

VIII. APPENDIX I  
METHOD FOR SAMPLING AND ANALYTICAL  
PROCEDURES FOR DETERMINATION OF SULFUR DIOXIDE

The following sampling and analytical method for analysis of sulfur dioxide in air employs absorption and oxidation in hydrogen peroxide solution followed by volumetric titration.

General Requirements

Sulfur dioxide concentrations shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sampling data sheets shall include:

- (1) The date and time of sample collection
- (2) Sampling duration
- (3) Volumetric flowrate of sampling
- (4) A description of the sampling location
- (5) Other pertinent information

Breathing Zone Sampling

Breathing-zone samples shall be collected as near as practicable to the worker's face without interfering with his freedom of movement and

shall characterize the exposure from each job or specific operation in each production area.

(a) Sampling Equipment

A calibrated personal sampling pump with flowmeter (range up to 2 liters/minute), a midjet impinger containing 15 ml of 0.3 N hydrogen peroxide absorbing solution, and an 0.8 micrometer nominal pore size cellulose membrane filter with filter holder shall be used for sample collections.

(b) Sampling Procedure

The filter is placed upstream of the impinger to collect any sulfuric acid mist or other airborne particulate sulfates prior to the air passing through the impinger. The filter holder is connected to the impinger inlet by a piece of flexible vinyl tubing as short as possible. The impinger outlet is connected to the personal sampling pump inlet by a piece of tubing of convenient length, but not in excess of 3 feet. The filter and impinger assembly is attached to the worker's clothing so as to sample from the worker's breathing zone. The sample is collected at a rate of 1 - 2 liters/minute for an appropriate length of time to attain a 100-liter air sample. If sulfur dioxide concentrations are expected to be greater than 100 mg/cu m of air, (approximately 40 ppm), a smaller air volume should be sampled but never less than 10 liters.

A minimum of 3 samples shall be taken for each operation (more samples if the concentrations are close to the standard) and averaged on a time-weighted basis. At least one blank impinger shall be provided

containing hydrogen peroxide solution through which no air has been sampled. One additional blank impinger shall be supplied with every 10 samples obtained.

### Shipping

After sampling, remove the glass stopper and impinger stem from the impinger bottle. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount of unused absorbing solution from a wash bottle, adding the wash to the impinger. Stopper the impinger tightly with plastic caps (do not seal with rubber), place in an upright position, and ship the impinger samples to the analytical laboratory in a suitable container to prevent damage in-transit. Special impinger shipping containers designed by NIOSH are available. Be certain that the impinger bottles are sealed very tightly to prevent leakage and subsequent loss of samples.

### Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the pump's indication. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been misused or if they have just been repaired

or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibrating instruments such as a wet test meter or dry gas meter can be used. The actual setup will be the same for all instruments. Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used.

(a) Flowmeter Calibration Test Method

The calibration setup for personal sampling pumps with the sampling system of a filter and a midjet impinger is shown in Figure XI-1.

(1) Procedure

(A) Check the voltage of the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the battery if necessary.

(B) Fill the impinger with 15 ml of the absorbing solution and place the cellulose membrane filter in the filter holder.

(C) Assemble the sampling train as shown in Figure XI-1.

(D) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and draw bubbles up the inside until they are able to travel the entire buret length without bursting.

(E) Adjust the pump rotameter to provide a flowrate of 1 liter/minute.

(F) Check the water manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (1 in. of Hg).

(G) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes for the bubble to move from one calibration mark to another. For a 1000-ml buret, a convenient calibration volume is 500 ml.

(H) Repeat the procedure in (G) above at least 2 times, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(I) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, and date and pump, and date and name of the person performing the calibration.

## Analytical

### (a) Principle of the Method

Sulfur dioxide in the air is absorbed and oxidized in 0.3 N hydrogen peroxide reagent. 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. The endpoint is determined as a change from yellow to pink.

