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COMMUNITY HEALTH ENVIRONMENTAL SURVEILLANCE STUDIES (CHESS) AIR POLLUTION MONITORING HANDBOOK: Manual Methods

Health Effects Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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COMMUNITY HEALTH ENVIRONMENTAL SURVEILLANCE STUDIES (CHESS)

AIR POLLUTION MONITORING HANDBOOK: MANUAL METHODS

By

Exposure Assessment Branch
Population Studies Division
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U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
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DISCLAIMER

This report has been reviewed by the Health Effects Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

LIST OF FIGURES

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Editor

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I. TOTAL SUSPENDED PARTICULATES (TSP)

I. TOTAL SUSPENDED PARTICULATES (TSP)

I.a. Hi- volume Sampler

1. Principle and Application

1.1 Measurement of mass concentration of suspended particulates in ambient air. Sample size collected is suitable for most other analyses.

1.2 Air is drawn into a covered housing through a filter with a high-flow-rate blower. Flow rate is 1.13 to 1.70 m^3/min. (40 to 60 ft^3/min.). This allows suspended particles with diameters of less than 100 μm (Stokes equivalent diameter) to reach the filter surface.[1] Particles of 100 to 0.3 μm diameter are ordinarily collected on glass fiber filters. Mass concentration of ambient air suspended particulates (μg/m^3) are computed by measuring the mass of collected particulates and the volume of air sampled.

2. Range and Sensitivity

2.1 An adequate sample can be collected in an atmosphere having concentrations as low as 1 μg/m^3 when the sampler is operated at an average flow rate of 1.70 m^3/min. for 24 hours. A satisfactory sample may be collected in 6 to 8 hours or less if particulate levels are higher than 400 μg/m^3. A standard sampling period is recommended for determination of average concentrations of suspended particulates in ambient air.

2.2 Weights are determined to the nearest milligram. Airflow rates are determined to the nearest 0.03 m^3/min. (1.0 ft^3/min). Times are determined to the nearest two minutes. Mass concentrations are reported to the nearest microgram per cubic meter.

3. Interferences

3.1 Oily particulate matter, such as photochemical smog or wood smoke, can block the filter and cause a rapid drop in airflow at an irregular rate.

3.2 Glass-fiber filters are comparatively insensitive to changes in relative humidity, but collected particles can be hygroscopic,[2] which may cause reduced air flow.

4. Precision, Accuracy and Stability

4.1 Collaborative testing indicates the relative standard deviation (coefficient of variation) for single analyst variation (repeatability of the method) is 3.0 percent. The corresponding value for multilaboratory variation (reproducibility of the method) is 3.7 percent.[3]

4.2 The sampler measurement accuracy of true average concentration depends upon constancy of airflow rates through the sampler. Airflow rates are affected by the concentration and nature of dust in the atmosphere. The error in the measured average concentration under extreme conditions may be more than ±50 percent of the true average concentration, depending on the amount of

true average concentration, depending on the amount of airflow rate reduction and on variation of the mass dust concentration with time in the 24-hour sampling period.[4] Periodic duplicate sampling should be used to assess accuracy.

5. Sampling Apparatus

5.1 Sampler. The sampler consists of three units: (1) faceplate and gasket, (2) filter adapter assembly, and (3) motor unit. Figure 1 shows a view of these parts, their relationship to each other, and assembly. The sampler must allow environmental air to pass through a 406.5 cm^2 (63 in^2) portion of a clean 20.3 by 25.4 cm (8 by 10 in) glass-fiber filter at a rate of at least 1.70 cm^3/min. The motor must operate continuously for 24-hour periods with input voltages ranging from 110 to 120 volts, 50-60 cycles alternating current. A third wire ground is necessary to meet safety requirements. The housing for the motor unit may be made in any way that allows the unit to remain airtight and leakfree. Variable transformers are used to set the initial flow at 1.70 m^3/min. (60 cfm).

5.2 Sampler Shelter. It is important that the sampler be correctly installed in a suitable shelter. The shelter must be made of materials that can withstand extremes of temperature, humidity, and all types of air pollutants. Properly painted exterior plywood or heavy-gauge aluminum serves well. The sampler must be mounted vertically in the shelter with the glass-fiber filter parallel to the ground. The shelter requires a roof to protect the filter from precipitation and debris. A design for a suitable shelter with a gable roof is shown in Figure 2.

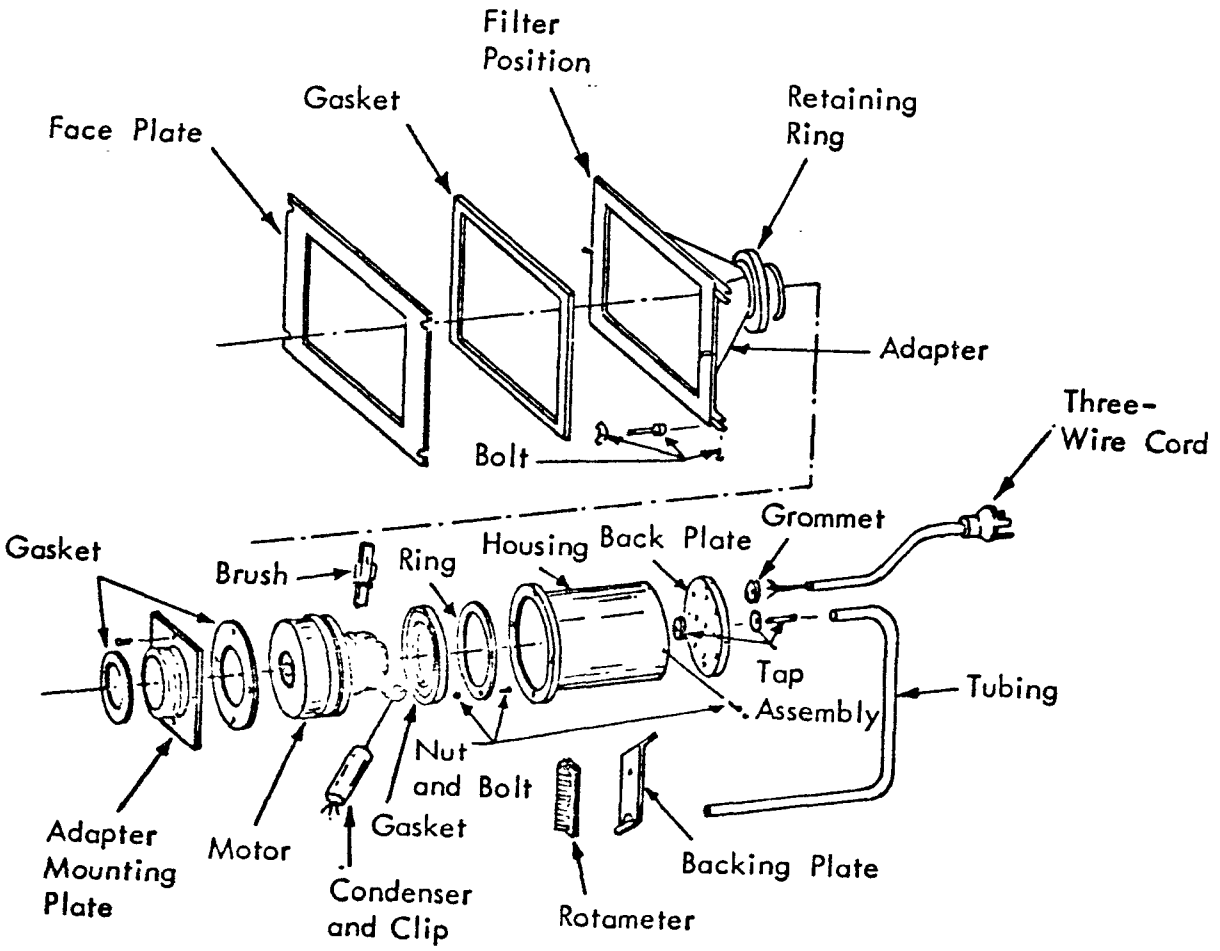


Figure 1 - Exploded view of typical high-volume air sampler parts

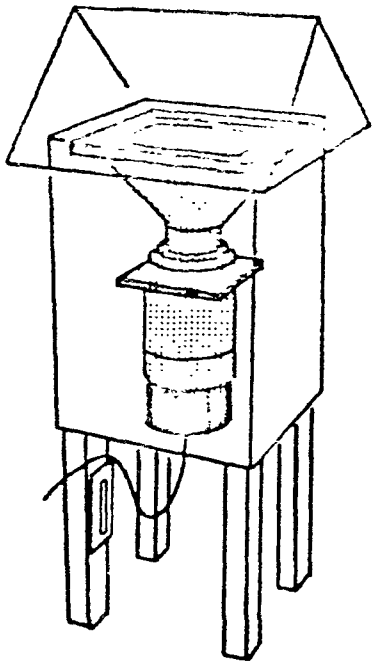


Figure 2 - Assembled Sampler and Shelter

The clearance between the main housing and roof should be 580.5 ± 193.5 cm^2 (90 ± 30 in^2). The main housing should be rectangular, with dimensions of about 29 by 36 cm (11½ by 14 in).

5.3 Rotameter. Marked in arbitrary units, frequently 0 to 70, and capable of being calibrated. Other devices of comparable accuracy may be used.

5.4 Filter media as discussed in 7.5.

6. Sampling Procedure

6.1 Filter Preparation. Expose filters to a light source. Inspect for pinholes, particles, or other imperfections. Do not use filters with visible imperfections. A small brush is useful for removing particles.

Equilibrate filters in the filter conditioning environment (15 - 35°C at less than 50 percent relative humidity) for 24 hours.

Weigh the filters to the nearest milligram. Record their weight and filter identification number. Do not bend or fold the filter before collecting the sample.

6.2 Sample Collection. Open the shelter, loosen the wing nuts, and remove the faceplate from the filter holder. Install a numbered, preweighed, glass-fiber filter in position (rough side up). Replace the faceplate without disturbing the filter. Fasten securely.

Undertightening will allow air leakage; overtightening will damage the sponge-rubber faceplate gasket.

A light application of talcum powder on the sponge-rubber faceplate gasket will prevent the filter from sticking.

In bad weather, the sampler may be taken to a protected area for filter change. Close the shelter roof and run the sampler for about 5 minutes. Connect the rotameter to the nipple on the back of the sampler and read the rotameter ball with rotameter in a vertical position. Estimate to the nearest whole number. Reading should be at the center of the ball.

If the ball fluctuates rapidly, tip the rotameter and slowly straighten it until the ball gives a constant reading. Record the initial rotameter reading, starting time, and date on the filter folder. Disconnect the rotameter from the nipple. (The rotameter should never be left connected to the sampler except when the flow is being measured.)

Sample for 24 hours and take a final rotameter reading. Record the final rotameter reading, ending time, and date on the filter folder. Data is voided if stop flow drops below 1.13 m^3/min. Remove the faceplate as described above and carefully take the filter from the holder, touching the outer edges only.

Fold the filter lengthwise so that only surfaces with collected particulates are in contact. Place in a manila folder. Record on the folder the filter number, location and other factors, such as meteorological condition or nearby building razing that could affect the results. If the sample is torn, wet, or incomplete, void it at this time.

To obtain a valid sample, the high-volume sampler must be operated with the same rotameter and tubing used in calibration.

6.3 Maintenance

6.3.1 Sampler Motor. Replace brushes every 25 days to prevent motor damage.

6.3.2 Faceplate Gasket. Replace when margins of samples are no longer sharp. The gasket may be sealed to the faceplate with rubber cement or double-sided adhesive tape.

6.3.3 Rotameter. Clean with alcohol for proper operation.

7. Analysis Apparatus

7.1 Filter Conditioning Environment. Balance room or desicator maintained at 15° to 35°C (normally 25°C) and less than 50 percent relative humidity.

7.2 Analytical Balance. Having a sensitivity of at least 0.1 mg and equipped with a weighing chamber designed to handle unfolded 20.3 by 25.4 cm (8 by 10 in) filters.

7.3 Light Source. Often a table of the type used to view X-ray films.

7.4 Numbering Device. Capable of printing identification numbers on the filters.

7.5 Filter Media. Glass-fiber filters with a collection efficiency of at least 99 percent (for particles of 0.3 cm diameter measured by the DOP test) are suitable for quantitative measurement of suspended particulate concentrations,[5] although some other medium, such as paper, may be desirable for some analyses. For more detailed analyses use filters that contain low background concentrations of the pollutant being investigated. Careful quality control is required to determine background values of these pollutants.

7.6 Set of Class 5 weights to standardize balance.

8. Analysis Procedure

8.1 After sampling, the filter is equilibrated again for 24 hours and reweighed. The weight of collected particulate matter is the weight of the filter after sampling less its tare weight. The filters may be subjected to detailed chemical analysis after weighing.

8.2 Calculations are expressed in micrograms of particulate matter collected for each cubic meter of ambient air sampled. The volume of air sampled is computed from the start-stop flow rates and time.

$$\text{microgram/m}^3 = \frac{\text{Total weight (micrograms)}}{\text{Volume of air sampled (cubic meters)}}$$

8.2.1 Sample Volume. Volume conversion: Convert the initial and final rotameter readings to true airflow rate, Q_i and Q_f, respectively. Use calibration curve obtained in Section 10.1.9.

Calculate volume of air sampled

$$V = \frac{Q_i + Q_f}{2} \times T$$

V = Air volume sampled, m^3

Q_i = Initial airflow rate, m^3/min.

Q_f = Final airflow rate, m^3/min.

T = Sampling time, min.

