac{W}{M} \times 2.80$$

N = normality of stock thiosulfate solution
M = volume of thiosulfate required, ml
W = weight of potassium iodate, grams

$$2.80 = \frac{10^3 \text{ (conversion of g to mg) x 0.1 (fraction iodate used)}}{35.67 \text{ equivalent weight of potassium iodate}}$$

6.2.7 Sodium Thiosulfate Titrant (0.01 N) - Dilute 100 ml of the stock thiosulfate solution to 1000 ml with freshly boiled distilled water.

Normality = Normality of Stock Solution X 0.100.

6.2.8 Standardized Sulfite Solution For Preparation of Working Sulfite-TCM Solution - Dissolve 0.30 g sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g sodium sulfite (Na_2SO_3) in 500 ml of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability). This solution contains the equivalent of 320 to 400 µg/ml of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 ml of the 0.01 N iodine into each of two 500-ml iodine flasks (A and B). To flask A (blank) add 25 ml distilled water, and to flask B (sample) pipet 25 ml sulfite solution. Stopper the flasks and allow to react for 5 min. Prepare the working sulfite-TCM Solution (6.2.9) at the same time iodine solution is added to the flasks. By means of a buret containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml starch solution and continue the titration until the blue color disappears.

6.2.9 Working Sulfite-TCM Solution - Pipet accurately 2 ml of the standard solution into a 100 ml volumetric flask and bring to mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution:

$$\mu g\ SO_2/ml = \frac{(A-B)\ (N)\ (32{,}000)}{25} \times 0.02$$

A = volume thiosulfate for blank, ml
B = volume thiosulfate for sample, ml
N = normality of thiosulfate titrant
32,000 = milliequivalent wt., μg
25 = volume standard sulfite solution, ml
0.02 = dilution factor

This solution is stable for 30 days if kept at 5°C. (refrigerator). If not kept at 5°C., prepare daily.

6.2.10 Purified Pararosaniline Stock Solution (0.2% nominal)

6.2.10.1 Dye Specifications - The pararosaniline dye must meet the following performance specifications: (1) the dye must have a wavelength of maximum absorbance at 540 nm when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid; (2) the absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), should not exceed 0.170 absorbance unit at 22°C with a 1-cm optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye; (3) the calibration curve (Section 8.2.1) should have a slope of 0.030 ± 0.002 absorbance units/μg SO_2 at this path length when the dye is pure and the sulfite solution is properly standardized.

6.2.10.2 Preparation of Stock Solution - A specially purified (99-100% pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20% concentration (Harleco*). If this cannot be obtained, the stock solution may be prepared by dissolving 0.200 g of the purified dye in 100 ml of 1 N hydrochloric acid in a 100 ml glass stoppered graduated cylinder. (See Scaringelli, et. al.[4] for the purification and assay procedures).

6.2.11 Pararosaniline Reagent - To a 250 ml volumetric flask, add 20 ml stock pararosaniline solution. Add an additional 0.2 ml stock solution for each per cent the stock assays below 100%. Then add 25 ml 3 M phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7. PROCEDURE

7.1 Sampling - Procedures are described for short term (30 min.) and for long term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Fixing sample volume at 30 liters maintains linearity between absorbance and concentration over this dynamic range. .01-.40 ppm

7.1.1 30-Minute Sampling - Insert a midget impinger into the sampling system, Figure 1. Add 10 ml TCM solution to the impinger. Collect sample at 1 liter/min. for 30 min. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Record the actual volume of air by multiplying the flow rate by the time in min. Remove and stopper the impinger. If the sample must be stored for more than a day before analysis, keep it at 5°C in a refrigerator (see 4.2).

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7.1.2 24-Hour Sampling - Place 15-20 ml TCM solution in a midget impinger or 50 ml in a larger impinger and collect the sample at 0.2 liter/min. for 24 hours. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Record the total volume of sample by multiplying the flow rate by the time in min. If storage is necessary, refrigerate at 5°C (see 4.2).

7.2 Analysis

7.2.1 Sample Preparation - After collection, if a precipitate is observed in the sample, remove it by centrifugation.

7.2.1.1 30 Minute Sample - Transfer the sample quantitatively to a 25-ml volumetric flask; use about 5 ml distilled water for rinsing. Delay analyses for 20 min. to allow any ozone to decompose.

7.2.1.2 24 Hour Sample - Dilute the entire sample to 25 ml for the midget impinger or 50 ml for the larger impinger, with absorbing solution. Pipet one-tenth of the sample into a 25-ml volumetric flask for chemical analyses. Bring volume to 10 ml with absorbing reagent. Delay analyses for 20 min.