### (b) Range and Sensitivity

The method is sensitive to 0.1 mg sulfur dioxide/cu m of air, assuming a 100 liter air sample. This would correspond to approximately 0.25 ppm of sulfur dioxide in air. The upper limit is the amount of sulfur dioxide absorbed in the hydrogen peroxide reagent and is at least 5 mg.

### (c) Interferences

Soluble particulate sulfates and sulfuric acid in the air sample would give erroneously high sulfur dioxide values; however, these can be eliminated by placing an 0.8 micron cellulose filter upstream of the impinger in the sampling train.

Metal ion interferences can be eliminated by either the use of the prefilter or, alternatively, by passing the solution through an ion exchange column.

Concentrations of phosphate ions greater than any sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate. The use of the prefilter should also remove phosphates.

(d) Accuracy and Precision

At 2.5 ppm, the accuracy is 5% with a relative standard deviation of 4%. At 25 ppm, the accuracy and relative standard deviation can be improved to about 1%.

(e) Advantages and Disadvantages

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

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

The analysis is relatively rapid and simple.

Spillage from the impingers is possible and could be hazardous if spilled into molten metal.

(f) Apparatus

- (1) Absorber-- glass midget impingers.
- (2) Personal sampling pump with flowmeter capable of sampling at a rate of 1-2 liters/minute.
- (3) 37 mm mixed cellulose ester filter, 0.8 micron nominal pore size.
- (4) Necessary glassware.
- (5) A buret of 10 ml capacity graduated in 0.05 ml subdivisions.
- (6) Daylight fluorescent lamp aids in identifying the endpoint.

(7) Ion exchange resin-- Strongly acidic cation exchange resin, 20-50 mesh, or equivalent. Ion exchange columns may be constructed using glass burets or tubing. A column with an inside diameter of 8 mm and 7 inches of resin has a capacity of approximately 25 milliequivalents.

(g) Reagents

(1) Alcohol-- isopropanol, reagent grade.

(2) Barium perchlorate, 0.005 M. Dissolve 2.0 g of barium perchlorate trihydrate in 200 ml of water and add 800 ml of isopropanol. Adjust pH to about 3.5 with perchloric acid. Standardize against 0.005 M sulfuric acid.

(3) Thorin-- prepare a 0.1-0.2% solution in distilled water.

(4) Standard sulfate solution-- prepare a 0.005 M solution of sulfuric acid and standardize by titration with 0.005 M sodium hydroxide solution or dissolve 0.7393 g anhydrous sodium sulfate in distilled water and dilute to 1 liter (1 ml = 0.5 mg sulfur dioxide). The sodium is removed by passage of the standard solution through the ion exchange column.

(5) Hydrochloric acid, 4 N-- add 300 ml concentrated HCl to 600 ml of distilled water. This is needed only to regenerate the column if the ion exchange procedure is used.

(6) Absorbing solution-- hydrogen peroxide, 0.3 N-- dilute 17 ml of 30% hydrogen peroxide solution to 1 liter with distilled water.



(h) Procedure

(1) Cleaning of equipment-- the glassware should be chemically clean. Wash in detergent and rinse with tap water and distilled water.

(2) Ion exchange procedure (used to purify standard sulfate solution)-- 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. 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 in the resin. One way this can be accomplished is by forcing air through the resin with a squeeze bulb to remove most of the distilled water from the ion exchange resin. One or 2 ml of sample is passed through the column and is discarded after air is again forced 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 in (i)(3) below.

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

(i) Analysis of Samples

(1) Measure the volume of the sample solution or dilute it to a given volume.

(2) If high air concentrations of metal ions are encountered which are not completely removed by the prefilter, samples may be passed through the ion exchange column by the procedure detailed in (h)(2) above.

(3) To a 10 ml aliquot, add 40 ml isopropanol. Adjust the pH, if necessary, to between 2.5 and 4.0 with perchloric acid. Add 1-3 drops of Thorin indicator and titrate with barium perchlorate, taking the change from yellow or yellow-orange to pink as the endpoint.

(4) Analyze the standard and absorbing solution blank in the same manner.

