

TRANSMITTAL OF RULES ADOPTED

FROM: WASHINGTON STATE AIR POLLUTION CONTROL BOARD
(Name of Agency)

TO: CODE REVISER
LEGISLATIVE BLDG (Southwest Corner, Ground Floor)
Olympia 98501

The enclosed Permanent rules , being order No. 13
Emergency rules

relating to (Name of rules or description of subject matter)

sulfur oxide. These rules and regulations create chapter 18-56 WAC and establish the air quality standard for sulfur oxide, the air quality objective, and the method of measuring and reporting.

(ALTERNATIVE A. Use only for adoption of permanent rules)

pursuant to Notice No. 2607 ① filed with the code reviser on 3-26-70 ② were regularly adopted as permanent rules of this agency at Spokane, Washington on 4-17-70 and are herewith filed in the office of the code reviser pursuant to chapter 34.04 RCW. The effective date of such rules shall be _____ ③

(ALTERNATIVE B. Use only for adoption of emergency rules)

pursuant to its finding that the immediate adoption of these rules is necessary for the preservation of the public health, safety, or general welfare and that observance of the requirements of notice and opportunity to present views on the proposed action would be contrary to the public interest, were regularly adopted as emergency rules of this agency at _____ on _____ and are herewith filed in the office of the code reviser pursuant to chapter 34.04 RCW.

Dated this 17th day of April 1970.

STATE OF WASHINGTON
FILED
MAY 18 1970
CODE REVISER'S OFFICE
KET # 2379 FILE # 1

WASHINGTON STATE AIR POLLUTION CONTROL BOARD
(AGENCY)
Wallace Lane MD
By Wallace Lane, M. D.
Chairman
Title

- ① NOTICE NUMBER AS APPEARS ON THE COPY OF NOTICE RETURNED TO YOU BY REVISER'S OFFICE (IF PROCEEDINGS WERE CONTINUED, USE NO. OF LAST NOTICE)
- ② STAMPED DATE AS APPEARS ON THE COPY OF NOTICE RETURNED TO YOU BY REVISER'S OFFICE (IF PROCEEDINGS WERE CONTINUED, USE DATE OF LAST NOTICE)
- ③ UNLESS A LATER DATE IS SPECIFIED IN THIS ORDER OR IS PRESCRIBED IN ANOTHER STATUTE, RULES ARE EFFECTIVE 30 DAYS AFTER FILING: RCW 34.04.040. LEAVE THIS SPACE BLANK EXCEPT IN SUCH SPECIAL CASES.

STATE OF WASHINGTON
STATE AIR POLLUTION CONTROL BOARD

PURSUANT to the authority vested in it by the laws of the State of Washington, particularly chapter 70.94 RCW, and pursuant to chapter 34.04 RCW, the State Air Pollution Control Board does hereby adopt as permanent rules and regulations chapter 18-56 WAC, pertaining to sulfur oxide. These rules and regulations, as attached hereto, establish the air quality standard for sulfur oxide, the air quality objective, and the method of measuring and reporting.

THIS order after being first recorded in the order register of this agency shall be forwarded to the Code Reviser for filing pursuant to chapter 34.04 RCW and chapter 1-12 WAC.

DONE in the City of Spokane, County of Spokane, State of Washington, this 17th day of April, 1970.

WASHINGTON STATE AIR POLLUTION CONTROL BOARD

Wallace Lane, M.D.
Wallace Lane, M.D., Chairman

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Chapter 18-56

SULFUR OXIDE STANDARDS

NEW WAC 18-56-010 PREAMBLE. In the interest of the people of the state of Washington, it is the objective of the state air pollution control board to obtain and maintain the cleanest air possible, consistent with the highest and best practicable control technology.

In areas where existing concentrations of sulfur oxides are lower than concentrations allowed by the standards enumerated below, degradation of the atmosphere should be minimized. The highest and best practicable control technology should be applied to all sources emitting sulfur oxides to the atmosphere unless it is determined by the responsible air pollution control agency that application of lesser technology is justified. Air quality standards should not be construed to encourage degradation of existing air quality.

NEW WAC 18-56-020 DEFINITIONS. (1) Air Quality Objective--The concentration and exposure time of a contaminant or multiple contaminants in the ambient air below which, according to available knowledge, undesirable effects will not occur.

(2) Air Quality Standard--An established concentration, exposure time and frequency of occurrence of a contaminant or multiple contaminants in the ambient air which shall not be exceeded.

(3) Primary Air Mass Station (PAMS-SO₂)--A type of station designed to measure contamination in an air mass and representing a relatively broad area. The sampling site shall be representative of the general area concerned and not be contaminated by any special source. The probe inlet shall be a minimum of twenty feet and a maximum of one hundred fifty feet above ground level. Actual elevation should vary to prevent adverse exposure conditions caused by surrounding buildings and terrain. The probe inlet shall be placed approximately twenty feet above the supporting rooftop.

(4) Primary Ground Level Monitoring Station (PGLMS-SO₂)--Stations designed to provide information on contaminant concentrations near the ground and provide data valid for the immediate area only. The probe inlet shall be ten to twenty feet above ground level with a desired optimum height of twelve feet. The probe inlet shall not be less than two feet from any building or wall. The sampling site shall be representative of the immediate area and not be contaminated by any unique source.

(5) Special Stations (SS-SO₂)--Any station that does not meet the criteria or purpose of the standard stations are defined as special stations.

NEW WAC 18-56-030 AIR QUALITY STANDARDS. Sulfur oxides in the ambient air, measured as sulfur dioxide at a primary air mass station, a primary ground level monitoring station, or a special station shall, not exceed the following concentrations averaged over the specified time periods:

(1) Four-tenths part per million by volume average for any one hour.

(2) Twenty five one hundredths part per million by volume average for any one hour day not to be exceeded more than two times in any consecutive seven days.

(3) One-tenth part per million by volume average for any one day (twenty-four hours).

(4) Two one hundredths parts per million by volume average for any one year.

NEW WAC 18-56-040 AIR QUALITY OBJECTIVE. In recognition of the need for continuing improvement of the quality of the air resource, it is the intent of the state air pollution control board to work toward the achievement of the following objective for sulfur oxides: The sulfur oxide concentration measured as sulfur oxide at a primary air mass station, primary ground level monitoring station, or special station shall not exceed 0.3 parts per million average for five minutes.

NEW WAC 18-56-050 METHOD OF MEASUREMENT. For determining compliance with this regulation, sulfur oxides shall be measured as sulfur dioxide by acidified peroxide reagent conductivity or colorimetric techniques approved by, and on file with, the state air pollution control board (Appendix 1). Other continuous and manual methods equivalent in sensitivity, accuracy, reproducibility and selectivity to the approved methods may be used after approval by the state air pollution control board.

NEW WAC 18-56-060 DATA REPORTING. Local and regional air pollution control agencies sampling for sulfur oxides shall notify the state office of air quality control of all violations of this regulation. The notification shall be submitted by the fifteenth of each month, summarizing the violations of the previous month, and by March 1st of each year if the annual standard was exceeded in the previous year. Summaries shall be on forms furnished by the state and shall provide the following information:

- (1) Location of sampler.
- (2) Type of station--air mass, ground level, or special station.
- (3) Time span involved (including specific hours, days, and year.
- (4) Actual concentrations recorded that exceeded the standard.
- (5) Action taken or planned to prevent recurrence.