8.2.2 Calculate mass concentration of suspended particulates

$$S.P. = \frac{(W_f - W_i) \times 10^{-6}}{V}$$

S.P. = Mass concentration of suspended particulates, $\mu g/m^3$

W_i = Initial weight of filter, g

W_f = Final weight of filter, g

V = Air volume sampled, m^3

10^{-6} = Conversion of g to μg

9. Calibration Apparatus

9.1 Calibration apparatus for hi-volume sampler.

9.1.1 Calibrated orifice with 18-hole plate. (18-hole plate simulates fresh filter.)

9.1.2 Manometer capable of reading from zero to 30 cm of water.

9.1.3 Hi-vol sampler with visi-float rotameter.

9.1.4 Variable voltage transformer (Variac).

9.1.5 Tube of general purpose clear glue.

9.1.6 Wrenches (2) for making various adjustments in the visi-float for calibration.

9.2 Orifice Calibration Equipment and Procedure

9.2.1 Orifice Calibration Unit. Consists of a metal tube 7.6 cm (3 in.) ID and 15.9 cm (6 1/4 in.) long with a static pressure tap 5.1 cm (2 in.) from one end.

The other end of the tube is flanged to hold a loose female threaded coupling that

screws onto the inlet of the sampler. An 18-hole metal plate is positioned with a rubber gasket between the orifice and sampler to simulate resistance of a clean glass-fiber filter. An orifice calibration unit is shown in Figure 3.

9.2.2 Differential Manometer. Capable of measuring to at least 30 cm (12 in.) of water.

9.2.3 Positive Displacement Meter. Calibrated in cubic meters or cubic feet, to be used as a primary standard.

10. Calibration Procedure

10.1 Sampler Procedure

10.1.1 Set up the sampler and materials according to Figure 4.

10.1.2 Insure that all connections are tight.

10.1.3 Zero the manometer by adjusting the fluid level.

10.1.4 Operate the hi-vol sampler with a clean filter at 30 cm of water for 3 to 5 minutes to seat the brushes.

10.1.5 Adjust the Variac until the manometer fluid level is slightly above the 30 cm manometer mark. This indicates that the sampler is capable of operating at the desired flow rate.

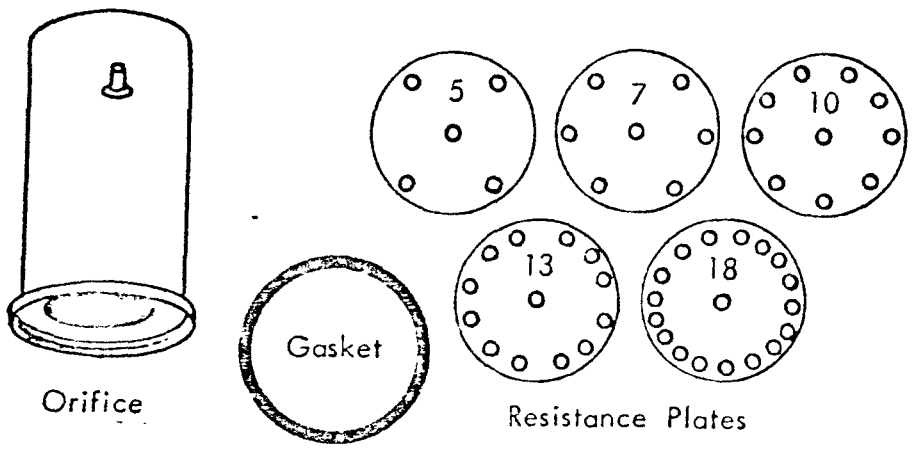
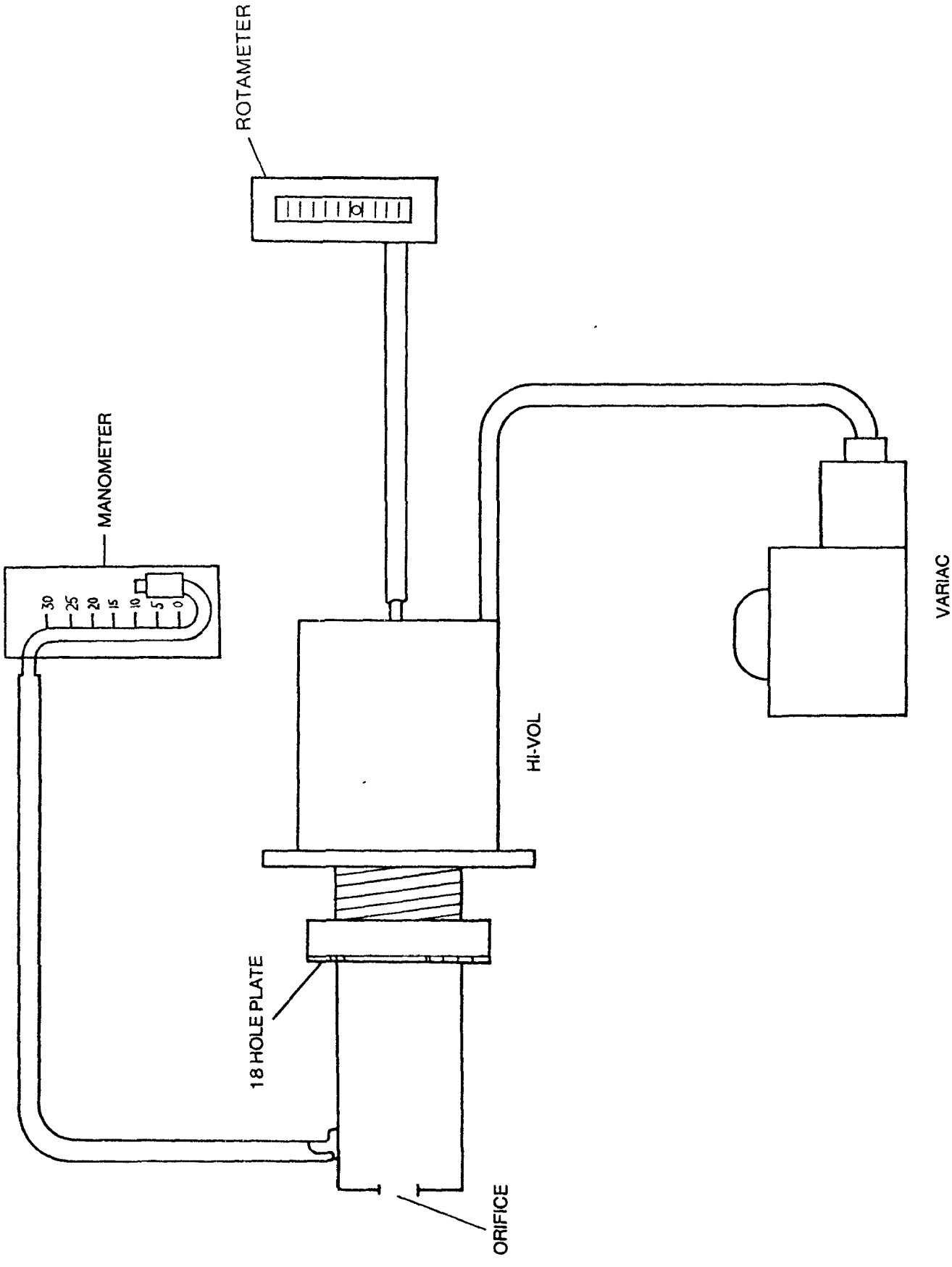


Figure 3 - Orifice Calibration Unit

Figure 4

HI-VOL ROTAMETER CALIBRATION



10.1.6 During the 3 - 5 minute seating of brushes, the rear portion of the sampler should be visually checked for excessive armature sparking. The armature should be replaced if it sparks.

10.1.7 Set the manometer to the centimeters of water that corresponds to a flow of 1.70 m^3/min. (60 cfm) from the calibration curve supplied with the orifice. This is the usual operation flow of the sampler in the field.

10.1.8 Adjust the visi-float to indicate 1.70 m^3/min. (60 cfm). Do this by adjusting the brass fitting at the top of the visi-float. Seal the fitting in position with a small amount of glue. Be careful so as not to plug the hole in front and just below the brass fitting.

10.1.9 Shut off motor, remove the filter, and attach the orifice calibration unit with 18-hole resistance plate in place. Operate the hi-volume sampler at a series of different, but constant, air flows (usually six). Use a variable transformer to change the flows. Record the reading of the differential manometer on the orifice calibration unit. Also record the readings of the rotameter at each flow. Read the center of ball.

Measure atmospheric pressure and temperature. Convert the differential manometer reading to m^3/min. (Q), using the plot in 10.2.2. Obtain a linear regression of Q and the rotameter reading. From this regression obtain a chart of rotameter reading vs flow. Increment the flows in 0.1 m^3/min. The chart is used by the field operator to obtain Q_i and Q_f.

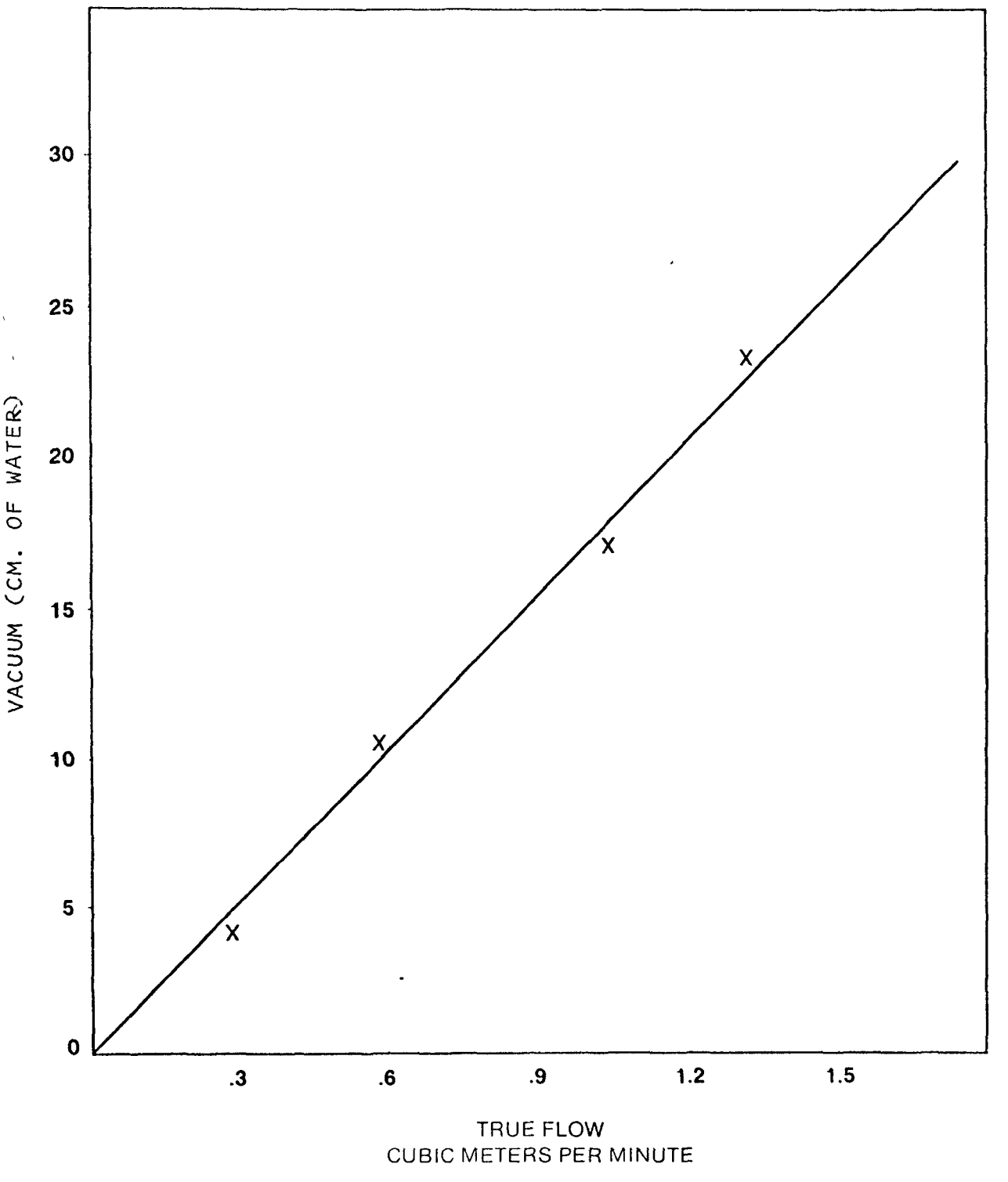
10.1.10 Plotting the Curve

10.1.10.1 Use graph paper (10 x 10 block to the inch) to plot a curve of centimeters of water vs. flow in m^3/min. as in Figure 5.

10.1.10.2 The actual calibration performed is the calibration of the visi-float. It is important to keep the visi-float paired with the hi-vol it was calibrated with due to varying differences from one hi-vol sampler to another. The visi-float number and the number appearing on the hi-vol sampler should be the same. Record this number and the calibration date on the curve.

Figure 5

HI-VOL ROTAMETER CALIBRATION CURVE



10.2 Orifice Procedure

10.2.1 Purpose. Since only a small portion of the total air sampled passes through the rotameter during measurement, the rotameter must be calibrated against actual airflow with the orifice calibration unit. The orifice calibration unit itself must be calibrated against the positive displacement primary standard (Roots-meter) before it can be used to calibrate the rotameter.