7.2.2 Determination - For each set of determinations prepare a reagent blank by adding 10 ml unexposed TCM solution to a 25-ml volumetric flask. Prepare a control solution by adding 2 ml of working sulfite-TCM solution and 8 ml TCM solution to a 25-ml volumetric flask. To each flask containing either sample, control solution or reagent blank, add 1 ml 0.6% sulfamic acid and allow to react 10 min. to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml 0.2% formaldehyde solution, then 5 ml pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 min. and before 60 min., determine the absorbances of the sample, reagent blank and the control solution at 548 nm using 1-cm optical path length cells. Use distilled water, not the reagent blank, as the reference. (NOTE! This is important because of the color sensitivity of the reagent blank to temperature changes which can be induced in the cell compartment of a spectrophotometer.) Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol after use. If the temperature of the determinations does not differ by more than 2°C from the calibration temperature (8.2), the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve (8.2). If the reagent blank differs by more than 0.03 absorbance unit, from that found in the calibration curve, prepare a new curve.

7.2.3 Absorbance Range - If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to six-fold with the reagent blank in order to obtain on-scale readings within 10% of the true absorbance value.

8. CALIBRATION AND EFFICIENCIES

8.1 Flowmeters and Hypodermic Needle - Calibrate flowmeters and hypodermic needle[8] against a calibrated wet test meter.

8.2 Calibration Curves

8.2.1 Procedure with Sulfite Solution - Accurately pipet graduated amounts of the working sulfite-TCM solution (such as 0, 0.5, 1, 2, 3, and 4 ml) into a series of 25-ml volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in .2.2. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within ± 1°C and in the range of 20 to 30°C. The temperature of calibration and the temperature of analysis must be within 2 degrees. Plot the absorbance against the total concentration in µg SO_2 for the corresponding solution. The total µg SO_2 in solution equals the concentration of the standard (Section 6.2.9) in µg SO_2/ml times the ml sulfite solution added (µg SO_2 = µg/ml SO_2 x ml added). A linear relationship should be obtained, and the y-intercept should be within 0.02 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Under these conditions the plot need be determined only once to determine the calibration factor (reciprocal of the slope of the line). (See Section 6.2.10.1 for specifications on the slope of the calibration curve). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 Procedure with SO_2 Gas - See Appendices.

8.3 Sampling Efficiency - Collection efficiency is above 98%; efficiency may fall off, however, at concentrations below 25 $\mu g/m^3$.[9,10]

9. CALCULATIONS

9.1 Conversion of Volume - Convert the volume of air sampled to the volume at standard conditions of 25°C, 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{(t + 273)}$$

V_s = volume of air at 25°C and 760 mm Hg
V = volume of air sampled, liters
P = barometric pressure, mm Hg
t = temperature of air sample, °C

Ordinarily, the correction for pressure is slight and may be neglected.

9.2 Sulfur Dioxide Concentration - Compute the concentration of sulfur dioxide in the sample by the following formula:

$$SO_2,\ \mu g/m^3 = \frac{(A - A_o)\ (10^3)\ (B)}{V_s}$$

A = sample absorbance,
A_o = reagent blank absorbance,
10^3 = conversion of liters to cubic meters
V_s = the sample volume corrected to 25°C and 760 mm Hg., liters

$$B = \frac{1}{\text{Slope of calibration curve, absorbance units/}\mu g} = \text{calibration factor, } \mu g/\text{absorbance unit}$$

9.2.1 <u>Conversion of $\mu g/m^3$ to ppm</u> - If desired, the concentration of sulfur dioxide may be calculated as ppm SO_2 at standard conditions as follows:

$$\text{ppm } SO_2 = \mu g\ SO_2/m^3 \times 3.82 \times 10^{-4}$$

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Gaseous Calibration - Certified permeation tubes containing liquified sulfur dioxide are available from the National Bureau of Standards and may be used for gaseous calibration.

(1) Commercially available permeation tubes* may be calibrated as follows: Obtain an FEP Teflon^R permeation tube that emits sulfur dioxide at a rate of 0.2 to 0.4 µg/min. (0.08 to 0.15 µl/min. at standard conditions of 25°C and 1 atmosphere.) A permeation tube with an effective length of 2 to 4 cm, and outer diameter of 0.63 cm will yield the desired permeation rate if held at a constant temperature of 20°C. Using the system shown in Figure 2, calibrate the tube gravimetrically at the intended operating temperature to a precision within ± 2 percent. The temperature of the tube must be controlled within 0.1°C. Permeation tubes are calibrated under a stream of dry nitrogen to prevent the formation of blisters in the walls and sulfuric acid inside the tube. Periodically, about every 4 days, remove the bubbler from the constant temperature bath and throughly dry the bubbler. Remove the permeation tube from the bubbler with a Teflon-tipped forcep and weigh the tube to the nearest 0.1 mg. Record weight and time to the nearest minute. Immediately return tube to bubbler and bubbler to bath. Plot gross weight (10 mg to the inch) against time (1000 minutes to the inch). Compute the slope of the linear portion from the line that best fits the points. Linear regression is recommended. Alternately, tubes can be rapidly calibrated using a coulometric SO_2 analyzer operating under ideal conditions.