The state agency shall notify the regional or local agencies of results of samples exceeding the standards within the agency jurisdiction on a monthly basis. This notification shall include:

- (1) Location.
- (2) Time span.
- (3) Standard exceeded.
- (4) Concentrations recorded.
- (5) Requests for reply, indicating action planned or taken to prevent recurrence.

WAC 18-56

APPENDIX 1

SAMPLING AND ANALYSIS
FOR
SULFUR DIOXIDE
IN
AMBIENT AIR

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Part 1

SULFUR DIOXIDE IN AMBIENT AIR MANUAL SAMPLING AND ANALYSIS PROCEDURES

DISCUSSION

These procedures are adapted with modification from the "Intersociety Committee Methods for Ambient Air Sampling and Analysis, Tentative Method of Analysis for Sulfur Dioxide Content of the Atmosphere (Colorimetric) 42401-01-69T," as published in Health Laboratory Science, 6, 228-236 (1968). Variation B of the reference method is used.

PRINCIPLE OF THE METHOD

Sulfur dioxide is absorbed from a measured air sample by aspirating the air through a solution of potassium tetrachloro-mercurate. This reacts to form a dichlorosulfitomercurate complex which is resistant to oxidation.^(1,2) Ethylenediaminetetraacetic acid, disodium salt (EDTA) is added to this solution to complex heavy metals that can interfere with the formation of the dichlorosulfitomercurate.^(3,4) After the absorption is completed, ozone in the solution is allowed to decay.⁽⁴⁾ The solution is treated first with sulfamic acid to destroy the nitrite anion formed from absorbed oxides of nitrogen.⁽⁵⁾ It is treated next with solutions of formaldehyde and purified acid-bleached pararosaniline containing phosphoric acid for pH control. Pararosaniline, formaldehyde, and the bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid, which behaves as a two-color pH indicator. The final solution is adjusted to pH 1.2 ± 0.1 by the addition of 3M phosphoric acid to the pararosaniline reagent. The wave length of maximum absorbance under these conditions is 575 millimicrons and the compound has a molar extinction of 37.0×10^3 .⁽⁴⁾

Atmospheric sulfur dioxide concentrations of interest usually range from a few pphm to several ppm. Higher concentrations (5 to 500 ppm), used in special studies, must be analyzed by using smaller gas samples. A rapid redox reaction occurs between Hg (II) and the sulfite ion, if concentrations of this ion exceed 500 ug/ml.⁽⁶⁾

Collection efficiency falls off rapidly below 0.01 ppm and varies with the geometry of the absorber, the size of the gas bubbles, and the contact time with the solution.^(7,8,9)

RANGE AND SENSITIVITY

The lower limit of detection of sulfur dioxide in 10 ml of TCM is 0.3 ul (based on twice the standard deviation), and represents a concentration of 0.01 ppm SO₂ in an air sample of 30 liters. Extrapolation to lower values cannot be made by taking larger volumes of air (e.g. 100 liters at 0.003 ppm).

Beer's law is followed through the working range of 0.1 - 1.0 absorbance units (0 - 35 ug SO₂ in 25 ml final solution).

INTERFERENCES

Interferences are eliminated by sulfamic acid for oxides of nitrogen,^(4,5) by time delay for ozone,⁽⁴⁾ and by EDTA and phosphoric acid for heavy metals.^(3,4) With this procedure, at least 60 ug of Fe (III), 10 ug of Mn (II), and 10 ug of Cr (III) in 10 ml of absorbing reagent can be tolerated. No significant interference was found with 10 ug of Cu (II) and 22 ug V (V).

PRECISION AND ACCURACY

The precision at the 95 per cent confidence level is 4.6 per cent.⁽⁴⁾

APPARATUS AND REAGENTS

APPARATUS

Absorber - A midget impinger should be used. The orifice of the impinger must not be more than 1/4 inch from the bottom of the absorber. The absorber is filled to the 10 ml mark with absorbing solution and a gas flow rate between 0.2 - 1.0 liter/min. is used. Bubble fracturing must occur as the bubbles strike the bottom. Two impingers are used in series to check for absorption efficiency. There should be no carry-over into the second impinger.

Air Volume Measurement - The air flow measuring device must be capable of measuring the air flow within ± 2 per cent. A wet or dry gasmeter or a calibrated rotometer is satisfactory. Calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.5 atmosphere pressure differential across the needle.⁽¹¹⁾ When using a critical orifice, the incoming air must be free of particulate matter.

Spectrophotometer or Colorimeter - The instrument must be suitable for measurement of color at 575 millimicrons. The wavelength calibration of the instrument must be verified.

REAGENTS. All chemicals must meet the ACS specifications for reagent chemicals.

Distilled Water - Distilled water must conform to the ASTM D1193 Standard for non-Referee Reagent Water. It must be free from oxidants.

Absorbing Reagent - 0.04M Potassium Tetrachloromercurate (TCM), (K_2HgCl_4) - Dissolve 10.86 g mercuric chloride (CAUTION: Highly poisonous. If it comes in contact with skin, flush off with water immediately), 5.96 g of potassium chloride and 0.066g of EDTA disodium salt in water and dilute to 1 liter in a volumetric flask. The absorbing reagent is normally stable for 6 months, but should be discarded if a precipitate forms.

Sulfamic Acid - 0.6 per cent - Dissolve 0.6 g of sulfamic acid in 100 ml of distilled water. Prepare fresh daily.

1-Butanol - Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Check by shaking 20 ml of 1-butanol with 5 ml of 20 per cent KI . If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide.

Buffer Stock Solution (pH 4.69) - Dissolve 13.61 g of sodium acetate trihydrate in distilled water in a 100 ml volumetric flask. Add 5.7 ml of glacial acetic acid and dilute to volume.

1.0 N Hydrochloric Acid - Dilute 86 ml of 11.6 HCl (36 per cent) HCl to 1 liter with distilled water.

Purified Pararosaniline, 0.2 per cent Stock Solution - It is recommended that the "Harleco #64327 purified 99% pararosaniline hydrochloride solution*" be used as the 0.2 per cent stock solution.

If a purified 99% pararosaniline dye* is used, dissolve 0.200 g in 100 mls of 1 N HCl.

If an impure dye is used, it must be purified as follows:

Equilibrate 100 mls 1-butanol and 100 mls 1N HCl by mixing in a 500 ml separatory funnel. Dissolve 0.1 g of pararosaniline hydrochloride (PRA) in 50 ml of the equilibrated acid and let stand for several minutes. Transfer the acid dye solution to a 125 ml separatory funnel containing 50 ml of the equilibrated 1-butanol and extract. The violet impurity will transfer to the

*Available from Harleco, Hartman-Leddon Company, Philadelphia, Pennsylvania 19143.

organic phase. Transfer the lower (aqueous) phase into another separatory funnel, add 20 ml of equilibrated 1-butanol and extract again. Repeat the extraction three more times with 10 ml portions of equilibrated 1-butanol. This should remove all of the violet impurity. (If the 1-butanol phase is still violet after 5 extractions, discard the lot of dye.) After the final extraction, filter the aqueous phase through a cotton plug into a 50-ml volumetric flask and dilute to volume with 1 N HCl. This stock solution will be yellowish red.

Dye Specifications - When assayed as described below, the maximum absorbance must be at 540 millimicrons, and the calculated purity must be greater than 95 per cent.

When used as described in the analytical procedure, the reagent blank must not exceed 0.050 absorbance units using a 1 cm cell.