10.2.2 Orifice Calibration Unit. Attach the orifice calibration unit to the intake end of the positive displacement primary standard. Connect one end of a differential manometer to the differential pressure tap of the orifice calibration unit. Leave the other end open to the atmosphere. Operate the high-volume motor blower unit so that you get a series of different, but constant, airflows (usually six) in definite time periods. Record the reading of the differential manometer at each airflow. Obtain the different constant airflows by varying the sampler voltage using a variable transformer or by placing a series of resistance plates (Figure 6), one at a time, between the calibration unit and the primary standard. Placing the orifice before the inlet reduces the pressure below atmospheric at the inlet of

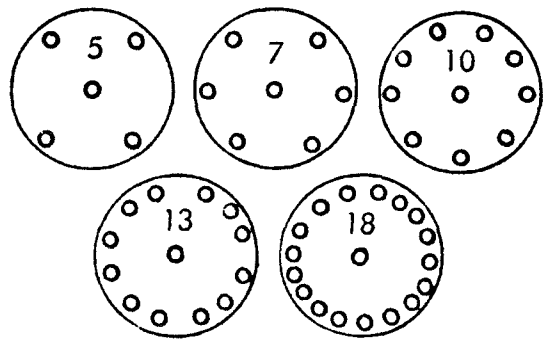


Figure 6 - Resistance plates

the primary standard; thus a correction must be made for the increase in volume caused by decreased inlet pressure. This correction is made by applying the equation in 10.2.4.

Attach one end of a second differential manometer to the inlet pressure tap of the primary standard. Leave the other end open to the atmosphere. During each of the constant airflow measurements made above, measure the true inlet pressure of the primary standard with this second differential manometer. Measure atmospheric pressure and temperature. Correct the measured air volume to true air volume as directed above. Then obtain true airflow rate, Q, as directed in 10.2.4. Q is defined as the corrected volume divided by the time of flow measured at each reading (Equation B). Plot the differential manometer readings of the orifice unit vs. Q.

10.2.3 All calibration measurements shall be computed using existing temperature and pressure. Then these measurements may be corrected to S.T.P. 25°C @ 760 nm pressure.

10.2.4 Orifice Calculations. Calculate the air volume measured by the positive displacement primary standard.

Equation A:

$$V_a = \frac{(P_a - P_m)}{P_a} \quad (V_M) \quad \frac{T_a}{T}$$

where:

V_a = True air volume at atmospheric pressure, m^3

T_a = Temperature at which primary standard is calibrated

T = Temperature at which calibration is conducted

P_a = Barometric pressure, mm Hg

P_m = Pressure drop at inlet of primary standard, m^3.

Conversion Factors:

Inches Hg x 25.4 = mm Hg

Inches water x 73.48 x 10^{-3} = inches Hg

Cubic feet air x 0.0284 = cubic meters air

True Airflow Rate:

Equation B:

$$Q = \frac{V_a}{T}$$

where:

Q = Flow rate, m^3/min.

T = Time of flow, min.

REFERENCES

1. Robson, C. D. and K. E. Foster, "Evaluation of Air Particulate Sampling Equipment," Am. Ind. Hyg. Assoc J. 24, 404 (1962)

2. Tierney, G. P. and W. D. Conner, "Hygroscopic Effects on Weight Determination of Particulates Collected on Glass-Fiber Filters," Am. Ind. Hyg. Assoc J. 28, 363, (1967)

3. McKee, Herbert C., Ralph E. Childers and Oscar Saeng, Jr., "Collaborative Study of Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Published by Southwest Research Institute, San Antonio, Texas, June 1971, Under EPA Contract #70-40.

4. Harrison, W. K., J. S. Nader and F. S. Fugman, "Constant Flow Regulators for High-Volume Air Sampler," Am. Ind. Hyg. Assoc. J. 21, 114-120 (1960).

5. Much material used is from the Federal Register, Vol. 36, No. 228, Thursday, Nov. 25, 1971.

I.b. SUSPENDED NITRATES (SN)

I.b. SUSPENDED NITRATES (SN)

1. Principle and Applicability

1.1 Suspended nitrates are collected on the hi-vol filter (Reference Sect. 1.0). Nitrate concentrations are determined by analyzing a portion of the exposed filter.

A strip of the filter is put into a flask with distilled water and refluxed. The extracted water soluble nitrates are reduced to nitrites by a copper-cadmium reductor column. The nitrite ion is reacted with sulfanilamide in acidic solution to form a diazo compound. This compound then couples with a N-1-naphthylene-diamine dihydrochloride to form a reddish-purple dye. They dye concentration, proportional to nitrate concentration, is determined spectrophotometrically at 540 nm.

1.2 Applicability. This method applies to the analysis of sulfates collected with the 24-hour hi-vol sampler.

2. Range and Sensitivity

The analysis method applies from 0.5 to 30.0 μg NO_3^-/ml.

3. Interferences

Metal ions can produce a positive error, i.e., divalent mercury and divalent copper can form colored complex ions with absorption bands in the region of color measurement.[1]

4. Precision and Accuracy

Precision and accuracy depend upon the region of the absorbance vs. concentration curve in which work is being done. Accuracies range between 3 and 10 percent.

5. Sampling Apparatus

Sampling apparatus is the hi-volume sampler described in the TSP procedure. (Reference Section 1).

6. Sampling Procedure

Sampling procedures are the same as in Section 6.1 in the TSP procedure. (Reference Section 1).

7. Analysis

7.1 Apparatus

7.1.1 Volumetric flasks, pipets, beakers, and graduated cylinders to prepare solutions. Use Class A glassware.

7.1.2 Vacuum Filtering Apparatus. Device which permits vacuum filtering directly into the receiver. This consists of a bell jar with a top opening, a side tabulation and a bottom plate. The Buchner funnel passes through the top opening and is sealed to the bell jar with a stopper. The bell jar should be tall enough to contain the polyethylene bottles used for storing the samples. The vacuum connection is made using the side tabulation. The filtering apparatus is shown in Figure 1.

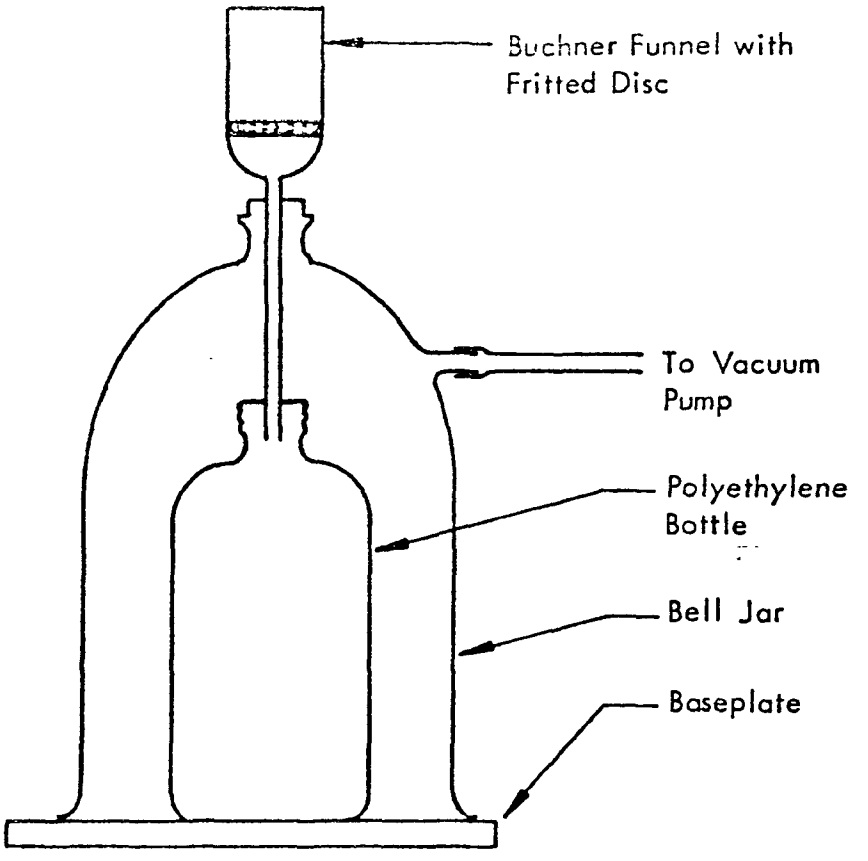


Figure 1 - Vacuum Filtering Apparatus

7.1.3 Vacuum Pump. Any device which can maintain a vacuum of at least 64 cm of Hg. Mechanical pumps or water aspirators may be used.

7.1.4 Polyethylene Bottles. Bottles with a capacity of 60 ml (2 oz) fitted with polyseal caps.

7.1.5 pH Meter. Capable of measuring pH to nearest 0.1 pH units over a range of 0-14.

7.1.6 Glass Bottles (brown). 500 ml glass bottles with polyseal caps.

7.1.7 Pump Tubing. Flow rated tubing of the capacities shown in Figure 2. Silicone rubber tubing in place of the standard pump tubing is highly recommended. Standard pump tubing should be replaced every day if used. Other available tubing has correspondingly longer life (3 weeks) with silicone rubber tubing having performed satisfactorily for as long as 5 weeks. If a plasticized tubing is used, it should be washed with acetone followed by distilled water prior to its use.

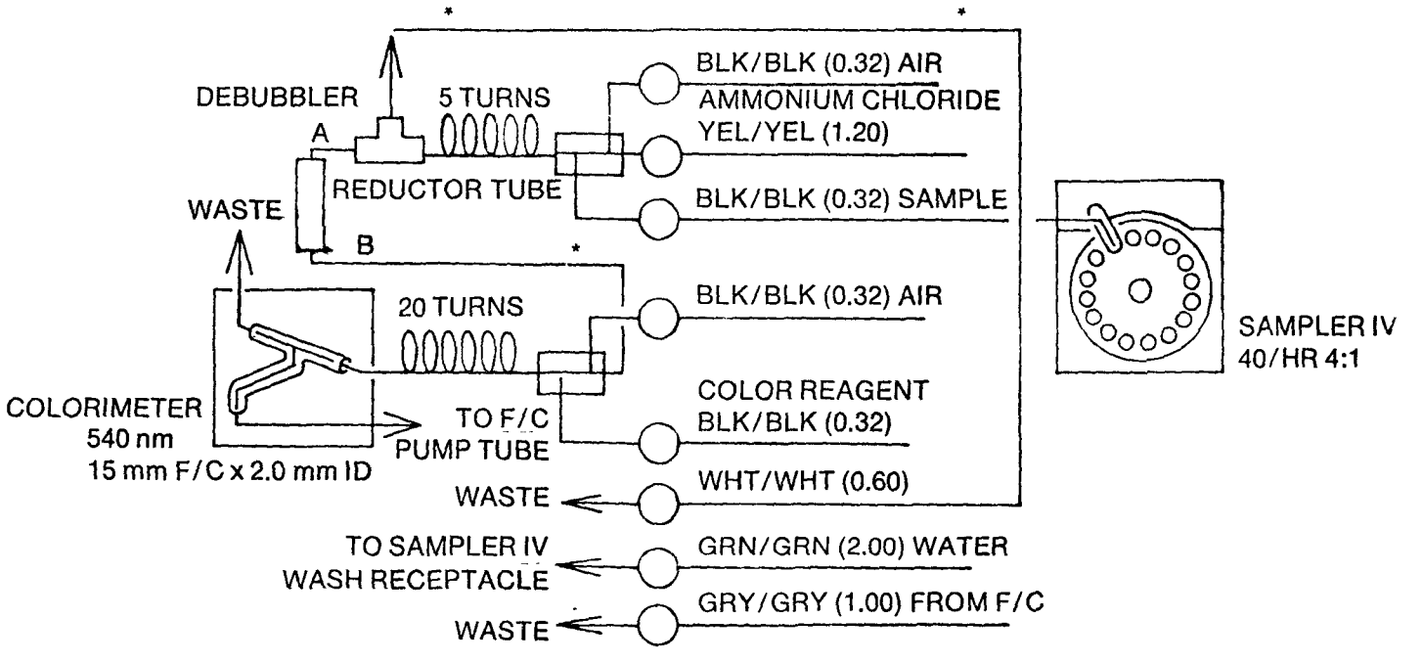
7.1.8 Erlenmeyer Flask. 125 ml with 24/40 joint.

7.1.9 Condenser. Water jacketed, 300 mm length with 24/40 joints.

7.1.10 Hot Plate. Suitable for sample extraction (7.2.1).

7.1.11 Pyrex Glass Wool.

Figure 2 - NITRATE AND NITRITE IN WATER



NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN. FLOW RATES ARE COLOR-CODED.

*0.034 POLYETHYLENE

7.1.12 Plastic Tubing. 10 cm (3.94 in) and 2.3 mm (0.09 in) I.D. Polyvinylchloride tubing, for ion exchange column (5.2.1.5).

7.1.13 Rubber Pipet Bulb.

7.1.14 Buchner Funnels. Buchner style 150 ml capacity with finepore fritter glass filter.

7.1.15 Instrument. Technicon Autoanalyzer II as listed below:

a. Sample turntable with variable sample rate and variable sample to wash ratio.

b. Proportioning pump: flow rates are varied by using flexible tubing of different diameters.

c. Mixing coils: use a 20-turn coil and a 5-turn coil.

d. Cadmium-copper reduction column: this U-shaped column is approximately 5 in. long and 1 - 1½ in wide. Pyrex glass tubing, 4 mm O.D., 2 m I.D., is used to build it.

7.2 Analysis Reagents

All reagents should conform to ACS specifications for reagent grade materials unless otherwise specified.

7.2.1 Ammonium Chloride. Weigh 20.0 g NH_4Cl (ammonium chloride) and place in a 2-liter volumetric flask. Add about 1000 ml alkaline water. (Adjust distilled water pH by adding

NH_4OH.) Swirl to complete solution. Dilute to the mark with alkaline water. Add 1.0 ml Brij-35* with a graduated pipet. Rinse the pipet twice with the solution. Store reagent at room temperature.

7.2.2 Color Reagent. Weigh .25 g NEDA [n-(naphthyl) -ethylene-diamine dihydrochloride] and 5.0 g sulfanilamide and place in a 500 ml volumetric flask. Add about 50 ml concentrated phosphoric acid ($H_3 PO_4$). Swirl to mix. Dilute to the mark with distilled water. Mix by inverting 3-4 times. Add .25 ml Brij-35* (wetting agent) with a 1 ml graduated pipet. Rinse the pipet twice with the solution. Mix well by inverting 10 - 15 times.