(2) A system designed for the preparation of standard concentrations of sulfur dioxide in the laboratory is shown in Figure 3. (Alternately, the apparatus shown in Figure 2 for gravimetric calibration and field use may be used.) Assemble the apparatus, consisting of a water-cooled condenser, a constant-temperature water bath maintained at 20°C, a cylinder containing pure, dry air or nitrogen, and appropriate pressure regulators, needle valves, and flow meters for the nitrogen and dry air diluent gas streams. The diluent gases are brought to temperature by passage through a 2-meter copper coil immersed in the water bath. Insert a calibrated permeation tube into the central tube of the condenser maintained at 20°C by circulating water from the constant-temperature bath and pass a stream of air or nitrogen over the tube at a fixed rate of approximately 50 ml/min. Dilute this gas stream to the desired concentration by varying the air flow rate. Normally this flow rate can be varied from 1.1 to 15 liters/min. The flow rate of the sampling system determines the lower limit for the flow rate of the diluent gases. With a tube permeating sulfur dioxide at a rate of 0.4 µg/min., the range of concentration of sulfur dioxide will be between 27 and 260 µg/m^3 (0.01 to 0.14 ppm), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate and use longer permeation tubes.

B. Procedure For Preparing Calibration Curves - One can prepare a multitude of curves by selecting different combinations of sampling rate and sampling time. (Calibration should be made under the same conditions used in sampling and analyses). Twenty-four hour samples must be calibrated for 24 hours. The above description represents a typical procedure for simulating ambient air sampling of short duration. The system is designed to provide an accurate

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*Available from Metronics, Inc. 3201 Porter Drive, Palo, Alto, Calif. 94304 and Analytical Instrument Developments, Inc. 250 S. Franklin St., West Chester, Pa. 19380.

measurement of sulfur dioxide in the range of 0.01 to 0.5 ppm. It can be modified easily to meet special needs. The concentration of standard SO_2 in air is computed as follows:

$$C = \frac{Pr \times 10^3}{R + r}$$

C = Concentration of SO_2, µg/m^3
Pr = Permeation rate, µg/min.
R = Flow rate of diluent air, liters/min.
r = Flow rate of diluent nitrogen, liters/min.

Data for a typical calibration curve are listed in Table I. A plot of the concentration of sulfur dioxide in µg/m^3 (X-axis) against absorbance of the final solution (Y-axis) will yield a straight line, the reciprocal of the slope of which is the factor for conversion of absorbance to µg/m^3. This factor includes the correction for collection efficiency. Any deviation from linearity at the lower concentration range indicates a change in collection efficiency of the sampling system. Actually, the standard concentrations of 25 µg/m^3 and below of sulfur dioxide are slightly below the dynamic range of the method. If this is the range of interest, the diluent air stream must be adjusted to deliver these lower concentrations, and the total volume of air collected must be increased to obtain sufficient color within the dynamic range of the procedure. The calibration factor must be reestablished, if collection efficiency differs significantly from that obtained above 25 µg/m^3. The remainder of the analytical procedure is the same as described in Section 7.

TABLE 1

TYPICAL CALIBRATION DATA

Concentrations of SO_2, µg/m^3	Amount of SO_2 in µg for 30 liters	Absorbance of sample (1-cm cells)
15	0.45	0.013
25	0.75	0.022
100	3.0	0.089
200	6.0	0.179
500	15.0	0.448
800	24.0	0.716
1000	30.0	0.895
1100	33.0	0.985

SO_2, µg/m^3 = A x F, Where:

F = 1.1 x 10^3 = factor, as derived from equation in 9.2.

A = Absorbance of solution for 30 liters of sample and a volume of 25 ml for the colored solution

Bibliography for Appendices

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4. Thomas, M. D. and Amtowar, R. E., "Gas Dilution Apparatus for Preparing Reproducible Dynamic Gas Mixtures in any Desired Concentration and Complexity", J. Air Poll. Cont. Assoc. 16, 618 (1966).