Assay Procedure - The pararosaniline stock solution need be assayed only once for each lot of dye.

Dilute 1 ml of the stock solution to 100 ml with distilled water in a 100 ml volumetric flask. Transfer a 5 ml aliquot to a 50 ml volumetric flask. Add 5 ml of buffer stock solution and dilute the mixture to 50 ml with distilled water. After 1 hour, determine the absorbance at 540 millimicrons. Determine the concentration of PRA by the formula: $5 \text{ PRA} = \frac{(\text{Absorbance}) (K)}{(\text{grams PRA})}$.

K equals 21.3 (Mean value after extensive purification of dye) for a 1 cm cell and a 0.04 mm slit width in a Beckman DU Spectrophotometer. The K factor must be determined for other instruments.

Pararosaniline Reagent - Add 20 ml of pararosaniline stock solution to a 250 ml volumetric flask. Add an additional 0.2 ml of stock solution for each per cent the stock assays below 100 per cent. Add 200 ml of 3N H_2PO_4 and dilute to 250 ml with distilled water. This reagent is stable for at least nine months.

Formaldehyde - 0.2 per cent - Dilute 5 ml of 40 per cent formaldehyde to 1 liter with distilled water. Prepare fresh daily.

STANDARDIZATION REAGENTS.

Stock Iodine Solution (0.1 N) - Place 12.7 g of iodine in a 250 ml beaker. Add 40 g of potassium iodide and 25 mls of water. Stir until dissolved and dilute to 1 liter with distilled water.

Dilute Iodine Solution (0.01 N) - Dilute 50 mls of the stock iodine solution to 500 mls with distilled water.

Starch Indicator Solution - Mix 0.4 g of soluble starch and 0.002 g of mercuric iodide (preservative) with water to form a slurry and add slowly to 200 ml of boiling water. Continue boiling until clear. Cool the solution and transfer to stoppered bottle.

Standard 0.1 N Sodium Thiosulfate Solution - Dissolve 25 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$) and 0.1 g of sodium carbonate (Na_2CO_3) in 1 liter of freshly boiled, cooled distilled water. Allow the solution to stand for one day before standardizing. Accurately weigh about 1.5 g of potassium iodate, primary standard grade, dried at 180°C. Dissolve in water and dilute to 500 mls in a volumetric flask. To standardize the sodium thiosulfate solution, pipette 50 ml of the iodate solution into a 500 ml iodine flask. Add 2 g of potassium iodide and 10 ml of a 1:10 dilution of concentrated hydrochloric acid. Stopper the flask. Wait 5 minutes and titrate to a pale yellow color with the thiosulfate solution. Add 5 ml of starch indicator solution and continue the titration until the blue color disappears.

Normality of thiosulfate = $\frac{\text{Wt. (grams KI0}_3) \times 10^3 \times 0.1}{\text{ml of titer} \times 35.67}$

Standard 0.01 N Sodium Thiosulfate Solution - Dilute 25 mls of the standard 0.1 N sodium thiosulfate solution to 250 mls with distilled water. This solution must be prepared fresh daily.

Standard Sulfite Solution - Dissolve 0.400 g of sodium sulfite (Na_2SO_3) in 500 ml of distilled water. This solution is equivalent to between 320 and 400 ug of SO_2 per ml. To standardize, pipette accurately 50 ml of the 0.01 N iodine into each of two 500 ml iodine flasks. To flask A (blank) add 25 ml of distilled water, and to flask B (sample) pipette 25 ml of the standard sulfite solution. Stopper the flasks and allow to react for 5 minutes. Titrate each flask in turn to a pale yellow color with standard 0.01 N sodium thiosulfate. Add 5 ml of starch solution and complete the titration. Calculate the concentration of sulfur dioxide in the standard solution as follows:

$$\text{SO}_2 \text{ ug/ml} = \frac{(A-B) N K}{V}$$

Where: A = number of ml for blank
B = number of ml for sample
N = normality of thiosulfate solution
K = 32,000 (micro equivalent weight for SO_2)
V = mls sample volume

Dilute Sulfite Solution - Immediately after standardization, pipette accurately 2 mls* of the standard sulfite solution into a 100 ml volumetric flask and dilute (to volume) with 0.04 M TCM. This solution is stable for a maximum of three days at room temperature and one week under refrigeration.

PREPARATION OF STANDARD CURVE

With Sodium Sulfite - Accurately pipette graduated amounts of the dilute sulfite solution (such as: 0, 1, 2, 3, and 5 ml) into a series of 25 ml volumetric flasks. Add sufficient 0.04 TCM to each flask to bring the volume to 10 ml. Then add the sulfamic acid, formaldehyde and pararosaniline reagents and distilled water as described in the analysis procedure. For greatest precision, a constant temperature bath is preferred. The temperature of calibration and analysis should be the same. A standard curve should be prepared for each analysis.

The absorbances of the solutions are plotted (as ordinates) against the equivalent values of SO_2 . A linear relationship is obtained. The intercept with the vertical axis of the line best fitting the points is usually within 0.005 unit of the reagent blank (zero standard) absorbance value. At least one control sample is included with each series of determinations to insure the reliability of the standard curve.

With SO_2 Permeation Tube - Permeation tubes^(a) that contain liquid sulfur dioxide can be used. The permeation characteristics of permeation tubes are furnished by the manufacturer, and may vary with manufacturers and batches of tubes. The permeation

*If a cell path length of 1-inch is used for absorbance measurement of the developed color, dilute 1 ml of the standard sulfite solution to 100 mls with 0.04 M TCM.

(a) Available from Metronics, Inc., 3201 Porter Drive, Palo Alto, California, 94304, and Polyscience Corporation, 909 Pitner Avenue, Evanston, Illinois, 20202.

characteristics may also vary as the tube ages. Therefore, each tube must be calibrated periodically to verify its permeation rate. This calibration can be made gravimetrically or volumetrically (12,15) and the tube can then be used to prepare standard concentrations of sulfur dioxide in air. Wet chemical analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of sulfur dioxide.

Standard concentrations of sulfur dioxide in air can be prepared by using one of the systems shown in Figures 1, 2, 3 and 4, or the equivalent.

The equipment shown in these systems consists of a water-cooled condenser, constant-temperature water bath maintained at any temperature between 20°C-30°C (measured to $\pm 0.1^\circ\text{C}$), cylinders containing pure dry nitrogen or pure dry air, 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 at least 6 feet of copper coil immersed in a water bath. Insert a calibrated permeation tube into the permeation chamber which is maintained at the desired temperature by circulating water from the constant-temperature bath (a). Pass a stream of dry air or nitrogen over the tube at a known rate. The gas stream is diluted to the desired sulfur dioxide concentration by the addition of clean, dry air (b). The flow rate of the air can be varied from 0.2 to 15 liters per minute depending upon the system used. The flow rate of the sampling system determines the lower limit for the flow rate of the diluent gas, and both must be measured to an accuracy of 1 to 2 per cent. The sulfur dioxide concentration can also be varied by changing the temperature and/or tubes in the permeation tube chamber.

Example of the Preparation of a Standardization Curve - The systems are designed to provide an accurate measure of sulfur dioxide in the 0.01 to 0.5 ppm range, but they can be modified to meet special needs.

For this example the volume of air passed through the absorption bubbler will be held constant at 30 liters and the SO₂ concentration will be varied in the air stream.