If the solids do not dissolve at once, place it in a dark area at room temperature. Mix every 5 to 10 minutes by inversion until the solids dissolve. Refrigerate in an amber container.

7.2.3 Stock Nitrate Solution. (1000 µg NO_3^-/ml) Dry the KNO_3 (reagent grade or better) over silica gel or some other drying agent. Do not heat in an oven! Weigh exactly 1.6305 g of KNO_3 and dissolve in distilled water to make 1 liter. Add a few drops of chloroform

* Technicon brand name

as a preservative. The concentration of this solution is 1000 μg NO_3^-/ml.

7.2.4 Nitrate Working Standards. Prepare the following standards by accurately pipetting the appropriate amounts of stock nitrate solution into volumetric flasks. Dilute to volume with distilled water and mix thoroughly. Prepare working standards daily.

A	.5	μg NO_3^-/ml
B	1	"
C	2	"
D	5	"
E	8	"
F	10	"
G	20	"
H	30	"

e.g., put .5 ml of stock solution in a 100 ml volumetric flask. Dilute to volume. This will yield:

$$\frac{.5 \text{ ml} \times 1000 \text{ μg } NO_3^-/\text{ml}}{100 \text{ ml}} = 5 \text{ μg } NO_3^-/\text{ml}$$

Prepare a larger volume of one of the standards to use in every 10th cup of the sample tray. This will allow the operator to check for drift and column degradation. Replace the column if this standard drops more than 3% below its value.

7.2.5 When preparing fresh stock nitrate solution, run a 5-point calibration curve for the new and old solutions.

7.2.6 Cadmium Filings. Use 99% pure cadmium filings by filing a cadmium bar. Rinse the filings once or twice with diethyl ether or 1 N HCl followed by distilled water. Allow the metal to air dry. Store in a stoppered bottle.

8. Analysis Procedure

8.1 Filter Preparation. Cut a 3/4" x 8" filter strip from the exposed glass fiber hi-vol filter with a paper cutter. Place the folded strip in a 125 ml Erlenmayer flask. Add 35 ml distilled water and reflux the solution for 30 minutes. Turn off the heat and cool the flask to room temperature. Rinse the inside surface of the condenser and adaptor with small amounts of water from the upper opening of the condenser. Disconnect the Erlenmayer from the condenser. Vacuum filter the aqueous extract through a fine sintered glass funnel into a 50 ml volumetric flask. Wash the remaining filter strip at least five times with distilled water. Filter through the same glass filter into the flask. Dilute to 50 ml. Transfer an aliquot of this solution to a capped culture tube for future use in the Technicon sample tray.

8.2 Preparation of the Nitrate Reductor Column. Fill the U-tube with distilled water. Insert a funnel into one end of the U-tube and partially fill with cadmium filings. Alternate U-tube ends and repeat this process until column is full of cadmium. Plug both ends with glass wool.

Attach one end of the column to the ammonium chloride line of the system pump. Run 1 N HCl through this line for 1 - 2 minutes. Then run distilled water 1 - 2 minutes.

Dissolve 2 g $CuSO_4 \cdot 5H_2O$ in distilled water.

Dilute to 100 ml. Obtain 10 ml of this solution and dilute to 50 ml.

Run the second dilute solution through the column exactly 1 minute. Rinse again for 1 - 2 minutes with distilled water. Reverse position of the U-tube and repeat Cu_2SO_4 solution for 1 minute and distilled water for 1 - 2 minutes. Remove plugs and squeeze out cadmium with forced distilled water into a small (50 ml) beaker. Wash with distilled water and decant small black particles. (These particles are colloidal copper oxide, the primary contaminant.) Repeat washings until water is clear. Air dry or dry in oven until just dry. This may now be stored for future use.

When ready to use the column fill the U-tube with distilled water. Add this mossy green copper covered cadmium until the column is full and most of the water has been displaced. Plug both ends with glass wool. Attach a water filled shunt across the U-tube to keep air from reaching the filings. It may be stored from day to day or when not in use in this manner.

8.2.1 The reductor column must be clean and have good flow characteristics for the system to operate satisfactorily.

8.2.2 Pump about 100 ml of distilled water containing 1 ml of stock nitrate solution through the column for initial activation of the reductor column.

8.2.3 The reductor column is 99% efficient.

8.3 Use the Technicon Autoanalyzer II for this analysis. Use a 560 nm interference filter and a 15 mm tubular flow cell in the colorimeter. Operate the sample turntable at 40 sample positions per hour with a ∿ 1:10 sample to wash ratio. Eight minutes elapse between sample pickup and appearance of corresponding peak on recorder chart.

8.3.1 Assemble the Technicon Autoanalyzer pump as shown in Figure 2. See the Technicon II manual for specific instructions. After assembling the system, without the reductor column, attach a shunt (small piece of tubing) between points A and B (Fig. 2). Place all pump tubes in their respective solution containers and check the flows. Put the sample line in a container of distilled water. Allow the system to run 5 - 10 minutes. Check the debubbler to be sure that no bubbles are entering the shunt. Attach the nitrate reductor column at point A first, taking care that no air bubbles enter the system. Then attach column at point B. Run the analyzer with a fresh ion exchange column until a stable baseline is obtained.

Pump the chemicals through the system to zero the instrument. Adjust the range with the standards to read out as desired on the strip chart recorder. These standard values will be used to plot the absorbance vs. concentration curve. A blank filter strip sample should be inserted in the analysis system after running the standards. This will establish the blank absorbance data required to calculate the final values. Determine the blank by analyzing 1% of the filters before use. Cut 3/4" x 8" strips from these filters for the analysis. Extract the nitrate concentration from these strips as described in Section 8.1. This solution will provide the sample to determine the background levels of NO_3^- in the blank filters.

8.3.2 After plotting the standard curve and running the blank sample, the system is ready to analyze samples. Use a mid-range standard every 10th sample to check for drift. The baseline will remain noisy with some tailing throughout the day. Peak height readings should therefore always be made by drawing a line connecting the baseline and measuring at the midpoint. Samples which exceed the absorbance of the highest standard of the calibration curve are diluted until the concentration falls within the calibration range. A broading of the colorimeter output with a corresponding loss

in peak height usually indicates that the pump tubing should be replaced. Silicone rubber tubing is recommended in place of the standard pump tubing.

8.3.3 Run a color blank on the samples if the extracts are highly colored or contain suspended particulate. Remove the NEDA from the coloring reagent. Run the analyzer with this reagent and with distilled water in the sample tube. (Other lines are run normally.) This will establish a baseline for determining the color absorbance values. These values are then used to calculate the final concentration. (Colored samples are not often found except in extremely polluted areas.)

8.3.4 Run a series of standards including a filter blank at the end of each day's analysis. Re-run a random 5-10% of the samples to maintain internal quality assurance.

8.3.5 Change the glass wool in the ion exchange column when it gets dirty. The column may be removed from the system to use the next day if it is not exhausted. Deterioration can be observed when the standard sample value decreases.

At the end of an analysis day, replace the column with a shunt. Place another water-filled shunt across the column openings to prevent air contacting column material.

8.3.6 Purge this system daily with distilled water. Do this by placing all chemical lines in water for 5 - 10 minutes. All liquid lines should be left filled with water until the next sampling time.

8.3.7 Samples should be processed within 2 - 3 days after cutting.

8.3.8 Where particulate matter is present, the solution must be filtered. Filter with a fine sintered glass filter.

8.3.9 It is critical that the water used in preparing reagents and standards be completely free of metallic ion contamination. Store reagents in glass bottles and avoid contact with air.

8.3.10 Obtain expanded ranges by using the standard calibration dial on the colorimeter. Refer to the Technicon II manual to operate the colorimeter and strip chart recorder.

8.4 Calculations

Plot the absorbance on the y axis and the concentration on the x axis for the eight points given in Section 7.2.4. Since Beer's Law is followed, a straight line is obtained by the equation:

$$Abs = a\ x + b$$

where Abs = absorbance

$a = NO_3^-$ concentration

the NO_3^- concentration ($\mu g/ml$) $= \frac{Abs - b}{x}$

$$\text{or} \quad \mu g\ NO_3^-/ml = \frac{Abs - b}{x}$$

(Equation 1)

Linearity correlation coefficients are usually greater than .9995.

Determine the actual $\mu g\ NO_3^-/ml$ by subtracting the blank and color concentrations from the sample concentration obtained from Equation 1. (Run standards before and after each analysis day. Establish the absorbance vs. concentration curve by averaging these data.)

Determine nitrate concentration found in the air by:

$$\mu g\ NO_3^-/ml = \frac{(\mu g\ NO_3^-/ml)\ 600}{m^3}$$

$$600 = \frac{\text{area of exposed filter (9" x 7")}}{\text{area of analyzed strip 3/4" x 7"}} \times \frac{\text{volume of liquid (50 ml)}}{}$$

$$600 = \frac{9 \times 7 \times 50}{3/4 \times 7}$$

[The actual filter is 8" x 10", but there is a ½" unexposed border around it. Include the unexposed area when cutting the filter. This makes a 3/4" x 8" slice.]

Determine the air volume in cubic meters by:

$$m^3 = \left(\frac{Q_i + Q_f}{2}\right) T$$

where Q_i and Q_f are the initial and final flows in m^3/min. T is the number of minutes the hi-vol sampler is run.

9. Calibration Apparatus

9.1 The sampler calibration apparatus is that of the hi-volume sampler method procedure in Section 9.0.

9.2 The analysis calibration apparatus consists of preparing a series of liquid standards and running these through the analysis system. These standards are discussed in Section 7.2.4.

10. Calibration Procedure

10.1 The calibration procedure is that outlined in Section 10.0 of the hi-vol sampler method.

10.2 The analysis calibration procedure consists of running a number of known concentrations through the system and obtaining a calibration curve of the colorimeter output (absorbance) vs. the input nitrate ion concentration. Run a new curve whenever it is necessary to make new standard solutions. Run curves for both old and new solutions.

REFERENCES

1. "Community Health Air Monitoring Program" (CHAMP), EPA Contract No. 68-02-0759

2. Morgan, G. B., et al.; "Automated Laboratory Procedures for the Analysis of Air Pollutants," Presented at the 59th Annual Meeting APCA, June 20-24, 1966, San Francisco.

3. "Nitrates Industrial Method," AA II 100-70 W, January 1971, Preliminary Methods, Technicon Autoanalyzer II Methodology.

4. Armstrong, F. A. J., et al. 1967 Deep Sea Res. 14, pp. 381-389.

5. Grasshoff, K., Technicon International Congress, June 1969.

6. Federal Water Pollution Control Administration Methods for Chemical Analysis of Water and Wastes, November 1969.

I.c. SUSPENDED SULFATES (SS)

I.c. SUSPENDED SULFATES (SS)

1. Principles and Applicability

1.1 Principles. Suspended sulfates are collected on the hi-vol filter (Reference Sect. 1). A portion of this filter is analyzed and concentrations are obtained utilizing the methylthymol blue (MTB) method of sulfate determination.

A strip of the filter is put into a flask with distilled water and refluxed. The resultant water soluble sulfate is treated with a reagent containing equivalent barium chloride and methylthymol blue. Prevent formation of a barium dye chelate by maintaining a pH of 2.8. After reaction between the sulfate and barium ions, an excess of methylthymol blue, equivalent to the sulfate present, remains. The pH is increased to 12.4 with sodium hydroxide and the unreacted barium forms a chelate with the dye. The excess dye, which is equivalent to the sulfate, is determined colorimetrically at 460 nm.

1.2 Applicability. This method applies to the analysis of sulfates collected with the 24-hour hi-volume sampler.

2. Range and Sensitivity

The analysis range is 3.0 to 95.0 μg $SO_4^{=}$/ml with the Technicon II linearizer.

3. Interferences

Heavy metal cations interfere by complexing the methylthymol blue. These ions are removed by passing through a cation exchange column.

4. Precision and Accuracy

Precision and accuracy depend upon the region of the absorbance vs. concentration curve in which work is being done.

5. Sampling Apparatus

The sampling apparatus is the hi-volume sampler described in the TSP hi-vol procedure (Refer to Sect. 1.0).

6. Sampling Procedure

Sampling procedures are identical to those listed under Section 6.1 in the TSP, hi-volume sampler document.

7. Analysis

7.1 Apparatus

7.1.1 Volumetric flasks, pipets, beakers, and graduated cylinders to prepare solutions. Use Class A glassware.

7.1.2 Vacuum Filtering Apparatus: Device which permits vacuum filtering directly into the receiver. This consists of a bell jar with a top opening, a side tabulation and a bottom plate. The Bunchner funnel passes through the top opening and is sealed to the bell jar with a stopper. The bell jar should be tall enough to contain the polyethylene bottles used for storing the samples. The vacuum connection is made using the side tabulation. The filtering apparatus is shown in Figure 1.

7.1.3 Vacuum Pump: Any device which can maintain a of at least 64 cm of Hg. Mechanical pumps or water aspirators may be used.

7.1.4 Polyethylene Bottles: Bottles with a capacity of 60 ml (2 Oz) fitted with polyseal caps.

7.1.5 pH Meter: Capable of measuring pH to nearest 0.1 pH units over a range of 0-14.