(j) Standardization

The barium perchlorate solution is standardized by titrating a 5 ml aliquot with 0.005 M sulfuric acid to the endpoint using Thorin as indicator. The molarity of the solution is calculated as follows:

$$M[\text{barium perchlorate}] = \frac{\text{ml}[\text{sulfuric acid}] \times M[\text{sulfuric acid}]}{\text{ml}[\text{barium perchlorate}]}$$

Periodic checks of the molarity of the barium perchlorate solution should be run following this same procedure.

If anhydrous sodium sulfate is used to standardize the barium perchlorate, it must first be ion-exchanged since sodium obscures the endpoint. A 5 ml aliquot of the 0.5 mg/ml sulfate solution is ample for standardization.

(k) Calculations

The analytical results are calculated on the basis of the following reactions:

sulfur dioxide + hydrogen peroxide = sulfuric acid

sulfuric acid + barium perchlorate = barium sulfate + 2 perchloric acid

$$\frac{\text{mg}[\text{sulfur dioxide}]}{\text{cu m}} = \frac{\text{ml}[\text{s}] \times \text{M}[\text{barium perchlorate}] \times \text{MW}[\text{sulfur dioxide}]}{\text{V}[\text{cu m}]} \times \frac{\text{V}}{\text{V}[\text{aliq}]}$$

ml[s] = ml of barium perchlorate solution needed  
to titrate the sample aliquot minus the  
blank value.

MW[sulfur dioxide] = molecular weight of sulfur  
dioxide = 64.

V[cu m] = volume of air sampled in cubic meters.

V[aliq] = volume of sample aliquot used for the  
titration in ml.

V = original volume of sample in impinger in ml.

OR

$$\text{sulfur dioxide (ppm) by volume} = \frac{\text{ml}[\text{s}] \times \text{M}[\text{barium perchlorate}] \times 24,450}{\text{V}[\text{l}]} \times \frac{\text{V}}{\text{V}[\text{aliq}]}$$

V[l] = volume of air in liters at 25 C.

24,450 = ml/mole that ideal gas occupies at 25 C.

IX. APPENDIX II  
METHODS FOR DETERMINATION OF  
EXPOSURE AREAS TO SULFUR DIOXIDE

Estimation of Concentration with Detector Tubes

(a) Atmospheric Sampling

(1) Equipment Used

A typical sampling train consists of a detector tube with a corresponding sampling pump. A specific manufacturer's pump may only be used with his detector tubes.

(2) Sampling Procedures

A specific procedure depends on the manufacturer's instructions but normally consists of breaking both tips off a detector tube, inserting the tube into the pump, and taking a specific number of strokes with the pump.

(3) Handling and Shipping of Samples

Detector tubes are not stable with time because the stain in some tubes fades in a few minutes. The tubes should be read immediately in accordance with the manufacturer's instructions and charts and no attempt should be made to save the used tubes.

(b) General Principles

Gas detector tubes contain a chemically impregnated packing which indicates the concentration of a contaminant in the air by means of a chemically produced color change. The color changes are not permanent or

stable, so the stained tubes must be read immediately after the samples are taken. The length of stain or the color intensity is read according to the manufacturer's instructions and may involve comparing the stain with a chart, a color comparator, or a direct concentration reading from calibration marks on the tube. Detailed descriptions are provided by individual manufacturer's instructions.

Tubes obtained from commercial sources which bear the certified seal of NIOSH are considered to adhere to the requirements as specified for Certification of Gas Detector Tube Units in 42 CFR Part 84 (38 FR 11458). A user may perform his own calibration on commercially acquired tubes by generating accurately known concentrations of sulfur dioxide in air and correlating concentration with stain length or color intensity.

The use of detector tubes with their respective pumps for compliance purposes is inappropriate because sampling times are necessarily very brief; thus, an excessive number of sampling periods would be required to permit calculation of a time-weighted average. In addition, the accuracy of detector tubes is limited [see (e) below].