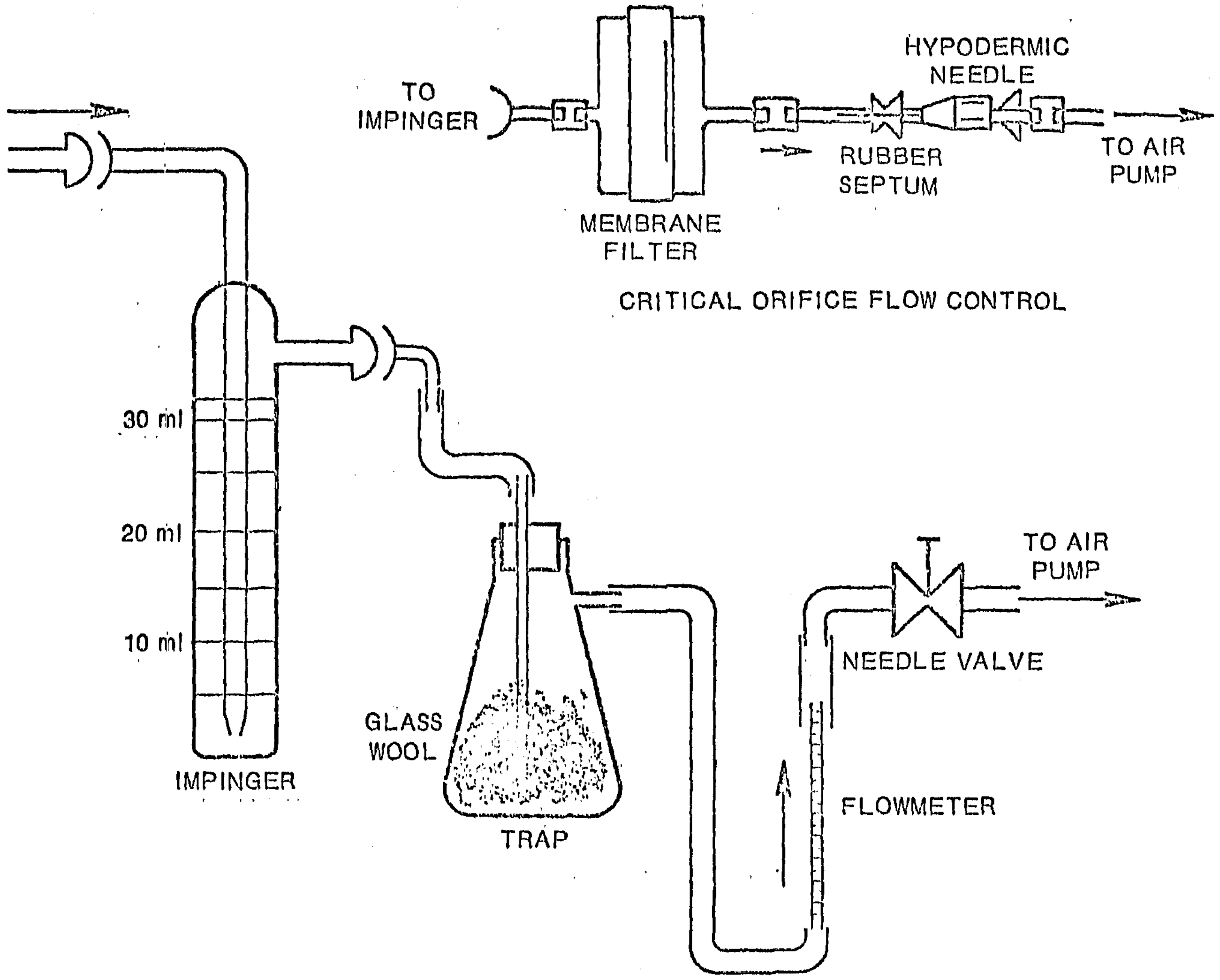


Figure 1. Sampling train.