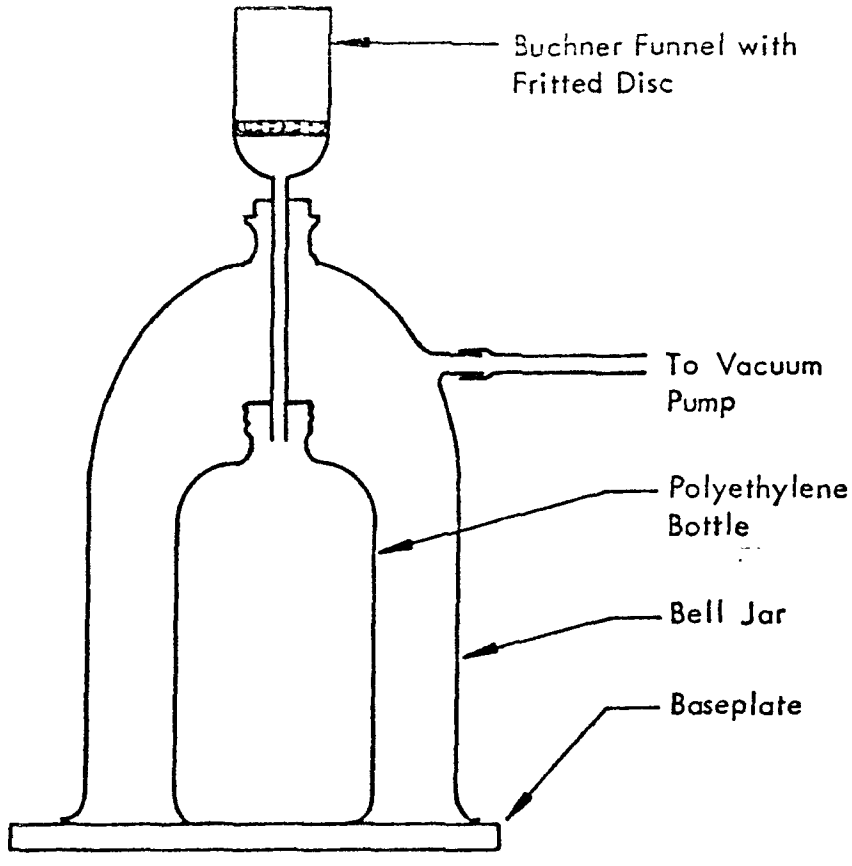


Figure 1 - Vacuum Filtering Apparatus

7.1.6 Glass Bottles (brown). 500 ml glass bottles with polyseal caps.

7.1.7 Pump Tubing. Flow rates tubing of the capacities shown in Figure 2. Silicone tubing is recommended and has a life of up to 6 weeks. Deviations from these flow rates are acceptable only to the extent that a proper calibration curve and acceptable quality control checks are obtained. The use of silicone rubber tubing in place of the standard pump tubing is highly recommended. Standard pump tubing should be replaced every day if used. Other available tubing has correspondingly longer life (3 weeks) with silicone rubber tubing having performed satisfactorily for as long as 5 weeks. If a plasticized tubing is used, it should be washed with acetone followed by distilled water prior to its use.

7.1.8 Erlenmeyer Flask. 125 ml with 24/40 joint.

7.1.9 Condenser. Water jacketed, 300 mm length with 24/40 joints.

7.1.10 Hot Plate. Suitable for sample extraction (7.2.1).

7.1.11 Pyrex Glass Wool.

7.1.12 Plastic Tubing. 10 cm (3.94 in) and 2.3 mm (0.09 in) I.D. Polyvinylchloride tubing, for ion exchange column (5.2.1.5).

The column consists of a length of glass tubing 7.5 in. long, 2.0 mm inner diameter, and 3.6 outer diameter. The column is then filled filled with the resin. Keep air out. Place glass wool plugs at each end to prevent the resin from escaping. These plugs should not restrict flow.

It is very important that no air bubbles enter the ion-exchange column. If air bubbles become trapped, the column should be repacked.

f. 15 mm flow cell colorimeter: a colorimeter of the phototube variety operated with an auxiliary power supply and amplifier for use at 460 nm and including a tubular flow cell. (The interference filters should be checked before use and at quarterly intervals for wavelength of maximum transmission.)

g. Recorder: 0-10 mv strip chart recorder.

h. Technicon linearizer: obtains readings directly proportional to concentration.

7.2 Analysis Reagents

7.2.1 Barium Chloride. (.006 m, ACD grade) Dissolve 1.4659 gm $BaCl_2.2H_2O$ in distilled water and dilute to 1000 ml in a volumetric flask. Mix well by inverting 10 to 15 times. Store at room temperature in a screw-top polyethylene container.

7.2.2 Methylthymol Blue. Weigh 0.1301 gm methylthymol blue. Add to a clean, dry 500 ml volumetric flask. (If a dry flask is unavailable, rinse a flask with about 10 ml alcohol and drain for at least 10 minutes.) Dissolve the dye with 25.0 ml (volumetric pipet) $BaCl_2$ solution. Add 4.0 ml 1 N HCl (volumetric pipet). Mix by swirling. Carefully add ethanol until the flask is 2/3 full, making sure all the dye in the neck of the flask is washed down. Swirl carefully to mix. Add more ethanol until the line is reached. Stopper and mix by inverting ONCE. If necessary, add more ethanol to bring the level to the mark. Now add 5.0 ml Brij-35 (Technicon trade name) and rinse the pipet twice in the dye solution. Stopper and mix by inverting ONCE. Carefully pour the solution into a brown storage bottle.

This reagent may be made daily. It should be stored in a refrigerator when not in use. Do not keep the reagent more than 3 days.

7.2.2 Comment. The ratio of MTB to Ba++ varies because of the impurities found in different lots of MTB dye. It may be possible to linearize the absorbance curve by slightly changing the MTB to BA++ ration. However, it is presently recommended to use the absorbance curve directly or a linearizer made specifically for the Technicon II system.

7.2.3 HCl (ACS) (1N). Add about 200 ml distilled water to a 500 ml graduated cylinder. Add (volumetric pipet) 25.0 ml concentrated HCl. Mix by swirling. Dilute with distilled water to 300 ml. Store at room temperature in a screw-cap polyethylene bottle.

7.2.4 NaOH (ACS) (0.18N). Dilute 9.0 ml (volumetric) 10N NaOH to 500 ml (volumetric). Mix well. Be sure the bottle contains at least 300 ml at the beginning of the run. Also be sure that the end of the line from the Technicon pump goes down to the bottom of the bottle.

7.2.5 NaOH (ACS) (10N). Prepare by dissolving 400 g NaOH pellets in boiled distilled water, cooling, and diluting to 1 liter with boiled distilled water. Store at room temperature in a polyethylene container.

7.2.6 Sodium (Tetra) Ethylenediamine Tetraacetate (EDTA) Cleaning Solution (Technical Grade). Weigh 6.75 g NH_4Cl and 26.9 EDTA, acid form. Add to a 1-liter

volumetric flask. Add about 500 ml water and swirl to form a suspension. Add 37 ml 10N NaOH and 57 ml concentrated ammonium hydroxide. Mix and dilute to 1 liter.

7.2.7 Ethanol. 95% U.S.P.

7.2.8 Ammonium Chloride. ACS Reagent Grade.

7.2.9 Concentrated Ammonium Hydroxide. ACS Reagent Grade, 28-30% NH_3.

7.2.10 Sodium Sulfate. ACS Reagent Grade, anhydrous.

7.2.11 Distilled Water. ACS Reagent Grade, having a specific conductance of 2 micromhos or less.

7.2.12 Potassium Chloride. ACS Reagent Grade.

7.2.13 Stock Sulfate Solution. Dissolve 1.4789 g sodium sulfate (Na_2SO_4), previously heated to 105°C for 4 hours and cooled in a dessicator. Dilute to 1000 ml with distilled water. This stock solution contains 1000 µg $SO_4^{=}$/ml. Store in a refrigerator. Prepare solution monthly and check the new against the old by running 5-point calibration curves.

7.2.14 Working Standards. Dilute 50.0 ml of stock solution containing 1000 µg $SO_4^{=}$/ml to 500 ml with distilled water. This intermediate sulfate solution contains 100 µg $SO_4^{=}$/ml. Prepare by pipeting (volumetric pipets) appropriate amounts of the stock sulfate solution into 100 ml volumetric flasks and diluting to volume with distilled water. These are prepared

daily. They may be used up to one week if well stoppered and in large volumes. Mix well by stoppering and inverting 10 to 15 times.

7.2.14.1 Prepare a series of working standards according to the following table:

Working Std. µg $SO_4^=$/ml	Volume of Std (to be diluted)	Final Volume (dilute with dist. H_2O)
60	60 ml of 100 µg $SO_4^=$/ml	100 ml
50	50 ml of 100 "	100 ml
40	40 ml of 100 "	100 ml
30	60 ml of 100 "	200 ml
20	20 ml of 100 "	100 ml
10	10 ml of 100 "	100 ml
5	5 ml of 100 "	100 ml

7.2.14.2 Standards to be used with linearizer:

A. 25 µg $SO_4^=$/ml

B. 40 "

C. 55 "

D. 70 "

E. 80 "

F. 90 "

Larger volumes of 30 µg $SO_4^=$/ml standard or 55 µg $SO_4^=$/ml are prepared to use as standards. When using the linearizer, a non-linearized calibration curve is first plotted by placing the linearizer in the direct mode. Using the non-linear curve, concentrations of standards are selected which fall at approximately 75% for each range of the linearizer. For

example, a concentration which falls at 15% of scale in the non-linearized mode should be selected as the standard for the 0-20% range of the linearizer. These concentrations as calculated are then used to set the linearizer as directed in the linearizer manual.

8. Analysis Procedures

8.1 Filter Preparation. Cut a 3/4 x 8" filter strip from the center of the exposed glass fiber hi-vol filter with a paper cutter. Cut the same section from each filter to maintain uniformity. The use of a template is suggested. Place the folded strip in a 125 ml Erlenmeyer flask. Add 35 ml distilled water and reflux the solution for 30 minutes. Turn off the heat and cool the flask to room temperature. Rinse the inside surface of the condenser and adaptor with small amounts of water from the upper opening of the condenser. Disconnect the Erlenmeyer from the condenser. Vacuum filter the aqueous extract through a fine sintered glass funnel. Wash the remaining filter at least five times with distilled water.

Vacuum filter the aqueous extract through a fine sintered glass funnel into a 50 ml volumetric flask. Wash the remaining filter strip at least five times with distilled water. Filter through the same glass filter into the flask.

Dilute to 50 ml. Transfer an aliquot of this solution to a capped culture tube for future use in the Technicon sample tray.

8.2 Analyzer Assembly and Use

8.2.1 Perform the sulfate analysis on a Technicon II Autoanalyzer. Use interference filters of 460 nm and a 15 mm tubular flow cell in the colorimeter. Operate the sample turntable at 30 sample positions per hour with a ∿1:3 sample to wash ratio. Eight minutes elapse between sample pickup and appearance of corresponding peak on recorder chart.

8.2.2 Assemble system with flows as shown in Figure 2. Refer to Technicon II manual for specific assembly instructions.

8.2.3 After assembling the system, attach a shunt (small piece of tubing) between points A and B (Fig. 2). Place all pump tubes in their respective solution containers and check the flows. Put the sample line in a container of distilled water. Allow the system to run 5 - 10 minutes. Check the debubbler to be sure that no bubbles are entering the shunt. Attach the ion exchange column at point A first, taking care that no air bubbles enter the system. Then attach column at point B. Run the analyzer with a fresh ion exchange column until a stable baseline is obtained. This usually requires a minimum of 2 hours. With the sample line in

deionized water, pump the chemicals through the system to zero the instrument. Adjust the range with the standards to read out as desired on the strip chart recorder or the linearizer printout. These standard values will be used to plot the absorbance vs. concentration curve, or to set the curve in the linearizer. A blank filter strip sample should be inserted in the analysis system after running the standards. This will establish the blank absorbance data required to calculate the final values. The blank is determined by analyzing 1% of the filters before use. Cut 3/4" x 8" strips from these filters for the analysis. Extract the sulfate concentration from these strips in the manner described in Section 8.1. This solution will provide the sample to determine the background levels of $SO_4^=$ in the filter.

8.2.4 After plotting the standard curve, the system is ready to analyze samples. Use a mid-range standard every 10th sample to check for drift. The baseline will remain noisy with some tailing throughout the day. Peak height readings should therefore always be made by drawing a line connecting the baseline and measuring at the midpoint. Samples which exceed the absorbance of the highest standard of the calibration curve are diluted until the concentration falls

within the calibration range. A broadening of the colorimeter output with a corresponding loss in peak height usually indicates that the pump tubing should be replaced. Silicone rubber tubing is recommended in place of the standard pump tubing.

8.2.5 Run a color blank on the samples if the extracts are highly colored or contain suspended particulate. Do this by diconnecting the MTB tube and running the analyzer without the MTB. Replace the MTB with ethanol and establish a new zero line with distilled water in the sample tube. The color absorbance values from the sample blanks should then be used in calculating the final concentration.

8.2.6 Run a series of standards including a filter blank at the end of each day's analysis. Rerun a random 5-10% of the samples to maintain internal quality assurance.

8.2.7 Change the glass wool in the ion exchange column when it gets dirty. The column may be removed from the system to use the next day if it is not exhausted. Deterioration can be observed when the standard sample value decreases.

At the end of an analysis day, replace the column with a shunt. Place another water-filled shunt across the column openings to prevent air contacting column material.

8.2.8 Purge this system daily with an EDTA solution. Do this by placing the methylthymol blue, sample, and the NaOH lines in water for 2-4 minutes. Then place them in the EDTA solution for 10 minutes. Wash system with water for 15 minutes before shutting down.

All liquid lines should be left filled with water after the system has been washed. A coating will slowly develop on the internal parts of the flow system. When the coating becomes noticeable, the mixing coils should be cleaned by pumping 1 N ammonium hydroxide through the system. The rate at which the coating develops is variable depending on the nature of the samples being analyzed. A coating will slowly build up on the flow cell windows which is not removed by the NH_4OH wash. This build-up is indicated by a loss in colorimeter sensitivity and may be corrected by washing the cell with 1 N HCl followed by an acetone and then a water wash.