(c) Range and Sensitivity

Certification standards require that certified tubes have a range from 1/2 to 5 times the time-weighted average concentration. The sensitivity varies with tube brands.

(d) Interferences

Interferences vary with tube brands. The manufacturer's instructions must be consulted.

(e) Accuracy

Certification standards under the provisions of 42 CFR Part 84 (38 FR 11458) specify reliability to within  $\pm 25\%$  of the actual concentration in the range 0.75 to 5 times the standard and  $\pm 35\%$  in the range from 0.5 up to, but not including, 0.75 times the standard.

(f) Advantages and Disadvantages

Unlike the hydrogen peroxide-barium perchlorate method, the use of detector tubes (and portable instruments) is relatively inexpensive and rapid. There is far less time lag than that experienced with laboratory analytical results. Rapid detecting units are valuable for determining whether a hazardous condition exists at a given location at a given time so that workers may be evacuated or suitable protective devices provided. In addition, industrial operators and process engineers need inexpensive and rapid tools for day-to-day evaluation of the atmospheric levels in a work area.

The accuracy of detector tubes is limited; at best they give only an indication of the contaminant concentration. In evaluating measurements performed with detector tubes, interferences, difficulty of endpoint readings, and possible calibration inaccuracies must all be considered.

## Measurement with Portable Instruments

### (a) Atmospheric Sampling

#### (1) Equipment Used

There are several different types of portable meters available for atmospheric sampling: portable variable path infrared analyzers, electroconductivity analyzers, and electrochemical membrane-type polarographic detectors. Any of the above mentioned instruments can be used to measure sulfur dioxide if they are properly calibrated before use.

#### (2) Sampling Procedures

The most important step is the meter calibration. Careful calibration should be performed in a laboratory prior to departure for the field. Known concentrations of sulfur dioxide can be generated from a dynamic permeation tube system.

The actual field sampling is conducted according to the manufacturer's instructions. Readings should be corrected if necessary for variables such as temperature, humidity, atmospheric pressure, etc, and recorded along with time, place, etc.

### (b) General Principles

Analysis is dependent on the type of meter used. The portable direct reading meters require no analysis because they usually provide usable concentration readings directly. Results obtained from the variable-path infrared analyzer and the electrochemical membrane-type polarographic detectors must be further analyzed and calculated to obtain concentration values.

(c) Range and Sensitivity

The range and sensitivity vary with the instrument used. These instruments generally have a greater sensitivity than detector tubes.

(d) Interferences

Again, these vary with the instrument. The most common interferences are water vapor, hydrogen sulfide, sulfates (gases and particulates), sulfur trioxide, and sulfuric acid. For the electroconductivity type detectors, strong interferences result from gases that affect the conductivity of the absorbing media.

(e) Advantages and Disadvantages

The benefits and drawbacks of portable instruments are essentially the same as for detector tubes discussed previously. Portable meters are generally more sensitive and more accurate than detector tubes. Also, when recording capability is possible, direct reading instruments have the advantage of continuous record availability.



X. APPENDIX III.

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material containing sulfur dioxide shall be provided in the appropriate section of the Material Safety Data Sheet or approved form. If a specific item of information is inapplicable, the initials "n.a." (not applicable) should be inserted.

(a) The product designation in the upper left-hand corner of both front and back to facilitate filing and retrieval. Print in upper case letters in as large a print as possible.

(b) Section I. Source and Nomenclature.

(1) The name, address, and telephone number of the manufacturer or supplier of the product.

(2) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; and the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(c) Section II. Hazardous Ingredients.

(1) Chemical or widely recognized common name of all hazardous ingredients.

(2) The approximate percentage by weight or volume (indicate basis) which each hazardous ingredient or the mixture bears to

the whole mixture. This may be indicated as a range of maximum amount, ie, 10-20% by volume; 10% maximum by weight.

(3) Basis for toxicity for each hazardous material such as established OSHA standard in appropriate units and/or LD50, showing amount and mode of exposure and species, or LC50 showing concentration and species.