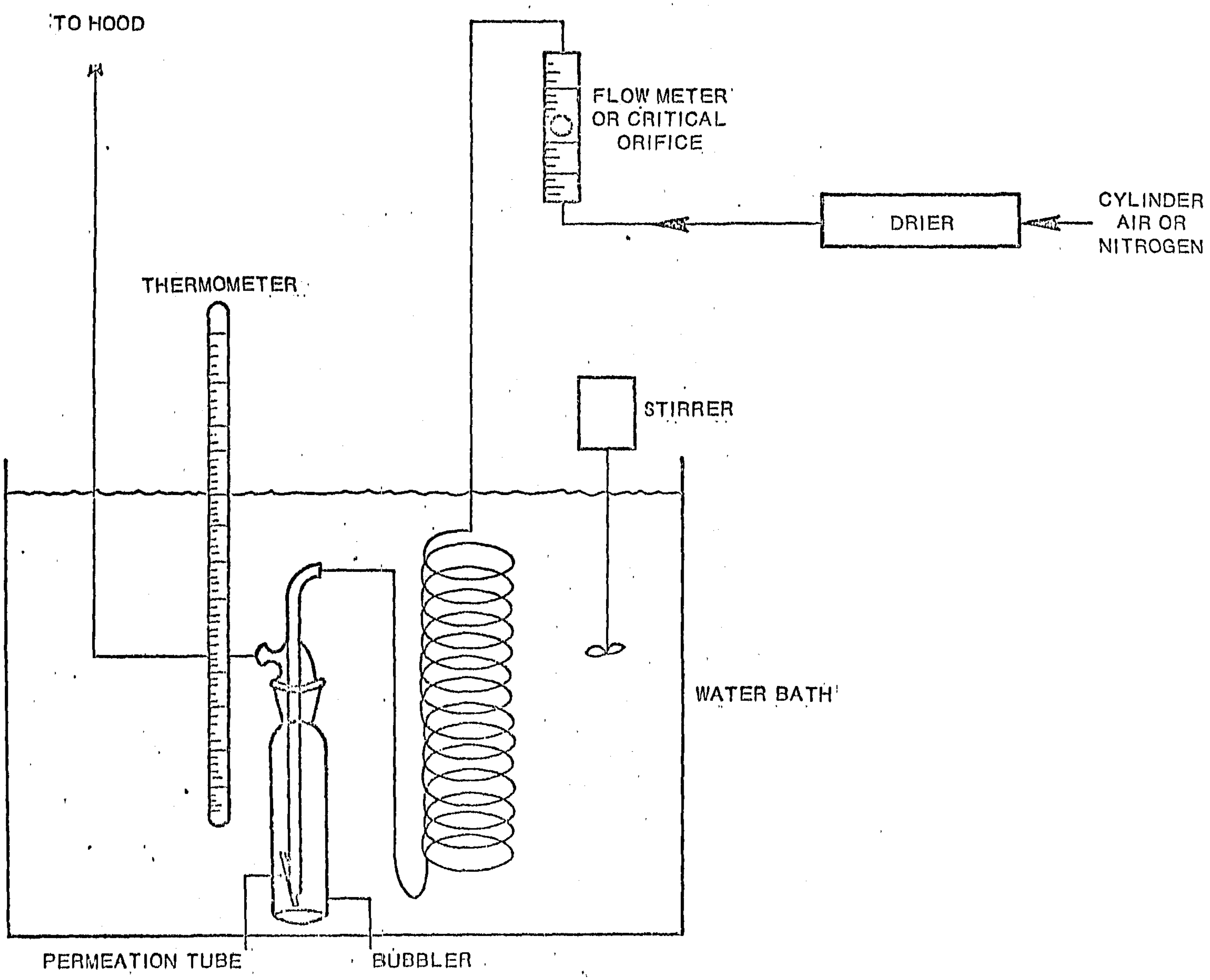


Figure 9. Apparatus for gravimetric calibration and field use.