8.2.9 Obtain alternate strip recorder ranges by using the Standard Calibration Dial on the colorimeter.

8.3 Calculations

$$\mu g\ SO_4^{=}/m^3 = \frac{(\mu g\ SO_4^{=}/ml)\ \ 600}{m^3}$$

Determine $\mu g\ SO_4^{=}/ml$ by subtracting the blank and color (if present) concentrations from the sample concentration

observed from the absorbance curve. (Run standards before and after each analysis day. Establish the absorbance vs. concentration curve by averaging these data.)

$$600 = \frac{\text{area of exposed filter (9" x 7")}}{\text{area of analyzed strip 3/4" x 7"}} \times \text{volume of liquid (50 ml)}$$

$$600 = \frac{9 \times 7 \times 50}{3/4 \times 7}$$

[The actual filter is 8" x 10", but there is a ½" unexposed border around it. Include the unexposed area when cutting the filter. This makes a 3/4" x 8" slice.]

Determine the air volume in cubic meters by:

$$m^3 = \left(\frac{Q_i = Q_f}{2}\right) T$$

where Q_i and Q_f are the initial and final flows in m^3/min. T is the number of minutes the hi-vol sampler is run.

9. Calibration Apparatus

9.1 The sampler calibration apparatus is that of the hi-volume sampler in Section 9.0 in that procedure.

9.2 The analysis calibration apparatus consists of preparing a series of liquid standards and running these through the analysis system. These standards are discussed in Section 7.2.8.

10. Calibration Procedure

10.1 The calibration procedure is that of the hi-volume sampler as outlined in Section 10.0 in that procedure.

10.2 The analysis calibration procedure consists of running a number of known concentrations through the system and obtaining a calibration curve of the colorimeter output (absorbance) vs. the input sulfate ion concentration.

REFERENCES

1. "Community Health Air Monitoring Program" (CHAMP), EPA Contract No. 68-02-0759.

2. Lazarus, A. L., et al., "A New Colorimetric Microdetermiation of Sulfate Ion," Automation in Analytical Chemistry (Vol. 1), New York: Mediad Corp., 1965. pp. 291-293.

3. Parr, S. W., et al. "Determination of Sulfur by Means of the Turbidimeter," Industrial Engineering Chemistry Annual Edition, 3:66-67, 1931.

4. "Sulfate in H_2O and Waste H_2O," Industrial Method 118-71, preliminary Method, Technicon Autoanalyzer II Methodology, Technicon Instrument Corp., Tarrytown, N.Y., 10591.

II. RESPIRABLE PARTICULATE (RSP)

II. RESPIRABLE PARTICULATE (RSP)

1. Principle and Applicability

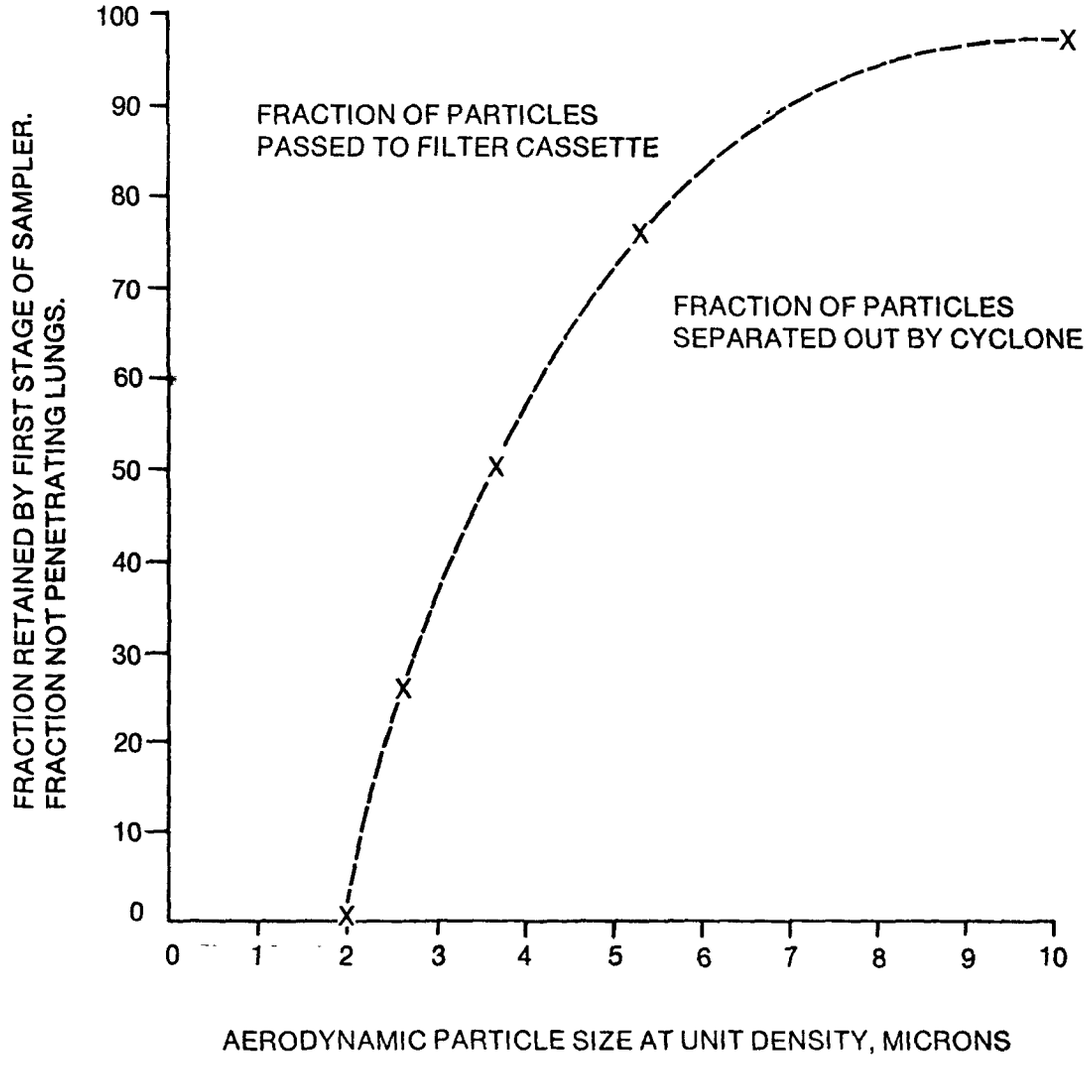
1.1 Particles moving in an air stream tend to follow their original straight line motion when streamlines of airflow are deflected by an obstacle. Using this principle, a cyclone separator divides the respirable, suspended particulates (RSP) of suspended airborne particles of less than 3.5 mm in diameter from the larger particles found in ambient air[1] (Figure 1). The air sample is first drawn through the cyclone where larger particles are removed and discarded by impaction and settlement. The small particles follow the air vortex, pass through the top of the cyclone and are captured on a filter media for weighing and further analysis.

1.2 Mass concentration of the fine fraction of matter found in ambient air is determined from the weight of samples collected and the volume of air passed through the train during each 24-hour sampling period. Mass concentration is expressed as micrograms per cubic meter ($\mu g/m^3$).

2. Range and Sensitivity

2.1 The sampler is operated for 24 hours at a flow rate of 9±.5 liters per minute. A meaningful sample will be obtained if the ambient air particulate concentration is at least 5 $\mu g/m^3$. Because of the small collection surface, the low concentration sampling range is sensitive to weighing procedures.

Figure 1 - "LOS ALAMOS" CURVE FOR FINE PARTICULATES



Filter and sampling weights are determined with an accurate balance. Weights are made to the nearest 0.01 milligram. Flow rates are measured to the nearest 0.1 liter per minute with a calibrated rotameter. Sampling times are recorded to the nearest minute.

2.2 RSP concentrations found in ambient atmospheres range to highs of over 200 $\mu g/m^3$. Minimum detectable concentrations are based on the accuracy of the balance.

3. Interferences

3.1 High humidity or rainfall pulled into the filter may dissolve the water-soluble portion of the sample.

3.2 The filter does not have water vapor gathering properties. The particles themselves, however, can be hygroscopic and introduce errors in weight determinations if samples are not carefully equilibrated to a fixed, environmentally controlled humidity and temperature level before weighing.

4. Precision and Accuracy

4.1 The accuracy of samplers measuring the true average concentration depends upon the degree of constant air flow maintained in the samplers and in making weight determinations of collected samples.

4.2 Results of duplicate sampling at the Durham, North Carolina Ambient Air Station have given a correlation coefficient of 0.97 for cyclone samplers. At an average mass concentration of 115 $\mu g/m^3$ of particulate matter in ambient air,

the measurement error determined by duplicate sampling averaged ±5 percent; at an average of 39 $\mu g/m^3$ the measurement error averaged 13 percent.

4.3 Start and stop flow rates are measured within 2 percent. This corresponds to the accuracy of the rotameter.

5. Sampling Apparatus

5.1 Cyclone. A 1.27 cm diameter stainless steel cyclone collector is used to separate the respirable fraction of the total suspended particulates. Only the smaller particles are collected on the filter.[2] The others fall to a cup at the bottom of the separator. This cyclone sampler is illustrated in Figure 2.

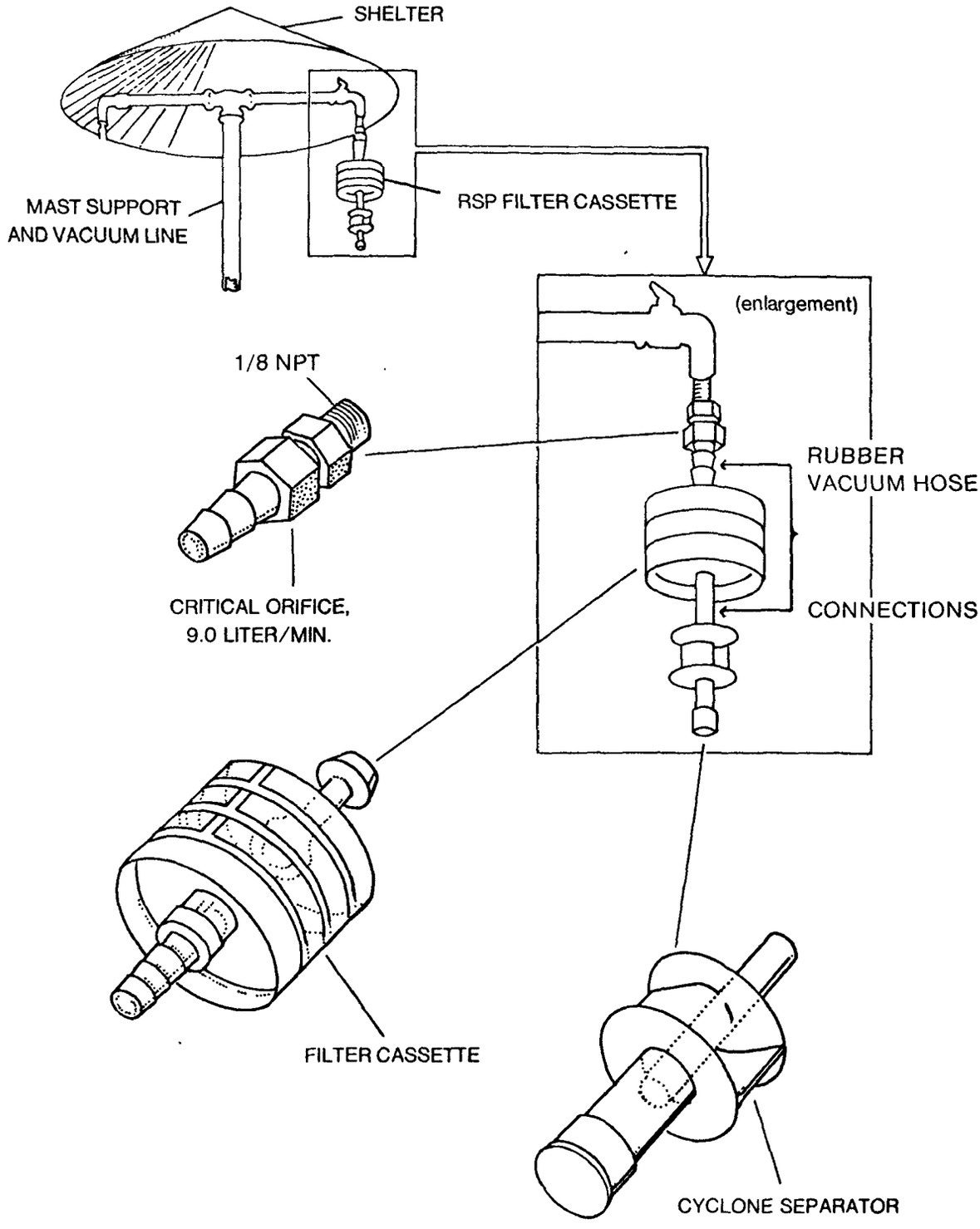
5.2 Cassette. An airtight plastic cassette is used to house the 37 mm preweighed filter and filter support. This cassette can be opened by hand to easily change filters.

5.3 Filter and Filter Support. The filter is a 37 mm circular glass-fiber filter. A porous material is placed on the back side of the filter for additional support. Other filter media may be substituted, but all should have a 99+ percent collection efficiency for particles under 3.5 μm diameter.

5.4 Critical Orifice. A limiting orifice will provide a constant flow of 9(±.5) liters per minute over a range of vacuums between 50.8 - 66.0 cm Hg (20 - 26 in.) on the pump gauge.