(d) Section III. Physical Data.

(1) Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure in millimeters of mercury; vapor density of gas or vapor (air=1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water=1); volatility, indicate if by weight or volume, at 70 degrees Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether=1); and appearance and odor.

(e) Section IV. Fire and Explosion Hazard Data.

(1) Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits in percentage by volume in air; suitable extinguishing media or agents; special fire fighting procedures; and unusual fire and explosion hazard information.

(f) Section V. Health Hazard Data.

(1) Toxic level for total compound or mixture, relevant symptoms of exposure, skin and eye irritation properties, principal routes

of absorption, effects of chronic (long-term) exposure, and emergency and first-aid procedures.

(g) Section VI. Reactivity Data.

(1) Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(h) Section VII. Spill or Leak Procedures.

(1) Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers holding residues, contaminated absorbents, etc.

(i) Section VIII. Special Protection Information.

(1) Requirements for personal protective equipment, such as respirators, eye protection, clothing, and ventilation, such as local exhaust (at site of product use or application), general, or other special types.

(j) Section IX. Special Precautions.

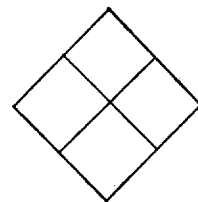
(1) Any other general precautionary information such as personal protective equipment for exposure to the thermal decomposition products listed in Section VI, and to particulates formed by abrading a dry coating, such as by a power sanding disc.

(k) The signature of the responsible person filling out the data sheet, his address, and the date on which it is filled out.

PRODUCT DESIGNATION

**MATERIAL SAFETY  
DATA SHEET**

Form Approved  
Budget Bureau No.  
Approval Expires  
Form No. OSHA



SECTION I SOURCE AND NOMENCLATURE	
MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, ZIP Code)	
TRADE NAME AND SYNONYMS	CHEMICAL FAMILY
CHEMICAL NAME AND SYNONYMS	FORMULA

SECTION II HAZARDOUS INGREDIENTS					
BASIC MATERIAL	APPROXIMATE OR MAXIMUM % WT. OR VOL.	ESTABLISHED OSHA STANDARD	LD 50		LC 50
			ORAL	PERCUT.	SPECIES

SECTION III PHYSICAL DATA			
BOILING POINT	°F.	VAPOR PRESSURE	mm Hg.
MELTING POINT	°F.	VAPOR DENSITY (Air=1)	
SPECIFIC GRAVITY (H <sub>2</sub> O=1)		EVAPORATION RATE ( _____ =1)	
SOLUBILITY IN WATER	Pts/100 pts H <sub>2</sub> O	VOLATILE	% Vol.                      % Wt.
APPEARANCE AND ODOR			

SECTION IV FIRE AND EXPLOSION HAZARD DATA		
FLASH POINT	FLAMMABLE (EXPLOSIVE) LIMITS	UPPER
METHOD USED		LOWER
EXTINGUISHING MEDIA		
SPECIAL FIRE FIGHTING PROCEDURES		
UNUSUAL FIRE AND EXPLOSION HAZARDS		

PRODUCT DESIGNATION

**SECTION V HEALTH HAZARD DATA**

TOXIC LEVEL

CARCINOGENIC

PRINCIPAL ROUTES OF ABSORPTION

SKIN AND EYE IRRITATION

RELEVANT SYMPTOMS OF EXPOSURE

EFFECTS OF CHRONIC EXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

**SECTION VI REACTIVITY DATA**

CONDITIONS CONTRIBUTING TO INSTABILITY

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

INCOMPATIBILITY (Materials to Avoid)

HAZARDOUS DECOMPOSITION PRODUCTS

**SECTION VII SPILL OR LEAK PROCEDURES**

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

WASTE DISPOSAL METHOD

**SECTION VIII SPECIAL PROTECTION INFORMATION**

VENTILATION REQUIREMENTS LOCAL EXHAUST

PROTECTIVE EQUIPMENT (Specify Types) EYE

MECHANICAL (General)