The concentration of SO₂ in the air sample is computed as follows: $C = \frac{Pr \times M}{R \times F}$ Where: C = Concentration of SO₂ in ppm
Pr = Permeation rate in ug/min
M = Reciprocal of vapor density, 0.382 ul/ug
R = Flow rate of diluent air, liter/min.

(a) The tube must be temperature equilibrated in the permeation chamber for at least four hours and preferably overnight.

(b) Clean dry air may also be prepared by passing ambient air from a relatively uncontaminated outside source through absorption tubes packed with activated carbon and soda-lime followed in series by an efficient fibre glass filter.

Data for a typical calibration curve are listed in Table 1.

TABLE 1 TYPICAL CALIBRATION DATA

Concentrations of SO ₂ ppm.	Amount of SO ₂ in ul for 30 liters	Absorbance of Sample
0.005	0.15	0.01
0.01	0.30	0.02
0.05	1.50	0.12
0.10	3.00	0.23
0.20	6.00	0.47
0.30	9.00	0.70
0.40	12.00	0.94

For long-term sampling, the conditions can be adjusted to collect 300 liters of sample in a larger volume of absorbing reagent. An aliquot representing 0.1 of the volume can then be taken for the analysis and the remainder of the procedure is the same as described in the analysis section of this method.

CALCULATIONS. Compute the concentration of sulfur dioxide in the sample by the following formula: $\text{ppm} = \frac{(A-A_0) B (0.382)}{V}$

Where: A is the sample absorbance.

A₀ is the point at which the curve crosses the y-axis. Refer to curve example below.

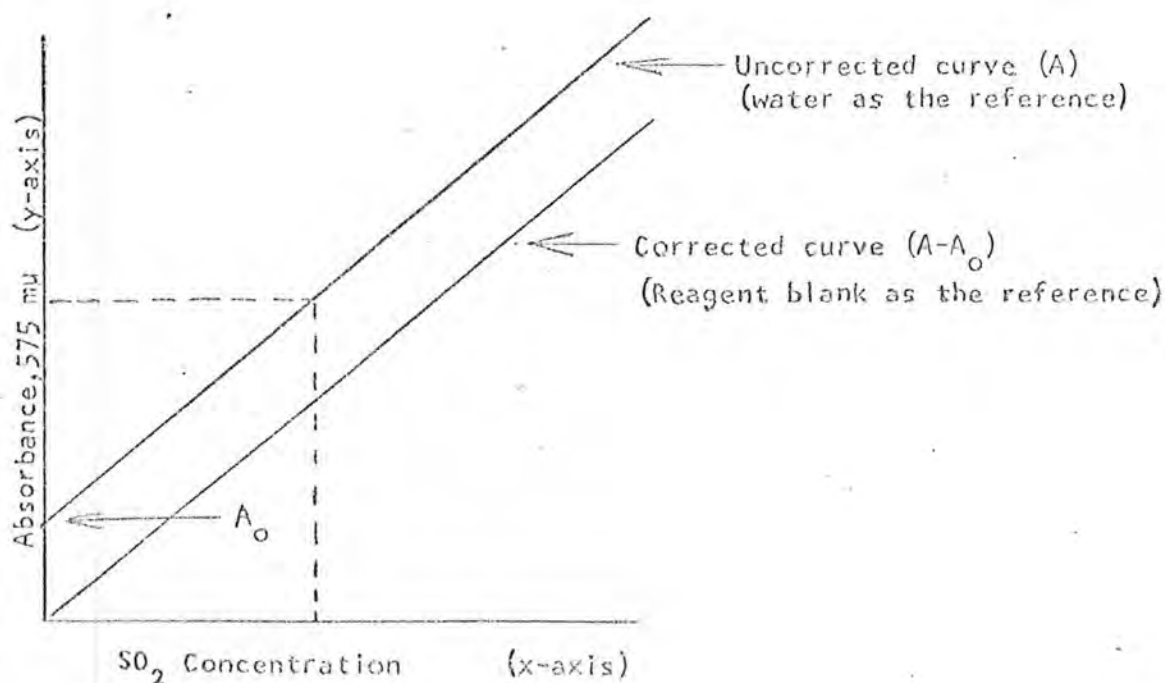
B is the calibration factor, ug/absorbance unit.

0.382 is the volume (ul) of 1 ug SO₂ at 25°C, 760 mm Hg.

V is the sample volume in liters corrected to 25°C and 760 mm Hg (by PV = nRT).

The micrograms of SO₂ in the sample can also be taken directly from curve A and substituted for (A-A₀)B in the above formula.

Example of a Standard Curve.



NOTE: Λ_0 is the point at which the curve crosses the y-axis. The reagent blank absorbance should be within 0.005 units of the absorbance at this point and usually is the same as Λ_0 .

SAMPLING AND ANALYSIS PROCEDURE

Collection of Sample - Place 10 ml of 0.04 M TCM absorbing solution in the absorber. Two absorbers are connected in series to check for complete absorption. Connect the sampling probe upstream of the absorber with glass, stainless steel, or Teflon. Rigid tubing may be joined with butted joints under polyethylene tubing. A trap and calibrated air flow meter, and/or a gas meter equipped with thermometer and manometer are placed between the probe and the pump. Instead of the flowmeter or gas meter, a hypodermic needle in parallel with a manometer can be used as a critical orifice if the pump can maintain a differential pressure of at least 0.5 atmosphere across the needle. The duration and rate of air flow selected depend on the concentration of sulfur dioxide being measured. For best results, rates and sampling time should be chosen to absorb 0.5 to 3.0 μg (0.2 to 1.3 μl at 760 mm Hg, 25°C) of sulfur dioxide per ml of absorbing solution. Shield the absorbing reagent from direct sunlight during and after sampling by covering the absorber with a suitable wrapping, such as aluminum foil, to prevent deterioration. Samples should not be stored for more than a few hours. However, if the sample must be stored before analysis, keep it refrigerated at 5°-10°C. If a precipitate is observed, remove it by centrifugation.

Analysis - After collection, transfer the sample quantitatively to a 25 ml volumetric flask. Use about 5 ml of distilled water for rinsing. Wait 20 minutes before adding color developing reagents to allow any ozone to decompose. For each set of determinations, prepare a reagent blank by adding 10 ml of the unexposed absorbing reagent to a 25 ml volumetric flask. Add 1 ml of 0.6 per cent sulfamic acid to each flask and allow it to react for 10 minutes to destroy the nitrite ion formed from absorbed oxides of nitrogen. With volumetric pipettes, add 2.0 ml of the 0.2 per cent formaldehyde, then 5.0 ml of the pararosaniline reagent.

Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with distilled water. At 30 minutes after adding color developing reagent determine the absorbances of the sample and of the blank at 575 millimicrons. Use distilled water (not the reagent blank) as the reference. Do not allow the colored solution to stand in the colorimeter cell; otherwise, a film of dye may be deposited on the glass surfaces.

If the absorbance of the sample solution falls between 1.0 and 2.0, the sample can be diluted 1:1 with the reagent blank and the absorbance immediately determined again. Solutions with higher absorbances can be diluted up to six-fold with the reagent blank in order to obtain on-scale readings within 10 percent of the true absorbance value.

The SO_2 content of the sample is determined by comparison with a standard curve showing SO_2 concentration vs. absorbance. The accuracy of the curve must be verified for at least one point every four hours during any sequence of manual sampling and analysis. The accuracy of the curve must be verified each time fresh absorbing reagent or pararosaniline reagent is used and whenever the temperature during color development varies more than $\pm 2^\circ\text{C}$ from the temperature at which the standard curve was prepared.