5.5 Vacuum Pump. This pump must maintain a vacuum of at least 50.8 cm Hg (20 in.) and a 10.5 liter per minute flow.

Figure 2 - CYCLONE SAMPLER AND SHELTER ASSEMBLY



5.6 Connections. The vacuum system is connected by 1/4" O.D. tubing to the base of the cast iron pipe support. The cassette, cyclone, and orifice are connected with 1/8" I.D. heavy-walled vacuum hose (Figure 2). All connections between cassette, cyclone and orifice should be easily disassembled, but should seal tightly.

5.7 Shelter. The shelter (Figure 2) protects the filter and cassette from rain and snow.

5.8 Rotameter. The rotameter measures the 9 liters per minute flow to the nearest .1 liter. A calibration table is used with the rotameter to determine actual flows in the field.

6. Sampling Procedure

6.1 To field sample, connect the cyclone in series with a pre-weighed 37 mm filter and filter pad in the airtight plastic cassette (Figure 2). The cassette-separator assembly is attached by rubber tubing to the orifice. Leave the orifice attached to the mast support arm. Change it only when it becomes clogged. A vacuum pump moves ambient air through the train.

6.2 Samples are changed every 24 hours.

6.3 Check the flow at the beginning and end of each sampling period by replacing the cyclone with the rotameter. Record the start flow with a clean filter and the stop flow with a soiled filter.

6.4 As with all the manual sampling methods described, fill the data forms in at the time the sample is changed. (These data are extremely important to determine daily pollutant concentrations.)

Data include:

A. Start and stop times in military units (e.g., 3:45 p.m. = 1545) (T)

B. Start and stop flows in liters per minute (Sec. 8.6.1., Q_i, Q_f)

C. Start and stop dates

D. Initial and final weights (Sec. 8.6.2., W_i, W_f)

E. Flowmeter number

F. Pump serial number

G. Filter number

H. Orifice number

I. Any conditions which can affect the sample should be noted in the "Comment" section (e.g., high winds, local construction, severe rains, etc.)

6.5 The rotameter monitors the flow through each orifice. This flow must stay in the 8.5 - 9.5 liter per minute range. Replace any orifice not in this range.

7. Analysis Apparatus

7.1 Maintain the environmentally controlled chamber between 15-35°C and less than 50 percent relative humidity.

7.2 A balance capable of weighing to the nearest .01 milligram, ±.005 mg.

8. Analysis Procedure

8.1 Equilibrate all filters in the environmental chamber 24 hours before preweighing. Weigh the filters to the nearest 0.01 mg.

8.2 Place a filter in a cassette and assign a number to it.

8.3 Send the filter cassette to the field operator.

8.4 When the exposed filter cassette is returned, carefully remove the filter and equilibrate it in the chamber for 24 hours before its final weighing.

8.5 Record on the data card the initial and final weights.

8.6 Concentrations Determinations. a computer determines concentrations from the data forms completed by the field operator and laboratory personnel. Use the initial and final weights and flows to compute the RSP concentrations.

8.6.1 Determine volume of air sampled from the equation

$$V = \frac{Q_i + Q_f}{2} \times T$$

where V = air volume sampled, m^3

Q_i = initial airflow rate, m^3/min

Q_f = final airflow rate, m^3/min

T = sampling time, min.

8.6.2 Determine mass concentration of suspended particulates from the equation

$$S.P.= \frac{(W_f - W_i) \times 10^6}{V}$$

where S.P. = mass concentration of suspended particulate, $\mu g/m^3$

W_i = initial weight of filter, grams

W_f = final weight of filter, grams

10^6 = conversion of g to μ grams

9. Calibration Apparatus

9.1 Orifice Calibration Apparatus

9.1.1 Mass flowmeter equipped with a transducer capable of a range of 0 to 10,000 cc/min or 0 to 10 liters/min. (The mass flowmeter is periodically calibrated with a Brooks calibrator.)

9.1.2 A vacuum pump must maintain 50.8 cm Hg (20 in.) to provide a critical flow of 9 liters per minute.

9.1.3 Vacuum tubing

9.1.4 Needle valve

9.1.5 Short sections of heavy rubber vacuum hose.

9.1.6 RSP orifice and tubing connectors.

9.2 Rotameter Calibration Apparatus

9.2.1 Wet test meter (1 liter/revolution) or a mass flowmeter with digital read-out as in 9.1.1.

9.2.2 Vacuum source capable of at least 50.8 cm Hg (20 in.)

9.2.3 Vacuum tubing

9.2.4 Needle valve

9.2.5 Rotameter

9.2.6 Ring stand and clamps

9.2.7 Stop watch

9.2.8 Manometer and thermometer

10. Calibration Procedures

10.1 Orifice Calibration Procedure

10.1.1 Set up materials as shown in Figure 3, taking care that all connections are secure to prevent air leakage.

10.1.2 Allow the mass flowmeter 30 minutes warm-up time.

10.1.3 Place an orifice into the train with the arrow on the orifice pointed toward the vacuum source or the direction of the airflow.

10.1.4 Record the orifice number, calendar date, and operator's initials.

10.1.5 Check to make sure the needle valve is closed.

10.1.6 Start up the vacuum source.

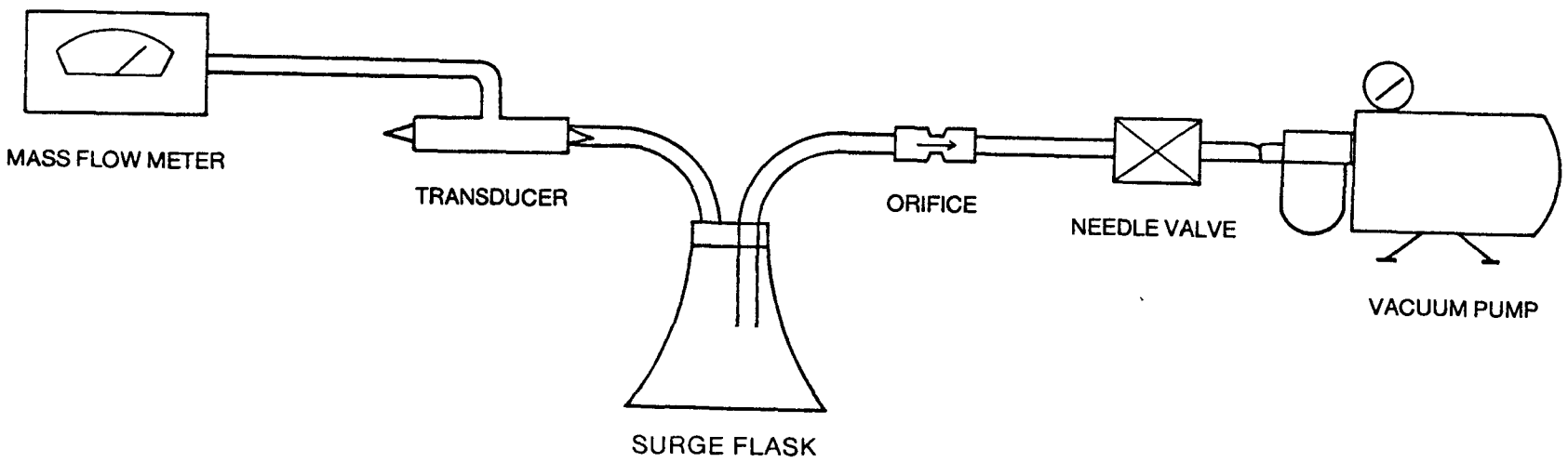
10.1.7 Regulate the vacuum to about 20 in. of vacuum. This prevents over-taxing the pump during calibration and also keeps the orifice at critical flow.

10.1.8 Open the needle valve slowly, until the mass flowmeter reading reaches a constant flow.

10.1.9 Record this flow as the critical or calibration point. The orifice is accepted or rejected at this point based on the flow. It is under these critical conditions that the orifice operates in the field.

10.1.10 The RSP sampling network calls for flows of 9 liters/min. during sampling. The tolerance of these flows if ±5 liters/min.

Figure 3 - RSP ORIFICE CALIBRATION



NOTE: The orifice should operate in a constant "critical flow" region. Filter loading and/or vacuum changes, however, could change this.

10.2 Rotameter Calibration Procedure

10.2.1 Set up materials shown in Figure 4. Make sure all connections are tight to prevent leakage.

10.2.2 Mount the rotameter in a vertical position.

10.2.3 Level the wet testmeter by using the bubble level and the screw legs.

10.2.4 Adjust the water level in the testmeter using distilled water, by either draining or adding water. The needle in the glass tube should just touch the water surface.

NOTE: Steps 10.2.3 - .4 are critical if an accurate calibration is to be obtained. A mass flowmeter may be used and steps 10.2.3 - .4 are eliminated.

10.2.5 Prepare data sheet as shown in Figure 5.

10.2.6 Record rotameter number, calendar date, room temperature, atmospheric pressure (P), and operator's initials.

10.2.7 Start up the vacuum pump, and adjust the needle valve until a stable reading is acquired on the rotameter. Read the center of the ball.

10.2.8 Allow for an equilibration period if the wet testmeter thermometer is much different from the room temperature.

Figure 4 - ROTAMETER CALIBRATION

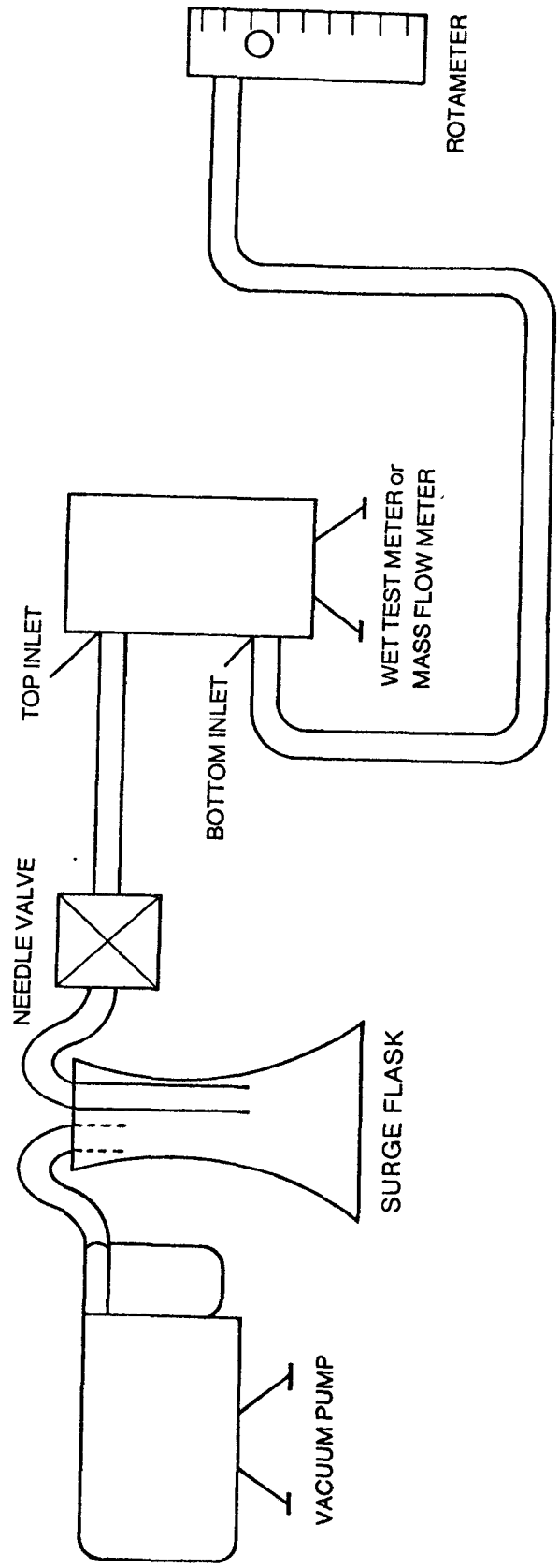


Figure 5: Typical data sheet

Rotameter Setting	V_1	V_1 corrected	Water Temp.	P	Vacuum	t time for each run	Flow= V_2/t
30	9.0 l						
40	9.0 l						
50	9.0 l						
60							
70							
80							
90							

10.2.9 Record the temperature in °C and the manometer readings in inches of water. Record the start value for the rotameter.

10.2.10 Start the stopwatch when the wet testmeter hand crosses a convenient mark.

10.2.11 Allow the wet testmeter to run freely until 9 liters of air have been pulled through.

10.2.12 Stop the watch and record the run time.

10.2.13 Record the rotameter stop value.

10.2.14 Make sure there have been no significant changes in the temperature or vacuum. (Not more than ½°C or .2" of water.)

10.2.15 Repeat steps 10.2.10 through .14 for readings on the RSP rotameter of 30, 40, 50, 60, 70, 80 and 90.

10.3 Calculation of Calibration Data

10.3.1 Calculate the total volume being pulled through the wet testmeter according to the calibrating conditions. Use the following formula:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

where P_1 = corrected pressure during calibration

T_1 = water temperature +273°C

V_1 = volume = 9 liters.

Conditions where rotameter is calibrated.

P_2 = Pressure = 760 mm Hg

T_2 = Temperature 298.15°K

V_2 = Volume in liters.

STP conditions.

10.3.2. Correct the pressure for water vapor pressure by taking the temperature readings in °C and referring to a vapor pressure chart. (One such chart is in the HANDBOOK OF AIR POLLUTION of the U. S. Dept. of Health, Education and Welfare.) Subtract this reading from the barometric pressure to get the corrected pressure, P_1.

10.3.3 Calculate the actual flow of reach rotameter reading. Divide actual volume (V_2), computed in steps 10.3.1 and .2, by the time taken for each flow measurement.