GLOVES

SPECIAL

RESPIRATOR

OTHER PROTECTIVE EQUIPMENT

**SECTION IX SPECIAL PRECAUTIONS**

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE

OTHER PRECAUTIONS

Signature \_\_\_\_\_

Address \_\_\_\_\_

Date \_\_\_\_\_

TABLE XI-1  
 PHYSICAL AND CHEMICAL PROPERTIES  
 OF SULFUR DIOXIDE

Formula	SO <sub>2</sub>
Formula Weight	64.06
Melting Point	-72.7 C (-99 F)
Boiling Point	-10 C (14 F)
Color	Colorless
Corrosivity	Anhydrous sulfur dioxide is noncorrosive to steel or other commonly used metals.
Odor and Taste	Characteristic, pungent.
Specific Gravity	1.434 (liquid) at 0 C (32 F)
Vapor Density	2.264 (air=1)
Solubility	22.8 g in 100 cc of water at 0 C, 0.58 g in 100 cc of water at 90 C; soluble in alcohol, acetic acid, and sulfuric acid.

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Derived from [1,2]

TABLE XI-2

OCCUPATIONS CONSIDERED TO FREQUENTLY  
INCLUDE EXPOSURES TO SULFUR DIOXIDE

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beet sugar bleachers	ore smelter workers
blast furnace workers	organic sulfonate makers
brewery workers	paper makers
diesel engine operators	petroleum refinery workers
diesel engine repairmen	preservative makers
disinfectant makers	protein makers, food
disinfectors	protein makers, industrial
firemen	refrigeration workers
flour bleachers	straw bleachers
food bleachers	sugar refiners
foundry workers	sulfite makers
fruit bleachers	sulfur dioxide workers
fumigant makers	sulfuric acid makers
fumigators	sulfuryl chloride makers
furnace operators	tannery workers
gelatin bleachers	textile bleachers
glass makers	thermometer makers, vapor pressure
glue bleachers	thionyl chloride makers
grain bleachers	wicker ware bleachers
ice makers	wine makers
meat preservers	wood bleachers
oil bleachers	wood pulp bleachers
oil processors	

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Derived from [3]

TABLE XI-3

OBSERVED AND EXPECTED DEATHS FROM RESPIRATORY CANCER,  
WITH STANDARDIZED MORTALITY RATIOS (SMR), BY COHORT  
AND DEGREE OF SO<sub>2</sub> EXPOSURE, 1938-63

Cohort	Respira- tory cancer mortality	Maximum exposure to SO <sub>2</sub> (12 or more months)*		
		Heavy	Medium	Light
All cohorts combined	Observed	46	23	39
	Expected	7.7	8.0	15.2
	SMR	597#	288#	257#
1	Observed	24	10	12
	Expected	3.4	1.7	5.1
	SMR	706#	588#	235##
2	Observed	13	6	8
	Expected	1.7	2.4	2.2
	SMR	765#	250	364#
3-5###	Observed	9	7	19
	Expected	2.6	3.9	7.8
	SMR	346#	179	244#
Number of persons in SO <sub>2</sub> category*		1,144	1,506	2,444

\*The remaining 2,953 men in the study worked less than 12 months in their category of maximum SO<sub>2</sub> exposure and had an SMR of 283#.

#Significant at 1% level.

##Significant at 5% level.

###Cohorts 3, 4, and 5 were combined, since observed and expected deaths were small for each cohort alone.

Cohort 1 = 15 or more years, with 15th year completed before 1938.

Cohort 2 = 15 or more years, with 15th year completed between 1938 and 1963.

Cohort 3 = 10-14 years.

Cohort 4 = 5-9 years.

Cohort 5 = 1-4 years.