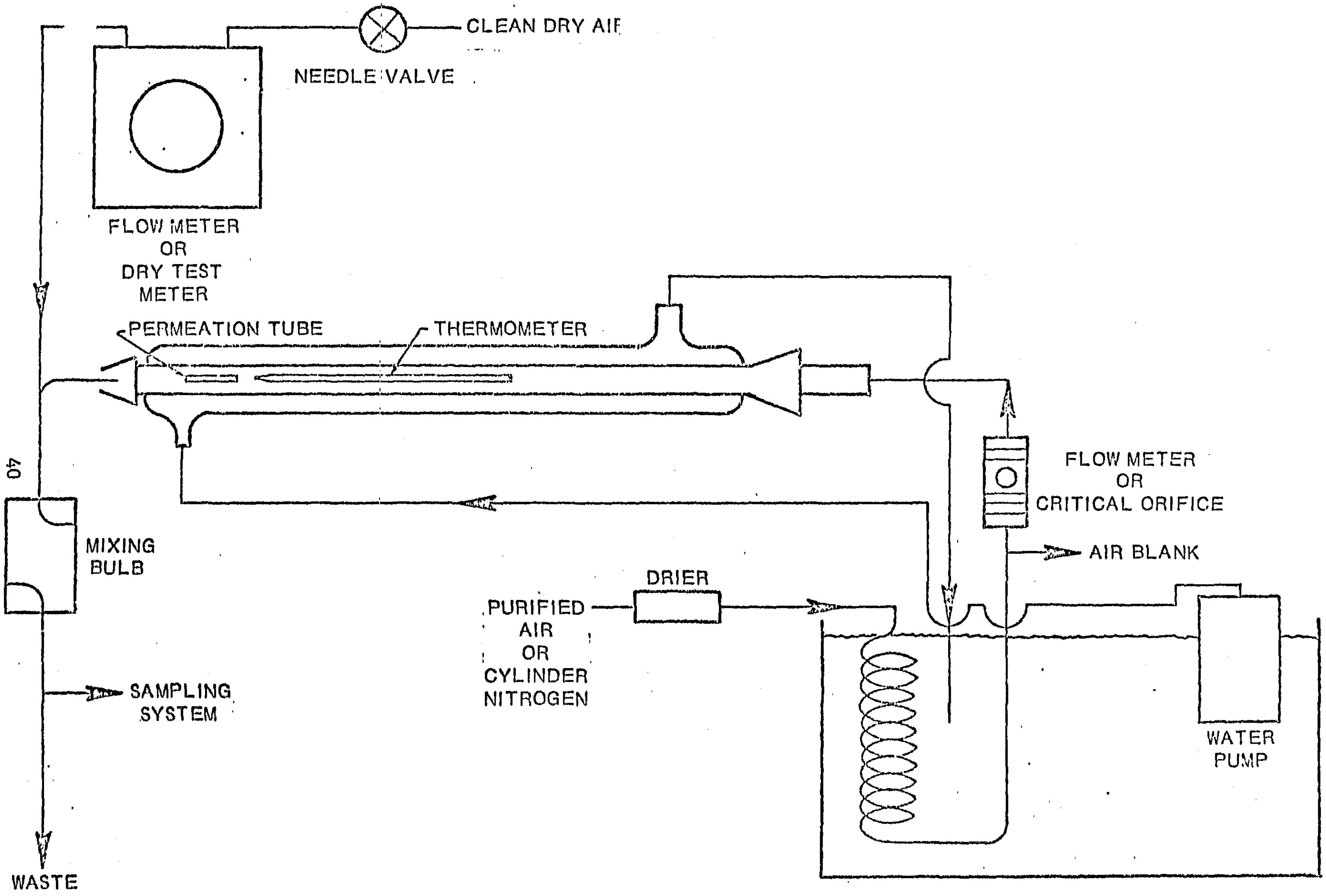
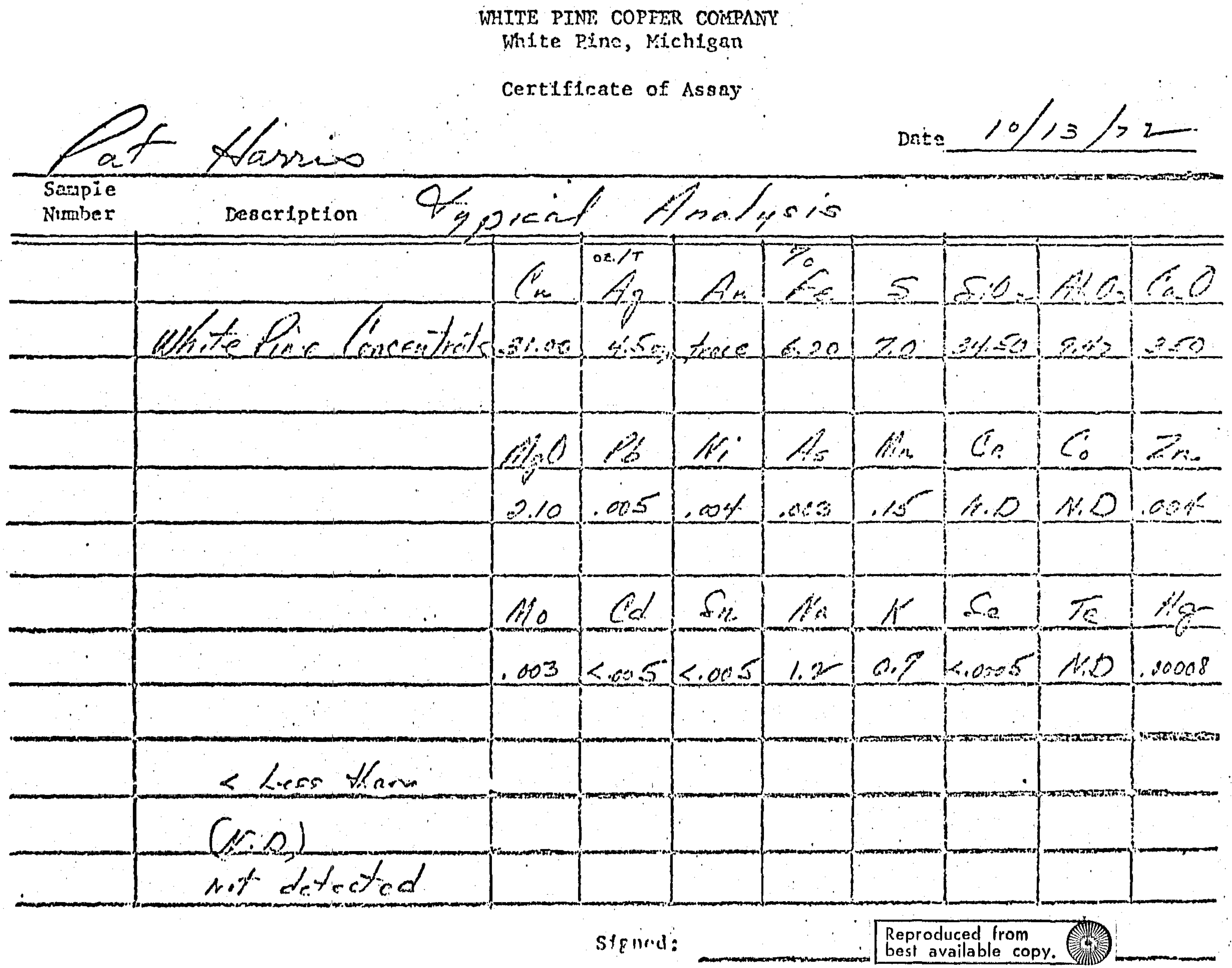