Part 2

SULFUR DIOXIDE IN AMBIENT AIR CONTINUOUS MONITORING

DISCUSSION

The acid-peroxide electro conductivity method shall be used for the continuous monitoring of sulfur dioxide in ambient air. The interference from other pollutants in the atmosphere should be determined for the particular area in which sampling is planned. Instrument manufacturers' specifications should list the magnitude of interference by specific gases. (16,17)

This method is used for the continuous automatic sampling, analyzing, and recording of SO_2 concentrations in outside ambient air in the concentration range from 0.01 to 2 ppm. The upper limit may vary from 1 to 5 ppm, depending upon reagent flow and airflow rates and on electronic amplification. Air is continuously admitted to the absorber where the SO_2 in the airstream is absorbed and oxidized by a liquid absorbent. The electrical conductivity of the resulting solution is continuously measured and recorded, and the readings obtained are proportional to the concentration of SO_2 in the sampled air.

REAGENTS

All chemicals used must be ACS analytical reagent grade.

The distilled water must conform to the ASTM D1193 Standard for Non-Referee Reagent Water.

Absorbing Solution - Prepare a distilled water solution containing 3×10^{-3} molar hydrogen peroxide (H_2O_2) and 5×10^{-5} normal sulfur acid (H_2SO_4). Two milligrams per liter of Dowicide B (2,4,5, trichlorophenate) or the equivalent are added to prevent algae growth. A non-ionic wetting agent is added to aid in the wetting of the reaction chamber of the monitoring instrument.

Before use, the solution must be analyzed to verify the reagent strength. The pH must be 4.2-4.8. The hydrogen peroxide concentration must be at least 3×10^{-3} molar. A suggested analytical method for peroxide is a potassium permanganate titration in strongly acid solution.

Absorbing Solution Preparation - Transfer 19 liters of distilled water to a suitable container such as a 5 gallon plastic bottle. Add 10.0 mls of 0.1 normal sulfuric acid, 4.2 mls of 30 per cent hydrogen peroxide, 8.0 mls of Kodak 200B non-ionic wetting agent and 10 mls of a 0.36 per cent Dowicide B solution. Mix thoroughly and analyze for reagent strength. Other volumes can be prepared by adjusting the reagent quantities proportionally.

Reagent Specificity - The acid in this particular reagent is for the purpose of maintaining the described pH and thus limiting interferences from acid gases. The acidified hydrogen peroxide absorbing reagent of pH 4.2-4.8 limits CO_2 , H_2S , and oxides of nitrogen interference as well as accelerating the absorption of SO_2 . The SO_2 is removed from the reaction zone by the peroxide oxidation to sulfate. This process also produces two hydrogen ions per molecule of SO_2 absorbed, which adds significantly to the reagent conductance. The oxidation step is specific to SO_2 , and the overall electro conductivity response to SO_2 is many times greater than that of the nitrogen oxides, CO_2 , and H_2S . (16)

APPARATUS (Figure 5)

Sampling Probe - The sampling probe can be made of Pyrex glass, 316 stainless steel or Teflon. The intake end is equipped

with a rain loop, and a loose glass wool filter is added to remove large particulate matter. This filter is positioned indoors, and, if necessary, inside the thermostatically controlled cabinet to prevent condensation of water vapor. The air sampling line, including the probe, should be kept as short as possible and still meet station requirements.

Absorber - A venturi scrubber or any reagent-air-contacting system capable of an absorbing efficiency of at least 98 per cent for all SO₂ concentrations is acceptable.

Air Flow Equipment - Use a flowmeter, needle valve, or other device capable of regulating flows with an accuracy of ± 2 per cent. A suitable device is recommended to continuously record the air flow rate on the conductivity recorder chart or shut off data input completely should error exceed ± 2 per cent of normal air flow.

Absorbing Reagent Flow - Use a metering pump, flowmeter, or other device capable of measuring flows with an accuracy of ± 2 per cent.

Pumps and Metering Devices - Air pumps and liquid metering devices must be variable and capable of the continuous accuracy described in air and reagent flow.

Instrument Temperature Control -

(1) Thermostatically Controlled Cabinet - The reagent feed lines, absorption column and conductivity cells shall be enclosed in an insulated compartment, with thermostatically maintained temperature control to $\pm 1^\circ\text{F}$.

(2) Unheated Cabinet - Instruments not equipped with temperature controlled cabinets must have conductivity cells incorporating thermistor compensation for temperature variation. The area in which the sampler is located must be free from large temperature changes.

Conductivity Electrodes - Two pairs of platinum dip electrodes are most commonly used. One pair measures the conductivity of the unreacted reagent and the other pair measures the conductivity of the reacted reagent.

Conductivity Recorder - Any instrument capable of recording the differential output of the conductivity cells in the SO₂ concentration range of zero to 2 ppm with an accuracy of ± 1 per cent of full scale is acceptable. The recorder should use chart paper of sufficient grid accuracy to determine a 24-hour average concentration of 0.05 ppm SO₂, on the 0-1 ppm full scale range.

Reagent Reservoir - Any inert container with sufficient volume to contain up to one week's supply of reagent can be used. The reagent must be protected from air pollutants by attaching soda lime and charcoal filters or the equivalent to the air inlet line.

Electronic Check - A means of checking by electrical impedance is recommended for all SO₂ analyzers. Checks of 25 per cent and 75 per cent are acceptable. Insertion of such a device may be manual or automatic. This shall be used only to check accuracy of the electronics and is not a substitute for dynamic calibration.

Zero Reference - A zero reference shall be made at least twice weekly. This will be accomplished by diversion of the normal sample stream through a filter capable of removing all traces of sulfur dioxide. This zero reference shall be stable to $\pm .005$ ppm for thirty minutes. Air and liquid flow rates shall indicate no greater than ± 2 per cent change during such a check period.

INSTRUMENT CALIBRATION PROCEDURES

Static Calibration Method - The instrument should be statically calibrated with sulfuric acid solutions of known composition corresponding to atmospheric SO₂ concentrations covering the

range of the instrument. For a 0-2 ppm instrument, calibration solutions corresponding to 0.5, 1.0, 1.5, and 2.0 ppm SO₂ are prepared by the addition of calculated amounts of dilute H₂SO₄ to the absorbing reagent. This method does not take into consideration absorption column efficiency and other factors; therefore, it cannot be used as a substitute for dynamic calibration but shall be done semi-annually in conjunction with the dynamic calibration.

Establish instrument zero by introducing the unexposed absorbing reagent in both the reference and sample conductivity cells. Calibration solutions are then substituted for the absorbing reagent in the sample conductivity cell. After normal operating temperatures and liquid flow rates have been established for each reference point, compare and record the instrument reading with the calibration solution equivalent SO₂ concentration. Adjust the instrument by means of the span control to indicate the correct concentration. Sulfur dioxide free air is now introduced directly into the system, as in normal operation. Air, free of sulfur dioxide, can be obtained by passing it through activated charcoal and soda lime. Adjust the instrument again, if necessary. A minimum of four reference points shall be recorded.

Do not adjust the span of temperature controlled instruments until the cabinet temperature has remained constant for at least 15 minutes.

Dynamic Calibration Method - The dynamic calibration methods take into account the collection efficiency of the absorbing column under standard flow conditions and shall be performed semi-annually along with static calibrations. Contact column changes will require dynamic and static recalibration. Conductivity cell replacement or replatinization requires only the static calibration reference.