Derived from [17]



TABLE XI-4  
 INHALATION EXPOSURES TO SULFUR DIOXIDE  
 AND/OR BENZO(a)PYRENE ATMOSPHERES

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Significant Pathological Findings in Rats Lungs

Exposure type	Number of animals	Advanced squamous metaplasia*	Squamous cell carcinoma*
Air	3	0/3	0/3
Air + carcinogen- irritant	21	1/21	2/21
Irritant	3	0/3	0/3
Irritant + carcinogen- irritant	21	2/21	5/21#

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\*Expressed as a ratio of tumors found to animals observed.

#Secondary squamous cell carcinoma in kidney.

Derived from [20]

TABLE XI-5  
 SULFUR DIOXIDE CONCENTRATIONS IN COPPER SMELTER(A)  
 AS DETERMINED WITH DETECTOR TUBES

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Belt Deck	none detected
Feed Floor Roaster Building	none detected
Between Decks	none detected
Fire Floor Roaster Building (4 of 6 roasters operating)	less than 1 ppm
Roaster Building Loading Area	none detected
Reverberatory Furnace Area (40% operating capacity, 1 of 2 furnaces operating)	7 ppm @0955 10 ppm @1125
(12% operating capacity, 1 furnace operating)	1 ppm @1405
Converters	none detected
Skimming Deck	none detected
Anode Casting	none detected

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Information prepared from NIOSH data.

TABLE XI-6

## SULFUR DIOXIDE CONCENTRATIONS IN COPPER SMELTER (B)

Date	Sampling Time	Remarks	ppm SO2	
Location: Reverberatory furnace area, chargers floor				
1/24/72	0909 - 0935	Tapped 0920-0930	Skimmed 0925-0940	10
"	0935 - 1008		Skimmed 0955-1010	26
"	1008 - 1034			44
"	1034 - 1100		Skimmed 1030-1045	23
"	1100 - 1142	Tapped 1120-1130	Skimmed 1100-1120	16
"	1311 - 1337			19
"	1337 - 1410	Tapped 1330-1340	Skimmed 1350-1410	9
"	1410 - 1437	Tapped 1405-1415	Skimmed 1425-1440	6
"	1437 - 1459	Tapped 1435-1445		10
1/25/72	1225 - 1247		Skimmed 1235-1240	17
"	1247 - 1314	Tapped 1245-1300	Skimmed 1300-1315	36
"	1314 - 1349			17
"	1349 - 1414	Tapped 1345-1400		34
"	1414 - 1450	Tapped 1430-1440	Skimmed 1415-1435	41
"	1450 - 1520	Tapped 1445-1455	Skimmed 1445-1455	24
"	1520 - 1603			1.6
"	1712 - 1737	Tapped 1715-1730	Skimmed 1705-1715	45
"	1737 - 1812	Tapped 1735-1745, 1750-1800		27
"	1812 - 1853	Tapped 1830-1845	Skimmed 1845-1900	25
"	1853 - 1925	Tapped 1910-1920	Skimmed 1915-1930	41
average SO2 concentration = 23 ppm				
Location: Main floor opposite skimming end				
1/24/72	0908 - 0932	Skimming Reverb. #2	0925-0945	4
"	0932 - 1005	" " "	0955-1010	2
"	1005 - 1033	" " "	1020-1045	1.6
"	1033 - 1107	" " "	1100-1120	0.4
"	1107 - 1140			1.2
"	1312 - 1340			3
"	1340 - 1414	" " "	1350-1410	1.1
"	1414 - 1440	" " "	1425-1440	0.6
"	1440 - 1502			0.6
1/25/72	1231 - 1249			9
"	1249 - 1328	" " "	1245-1300	4
"	1328 - 1355	" " "	1345-1400	7
"	1355 - 1420			3
"	1420 - 1447	" " "	1430-1440	3
"	1447 - 1528	" " "	1445-1455	2.3
"	1528 - 1608			0.3
"	1718 - 1750	" " "	1715-1730; 1735-45	1.6
"	1750 - 1817	" " "	1750-1800	3
"	1817 - 1855	" " "	1830-1845	3
"	1855 - 1923	" " "	1910-1920	5
average SO2 concentration = 2.5 ppm				

Information prepared from NIOSH data.