Figure 3. Permeation tube schematic for laboratory use.

Figure 2.



WHITE PINE COPPER COMPANY
White Pine, Michigan

Certificate of Assay

Pat Harris

Date 10/13/72

Sample Number	Description Typical Analysis								
		Cu	oz./T Ag	Au	% Fe	S	SiO_2	Al_2O_3	CaO
	White Pine Concentrate	31.00	4.50	trace	6.20	7.0	34.50	9.42	3.50
		MgO	Pb	Ni	As	Mn	Cr	Co	Zn
		2.10	.005	.004	.003	.15	N.D	N.D	.004
		Mo	Cd	Sn	Na	K	Se	Te	Hg
		.003	<.005	<.005	1.2	0.7	<.0005	N.D	.00008
	< Less than								
	(N.D.)								
	not detected								

Signed:

FIGURE 3

HYDROGEN PEROXIDE METHOD
FOR
SULFUR DIOXIDE

Analyte: Sulfur Dioxide	Method No.:
Matrix: Air	Range: 0.01 mg-5 mg
Procedure: Peroxide Absorption Titration with Barium Perchlorate	
Date Issued:	Collaboratively Tested:
Date Revised:	

1. Principle of the Method

1.1 Sulfur dioxide in the air is absorbed and oxidized in 0.3 normal hydrogen peroxide reagent.

1.2 The pH of the sample solution is adjusted with dilute perchloric acid. After isopropyl alcohol is added bringing the alcohol concentration to approximately 80% by volume, the resulting solution is titrated with 0.005 M barium perchlorate using Thorin as the indicator. There is a sharp change from yellow to pink at the end point.

2. Range and Sensitivity

This method.is sensitive to 0.1 mg sulfur dioxide per cubic meter assuming a 100 liter air sample. The upper limit is the amount of SO_2 absorbed in the hydrogen peroxide reagent and is at least 5 mg.

3. Interferences

3.1 Soluble particulate sulfates, and sulfuric acid in the air sample would give erroneously high sulfur dioxide values. However, these can be eliminated by placing a filter upstream of the impinger in the sampling train.

3.2 Metal ion interferences can be eliminated by passing the sample solution through an ion exchange resin.

3.3 Concentrations of phosphate ions greater than the sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate.

4. Precision and Accuracy

5. Advantages and Disadvantages

5.1 The samples are easily collected and conveniently shipped to the laboratory for analysis in glass vials.

5.2 The sulfuric acid formed is stable and nonvolatile, making this manner of collection of SO_2 desirable.

5.3 The analysis is relatively rapid and simple.

6. Apparatus

6.1 Absorber - Glass midget impingers or fritted bubblers.

6.2 Personal sampling pump with flow meter capable of sampling at a rate of 1.8 lpm.

6.3 125 ml erlenmeyer flasks.

6.4 30 ml beakers.

6.5 Buret - A buret of 10 milliliter capacity graduated in 0.05 milliliter subdivisions.

6.6 Daylight fluorescent lamp aids in identifying the end point.

6.7 Ion Exchange Resin - Dowex 50x8, 20-50 mesh, hydrogen form (Hach Chemical Co., Ames, Iowa).

6.8 One or more ion exchange columns may be constructed using a chromatographic column with fritted glass. A column with an inside diameter of 8 mm and 7 inches of resin has a capacity of approximately 25 milliequivalents.