Standard air-SO₂ mixtures may be prepared in a compressed gas cylinder, an ineft collapsible plastic bag or a temperature controlled permeation tube chamber. The gas mixtures from these containers are introduced directly into the monitoring instrument for calibration purposes.

Standard SO₂-air dilutions can be obtained commercially in compressed gas cylinders. (Most states have regulations regarding unlicensed pressurization of steel vessels.)

Collapsible inert plastic bags can be used by introducing a measured amount of SO₂ with a gas syringe. A measured amount of filtered air or nitrogen is then added to give the desired concentration.

The temperature controlled permeation chamber is the preferred method of obtaining standard SO₂-air dilutions. This method is discussed in full under "Preparation of Standard Curve" in the "Manual Sampling and Analysis Procedures" section.

The standard air-SO₂ mixture can be introduced simultaneously into the analyzer and the manual absorber. The instrument record is then adjusted to read SO₂ concentrations as determined by the manual method. A typical dynamic calibration system is shown in Figure 4.

CALIBRATION PROCEDURE

A complete examination of the monitoring instrument must be made to verify that it is in optimum operating condition before calibration. This examination must include:

- (1) The cleanliness of glass parts - all must be clean.
- (2) Verification of air and liquid flow meter calibration information.
- (3) An electrical impedance check - used fixed resistance

to assure that the instrument meets the manufacturer's specification.

(4) Checks of electronic tubes - replace those that have been used for six months or more.

(5) The recorder - verify that it gives a linear response and has had routine maintenance.

(6) All mechanical parts - verify that they are operating smoothly.

(7) Sample lines - replace if they are leaking, not clean or appear that they may fail because of age or other factors.

(8) Instrument maintenance - verify that the instrument has been maintained in accordance with the manufacturer's specification.

(9) Zero reference - the zero reference must be held for at least 30 minutes before calibration.

(10) The absorbing solution - it must show a pH of 4.2-4.8 and an H_2O_2 concentration of 3×10^{-3} molar. When it is installed in the instrument, all air bubbles that may collect in the reagent feed line must be removed.

(11) Instrument temperature - the temperature equilibrium must be $\pm 1^\circ\text{F}$.

(12) Air and liquid flow - both must be in equilibrium before calibration is started.

The calibration of the monitoring instrument with standard air- SO_2 mixtures must include the following:

(1) The chart reading must agree with ± 1 per cent of the standard atmosphere concentration as determined by the manual sampling and analysis section of this method.

(2) A minimum of four reference points in the regions of 10, 25, 50, and 100 per cent of the full chart scale must be determined to plot an instrument response curve.

(3) The instrument response to a standard air- SO_2 mixture must be maintained for a minimum of 15 minutes at each reference point.

INSTRUMENT PERFORMANCE SPECIFICATIONS

(1) Instruments shall be capable of operation with a full scale range of 0-1 ppm with an adjustment for higher ranges if required.

(2) Zero reproducibility of ± 1 per cent full-scale deflection over a 24-hour period.

(3) Linearity - for any sample and range, the analyzer shall give a recorded response which is within ± 2 per cent of full scale of a linear response to that sample. Reproducibility shall be ± 2 per cent of full scale for successive identical samples.

(4) Span drift - The distance between the recorded zero point on any range shall not drift by more than ± 1 per cent of full scale in 24 hours.

(5) Effect of zero and span adjustments - a 5 per cent manual adjustment of zero shall not change the span (the difference between zero point and span point) of the instrument by more than 1 per cent of full scale. A 5 per cent manual adjustment of span shall not change the zero point more than 1 per cent of full scale. Attenuation from one range to another shall not cause the recorded zero point to move by more than 1 per cent of full scale.

(6) Warm-up time - the analyzer shall be operating within specifications within one hour after connection to a source of power.

(7) Noise level - shall not exceed 1 per cent of any operating range (peak to peak).

(8) Effect of temperature and voltage - the analyzer shall maintain all specifications while operating within a surrounding

air temperature of 30°-120°F and subjected to line voltage variations of 95-125 volts AC.

(9) Speed of response - an analyzer shall indicate 90 per cent of the final reading one minute after the concentration at the instrument inlet has been changed.

(10) Interference - shall be specified by gas, related range of concentration in the atmosphere, and per cent of span interference for a sulfur dioxide range 0-2.0 ppm.

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PERMEATION TUBE SCHEMATIC FOR LABORATORY USE

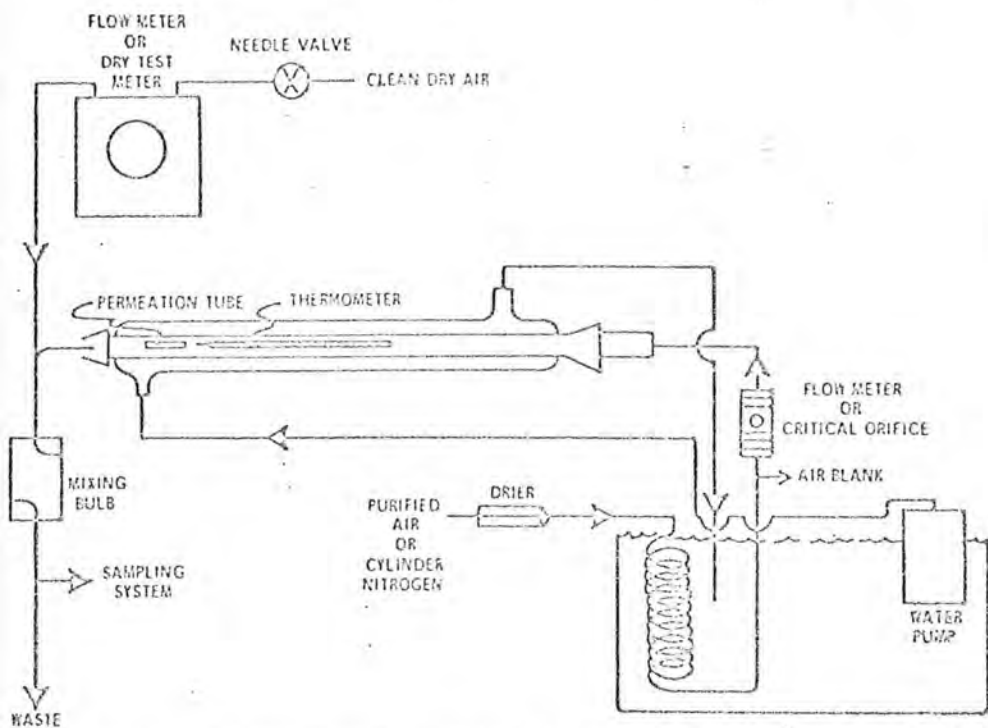


Figure 1—Gas dilution system for preparation of standard concentrations of sulfur dioxide for laboratory use by the permeation tube method.