TABLE XI-6  
(continued)

SULFUR DIOXIDE CONCENTRATIONS IN COPPER SMELTER (B)

1/26/72	Sampling time	Remarks	ppm SO2
	Location: Skimmer's platform for #7 converter		
"	1404 - 1447		25
"	1447 - 1532		17
"	1532 - 1617		2
"	1617 - 1645		6
"	1645 - 1723		9
"	1723 - 1800		4
"	1800 - 1843		1.5
	average SO2 concentration = 9 ppm		
	Location: Skimmer's platform for #6 converter		
1/26/72	1407 - 1445		26
"	1445 - 1531		19
"	1531 - 1615		5
"	1615 - 1644		15
"	1644 - 1722		10
"	1722 - 1759		3
"	1759 - 1842		0.8
	average SO2 concentration = 11 ppm		
	Location: Skimmer's platform for #4 converter		
1/26/72	1410 - 1443		17
"	1443 - 1530		11
"	1530 - 1614		3
"	1614 - 1642		6
"	1642 - 1720		11
"	1720 - 1757		7
"	1757 - 1840		3
	average SO2 concentration = 8 ppm		

Information prepared from NIOSH data.

TABLE XI-7

SULFUR DIOXIDE DETERMINATIONS IN COPPER SMELTER (B)  
USING DETECTOR TUBES

Date	Location	ppm SO <sub>2</sub>
1/13/72	Waste heat boiler #5, cleanout table, 8th floor @1323	20
"	Casting wheel near #2 anode furnace @1140	8
"	Converter platform #5 @1150	1
"	#23 conveyor belt (middle of gallery) @1030	12
"	Concentrate bin area @1015	20
"	Roaster acid plant control room @1025	14
"	#3 side #2 Reverb., chargers floor, middle @1035	10
"	#4 side @2 Reverb., chargers floor, middle @1040	9
"	#6 side #3 Reverb., chargers floor, middle @1045	5
"	@6 side #3 Reverb., chargers floor, skim end @1050	13
"	#7 side #4 Reverb., chargers floor, skim end @1055	>25(7*)
"	Over #3 side skimming bay during skimming	>25(4*)
1/14/72	#2 side @1 Reverb., chargers floor, skimming end @0935	17
"	#5 side #3 Reverb., chargers floor skimming end @0940	>25(5*)
"	Waste heat boiler #5, cleanout table, 8th floor @1015	>25
"	Junction #21 and #23 conveyor belts @1010	15
"	Top of fluosolids roaster @1005	9
"	Roaster and acid plant control room @1000	< 1
"	Skimming area #3 side, main level @0955	8
"	Tapping area, #6 side, main level @0940	>25(7*)
1/24/72	#2 side #1 Reverb., skimming end @1730	15
"	Between side #6 and #7, main floor, tapping on #6 side	5
1/25/72	Repair room, main floor, furnace area @0600	10
"	Repair room, main floor, furnace area @0800	5
"	Repair room, main floor, furnace area @1000	20
1/26/72	Between #5 and #6 converter, main floor @ desk @0600	5
"	North anode area @0610	< 1
"	#1 anode furnace @0625	2.5
"	Between #1 and #8 converters @0635	5
"	Between #1 and #2 converters @0640	5
"	Between #2 and #3 converters @0645	2.5
"	Between #3 and #4 converters @0650	2.5
"	Between #4 and #5 converters @0655	nil
"	Between #5 and #6 converters @0700	< 1
"	Between #6 and #7 converters @0706	< 1
"	South anode area @0710	< 1

\*The sulfur dioxide detector tubes operate by pulling a measured amount of air through the indicator tube 10 times. The \* indicates that the reading went off scale before the necessary 10. For example, 8\* means off scale after 8 times.

Information prepared from NIOSH data.

FIGURE XI-1

CALIBRATION SETUP FOR PERSONAL SAMPLING  
PUMP WITH FILTER HOLDER AND MIDGET IMPINGER