7. Reagents

7.1 Alcohol - Isopropanol, reagent grade.

7.2 Barium Perchlorate, 0.005 M - Hach Chemical Co., Ames, Iowa.

7.3 Thorin - Prepare a 0.1% solution in distilled water.

7.4 Standard Sulfate Solution, (1.00 ml = 0.50 mg SO_4) - Dissolve 0.7393 g anhydrous Na_2SO_4 in distilled water and dilute to one liter. The sodium is removed by passage of the standard through the ion exchange column.

7.5 Hydrochloric Acid, 4 N - Add 300 ml conc. HCl to 600 ml of distilled water.

7.6 Absorbing Solution - Hydrogen Peroxide, 0.3 N - Dilute 17 ml of 30% H_2O_2 solution to one liter with distilled water.

7.7 Perchloric Acid, 1.8% - Dilute 25 ml of reagent grade perchloric acid (70-72%) to one liter with distilled water.

8. Procedure

8.1 Cleaning of Equipment - The glassware should be chemically clean. Wash in detergent, and rinse with tap water and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Sulfur dioxide is absorbed in 15 ml of hydrogen peroxide absorbing solution in an impinger.

8.2.2 Air is drawn through the impinger by means of a personal sampling pump at the rate of 1.8 liters per minute. A minimum of 100 liters of air should be sampled. If SO_2 concentrations greater than 100 milligrams per cubic meter of air are expected, smaller air volumes should be collected.

8.2.3 With each batch of samples, a hydrogen peroxide absorbing solution blank should be submitted for analysis.

8.2.4 After the sample solutions from the impingers are transferred into vials, the vials are shipped in a suitable container to prevent damage in transit.

8.3 Ion Exchange Procedure

8.3.1 When about two thirds of the capacity of the resin has been exhausted (deterioration in sharpness of the end point), regenerate the resin by passing 30 ml of 4 N hydrochloric acid through the column. After thorough washing with distilled water, the column is ready for use.

8.3.2 Since small volumes of sample solution are passed through the ion exchange column, care must be taken not to dilute the sample with distilled water that remains on the resin. One way this can be accomplished is by blowing some air through the resin with a squeeze bulb to remove most of the distilled water from the ion exchange resin. One or two milliliters of sample is passed through the column and is discarded after air is again blown through the resin. The remainder of the sample is then passed through the ion exchange column, and an aliquot is titrated according to the general procedure (Section 8.4.3).

8.3.3 The column is flushed with distilled water between samples to prevent contamination from the previous sample.

8.4 Analysis of Samples

8.4.1 Measure the volumn of the sample solution or dilute it to a given volume.

8.4.2 Although all samples may be passed through the ion exchange column, it is necessary to do so only when the metal concentration exceeds that of the sulfate. The ion exchange procedure is detailed in Section 8.3. When the ion exchange step is not necessary, add 1 drop of perchloric acid to a 10 ml aliquot so that the pH is 2.5 to 4.

8.4.3 To the 10 ml aliquot in a 125 erlenmeyer flask, add 40 ml of alcohol and 1 drop of Thorin indicator. Titrate with barium perchlorate, taking the change from yellow or yellow-orange to pink as the end point.

8.4.4 Analyze the standard and absorbing solution blank in the same manner.

9. Calibration and Standards

9.1 Instruction for the preparation of the sulfate standard is presented in Section 7.4. Since sodium obscures the end point, it must be removed. Fifty milliliters of standard may be passed through the ion exchange column and stored in a bottle for later use. A five milliliter aliquot is ample for standardization when using a 10 ml buret.

10. Calculations

The analytical results are computed on the basis of the following reaction:

$$SO_2 + H_2O_2 = H_2SO_4$$

$$\frac{\text{mg } SO_2}{M^3} = \frac{(A-B) \times C \times E \times 0.333}{D \times F \times G}$$

A = milliliters of sample titrant
B = milliliters of sample reagent blank titrant
C = milliliters of standard titrated
D = milliliters of standard titrant
E = volume in milliliters of sample solution
F = milliliters of sample titrated
G = cubic meters of air sampled
0.333 in the above formula is the product of:

$$\frac{0.5 \text{ mg } SO_4}{1 \text{ ml standard}} \times \frac{SO_2\ (64.06)}{SO_4^{=}\ (9606)}$$

11. References

11.1 Fritz, J. S., and Yamamura, S. S., Anal. Chem., 27, 1461 (1955)

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