PERMEATION TUBE SCHEMATIC FOR FIELD USE

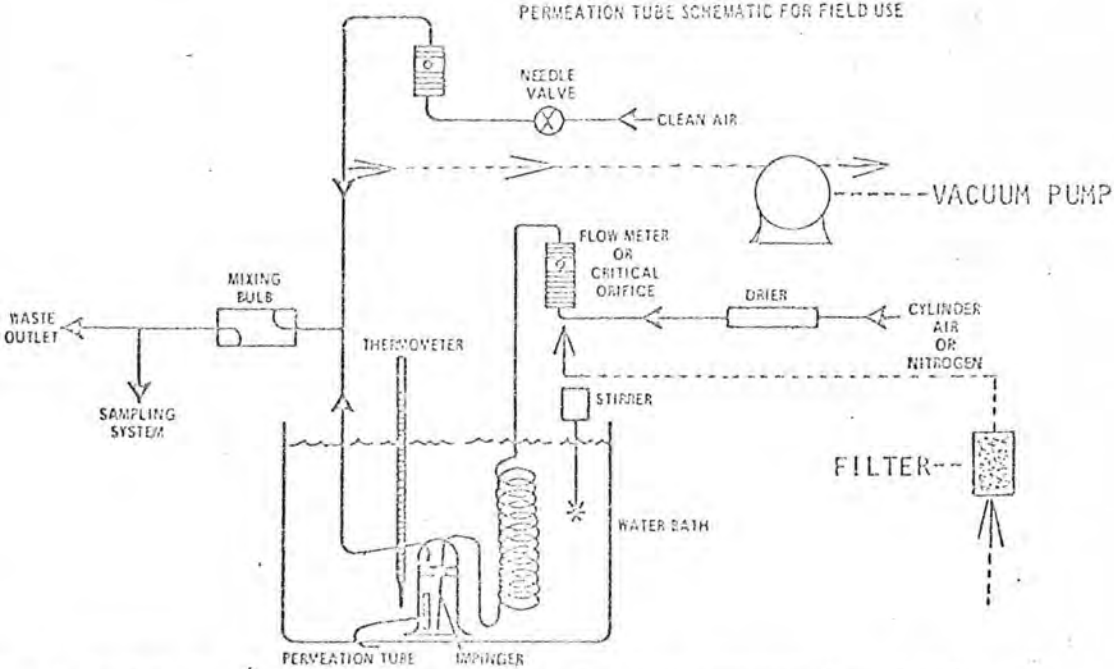
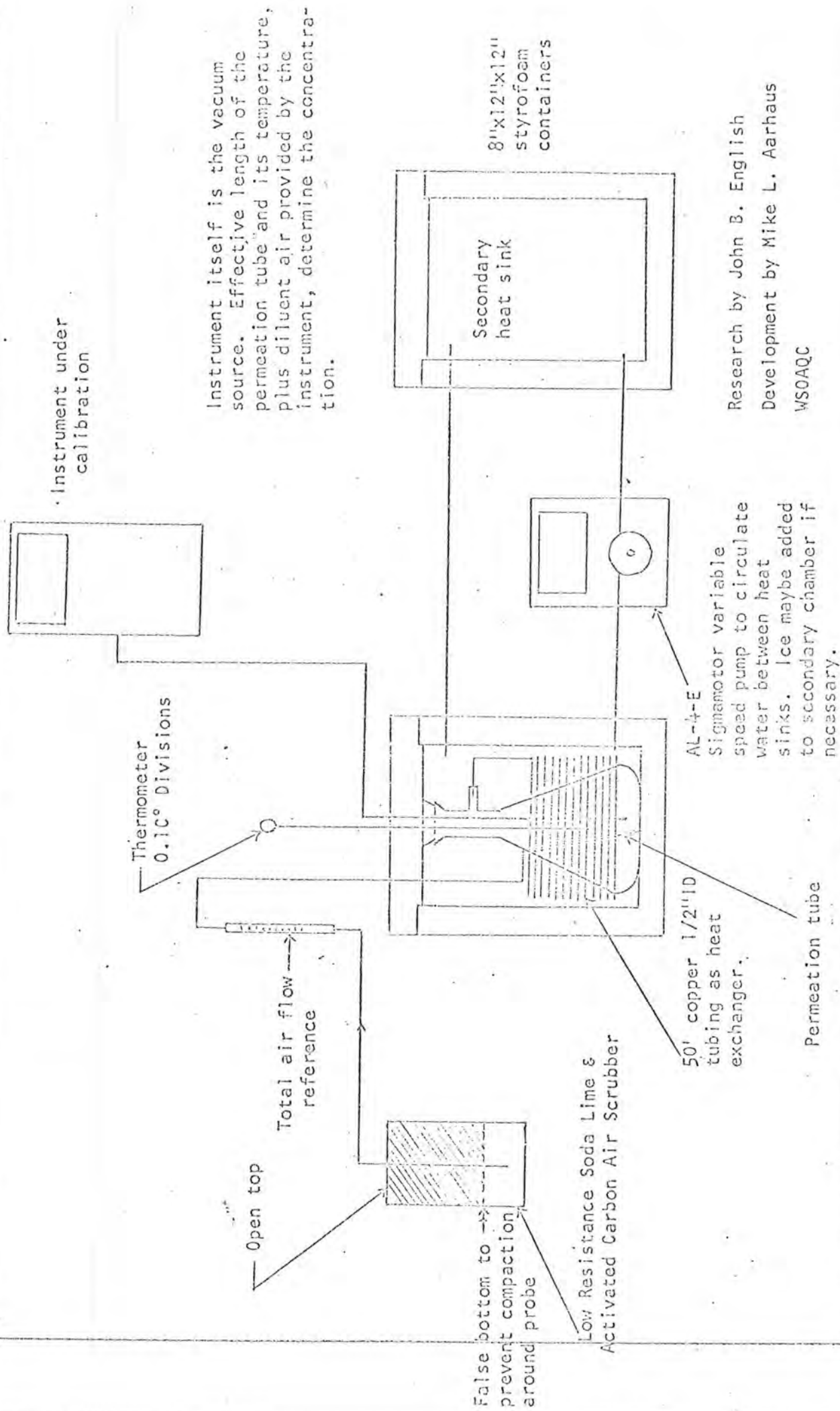


Figure 2—Gas dilution system for preparation of standard concentrations of sulfur dioxide for field use by the permeation tube method.

Dotted lines - Optional Vacuum System
 Filter - Low Pressure Soda Lime/Activated Charcoal

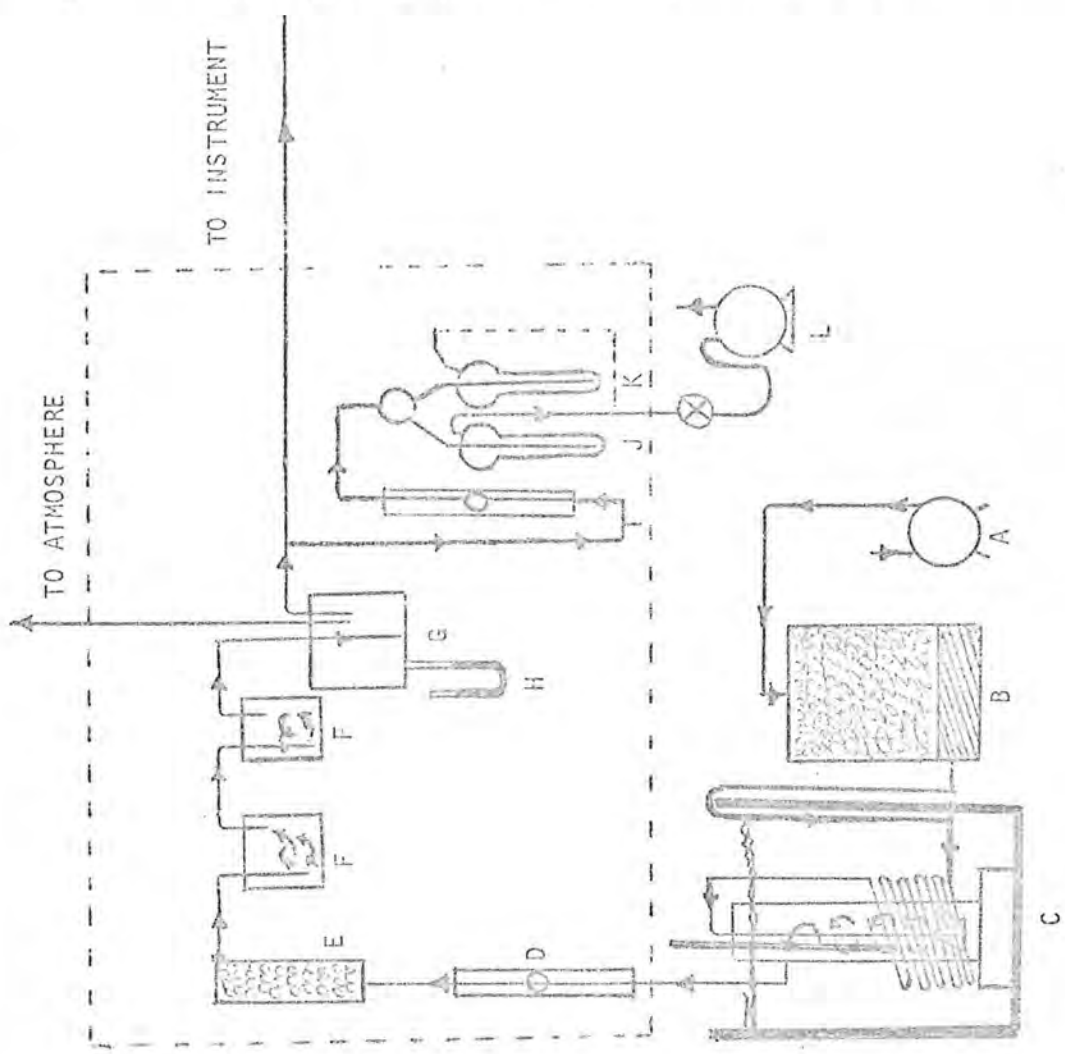
CALIBRATED PERMEATION TUBE GAS DISPENSING APPARATUS



NOTE: The method is limited to total flow sampling procedure because of the inadequate gas mixing characteristics of the system.

FIGURE 3

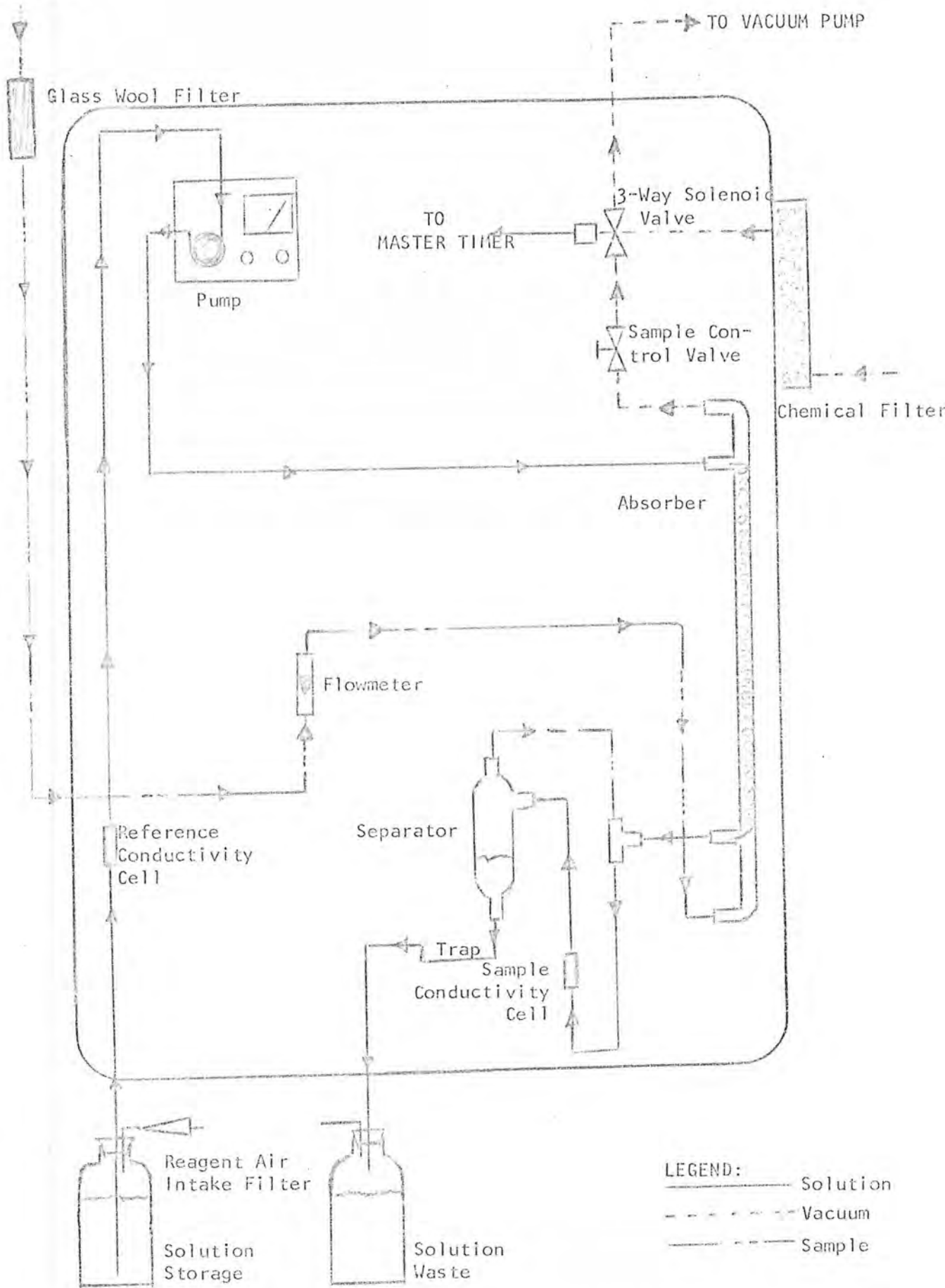
- A. Pump - providing flow through scrubber. Temperature, bath, and calibration panel.
- B. Chemical Scrubber - 8-12 mesh soda lime or equivalent (top) glass wool particulate filter (bottom) providing dry SO₂ free air
- C. Circulating Water Bath controlled to 0.1°C. Permeation chamber (Greenburg-Smith Impinger) thermometer inside, 50' coiled copper tubing inline with gas stream from scrubber to impinger to temperature condition gas sample.
- D. Variable area flowmeter (total volume flow reference)
- E. Glass column packed with helices (Teflon or glass) for initial mixing (optional)
- F. Mixing chambers
- G. Sampling chamber (vented to atmosphere)
- H. Manometer (1/4" water column positive pressure)
- I. Variable area rate meter for impinger flow reference
- J. Ballast impinger to maintain dynamic flow to impinger system through wet chemistry sample is not being taken.
- K. Sample impinger (vacuum source transferred from one impinger to another)
- L. Vacuum pump



DYNAMIC GAS DISPENSING SYSTEM

FIGURE 4

SAMPLE IN



GENERAL FLOW DIAGRAM FOR SULFUR DIOXIDE ANALYZER

FIGURE 5