10.3.4 Repeat steps 10.3.1, .2, and .3 for each rotameter calibration point.

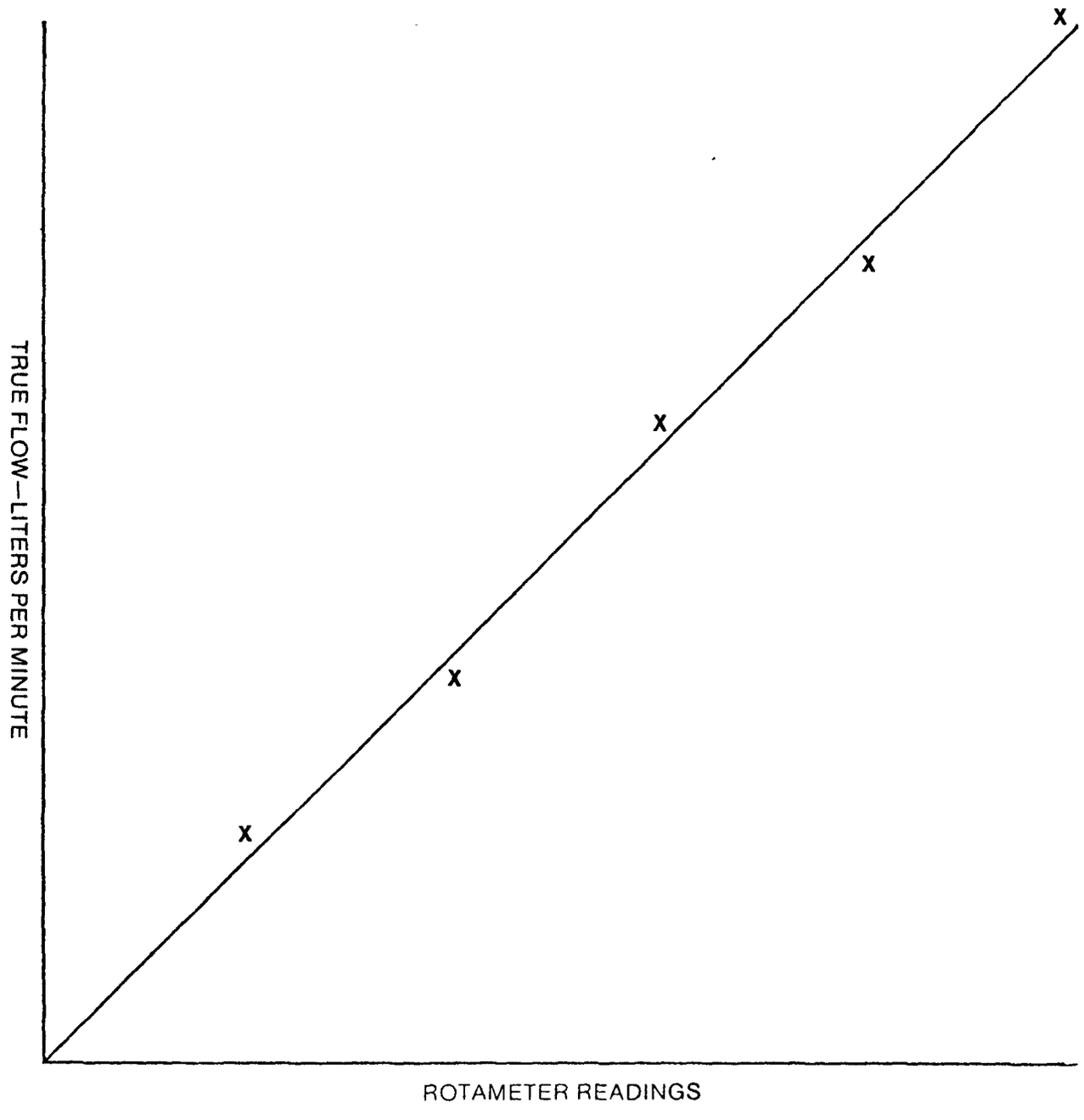
10.3.5 A standard referenced mass flowmeter with a digital read-out can be used to provide a quicker method to calibrate the rotameters. A water vapor pressure correction is unnecessary when using this mass flowmeter. Therefore, P can be used directly.

10.4 Plotting the Graph

10.4.1 Plot all points carefully on regular graph paper (10 x 10 to the inch). See Figure 6.

10.4.2 Obtain a linear regression of these points. From this regression obtain a chart of rotameter reading vs flow. Increment the flow in 0.02 l/min. increments. Tape this chart to the side of the rotameter. The chart is used by the field operator to obtain Q_i and Q_f.

Figure 6 - ROTAMETER CALIBRATION CURVE



REFERENCES

1. Aerosol Technology Committee, American Industrial Hygiene Assoc., "Guide for Respirable Mass Sampling," Am. Ind Hyg. Assoc. J. 31:133 (1970)

2. Burton, R. M., et al., "Development of Fine Particulate Sampling Methods in Support of CHESS Health Studies," EPA In-house Report.

III. SULFUR DIOXIDE (SO_2)

III. SULFUR DIOXIDE (SO_2)

1. Principle and Applicability

1.1 A stable dichlorosulfitomercurate complex, formed by absorption of SO_2 from air in a potassium tetrachloromercurate solution, is reacted with pararosaniline and formaldehyde by controlling the flow rates of sample and reagents.[1] A pararosaniline methyl sulfonic acid dye is formed. The absorbance, proportional to the SO_2 concentration, is measured colorimetrically and converted to an electrical signal. The signal is displayed in either digital or analog form on a readout device.

1.2 The method applies to integrated 24-hour samples of SO_2 in ambient air. Collected samples are analyzed by an automated procedure in a laboratory.

2. Range and Sensitivity

2.1 Concentrations of sulfur dioxide in the range of 25 to 1050 $\mu g/m^3$ (0.01 to 0.40 ppm) can be measured under the conditions given. Concentrations below 25 $\mu g/m^3$ can be measured by sampling larger volumes of air, but only if the absorption efficiency of the particular system is first determined. Higher concentrations can be measured by using smaller gas samples, a larger collection volume, or a suitable dilution of the collected sample. Beer's Law is followed through the analysis range of 0.02 - 1.4 μg SO_2/ml.

2.2 The lower limit of detection of sample analysis is estimated to be 0.02 μg SO_2/ml.[2] This value would represent a concentration of 4 μg SO_2/m^3 (0.0015 ppm) in a 24-hour sample. However, the minimum detectable concentration is 25 μg SO_2/ml, unless the measurement reliability of concentrations less than 25 μg/m^3 can be determined by the absorption efficiency at low levels.

3. Interferences

3.1 The effects of the known interferences have been minimized or eliminated.[3*] Interferences by oxides of nitrogen are eliminated by sulfamic acid,[4] ozone by time-delay,[5] and heavy metals by EDTA (ethylenediaminetetraacetic acid, disodium salt) and phosphoric acid.[6,7] At least 60 μg Fe (III), 10 μg Mn (II), and 10 μg CR (III) in 10 ml absorbing reagent can be tolerated. No significant interference has been found with 10 μg Cu (III) and 22 μg V (V).

4. Precision, Accuracy, Stability, and Efficiency

4.1 Precision. Estimates of the relative standard deviation for 24-hour samples at concentrations of 100, 350, and 900 μg SO_2/m^3 (0.037, 0.13, and 0.34 ppm, respectively) are 4.2, 0.4, and 0.8 percent.

4.2 Accuracy. No data on accuracy are available.

*See Editor's Note

*Editor's Note:

Recent unpublished EPA studies by the Environmental Monitoring Support Laboratory (EMSL) indicate that SO_2 concentrations in solution decay with increasing temperatures. Changes range from .9% per day at 20°C to 73% per day at 50°C.

To eliminate this problem sampling should be done at a constant temperature of 25°C or less and the exposed sample kept at 5°C until analyzed.

4.3 Stability. The presence of EDTA enhances the stability of SO_2 in solution. The rate of decay is independent of SO_2 concentration,[8] but temperature dependent. At 22°C, loss of SO_2 occurs at the rate of 1% per day. Samples stored at 5°C (e.g., in a refrigerator) for 30 days show no detectable loss of SO_2.

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

5. Sampling

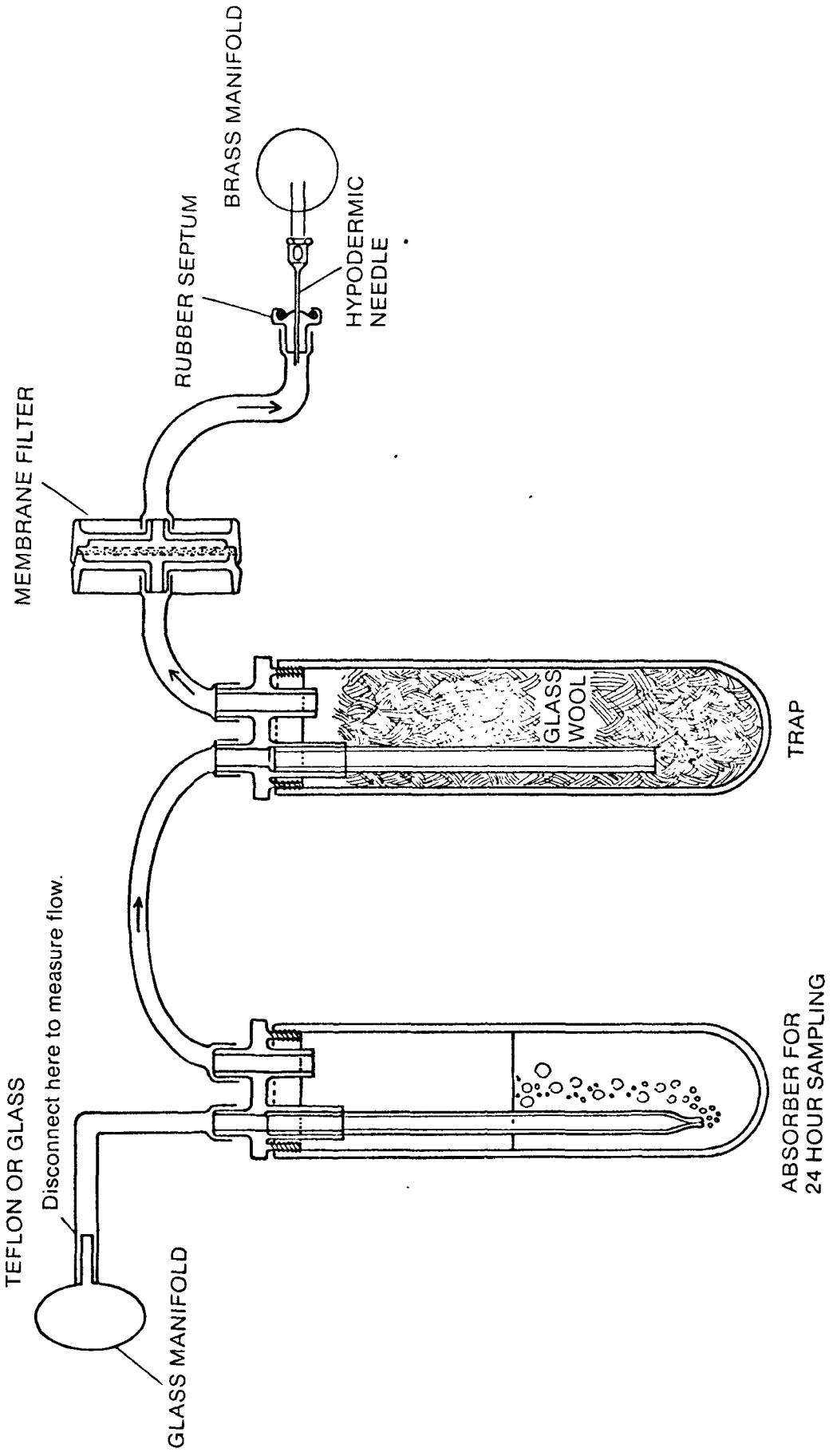
5.1 Apparatus

5.1.1 Sampling Train. A sampling apparatus diagram is shown in Figure 1. The apparatus section, or sampling train, between the glass intake manifold and the copper vacuum manifold is generally supported in a "bubbler box," Figure 1-a.

5.1.2 Probe. Teflon, polyethylene, or glass tube with an inverted polypropylene or glass funnel at the end.

5.1.3 Absorption Tube. Polypropylene tube 164 x 32 mm, equipped with a polypropylene two-port cap. Do not use rubber stoppers as they cause high and varying blank values. A restricted orifice glass tube is used to disperse gas. The 152 mm tube, 8 mm O.D. - 6 mm I.D., should

Figure 1 - SAMPLING SYSTEM



Other bubbler samplers may be used at the same time when this box arrangement is employed.

5.1.9 Pump. Capable of maintaining the minimum vacuum and flows required for the 24-hour sample. A vacuum of 0.7 atmosphere or greater is necessary.

5.2 Reagents

All reagents should conform to ACS specifications for reagent grade materials unless otherwise specified.

5.2.1 Sodium Hydroxide. ACS Reagent Grade.

5.2.2 Sodium Arsenite. ACS Reagent Grade.

5.2.3 Absorbing Reagent. Dissolve 4.0 g sodium hydroxide in distilled water, add 1.0 g of sodium arsenite and dilute to 1000 ml with distilled water.

6. Sampling Procedure

6.1 Assemble the sampling apparatus as shown in Figure 1. Connect components upstream from the absorption tube with teflon tubing. Connect glass tubing with dry ball joints or with butt-to-butt joints of tygon, teflon, or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated mark on the absorption tube.

6.2 Insert the flowmeter into the sample line between the glass manifold and the sample bubbler to measure the flow. Note this flow and remove the flowmeter from the system.

This process is done immediately after inserting a new unexposed bubbler tube and just before it is taken off line 24 hours later. Check the system for leaks if the flow rate before sampling is not between 180 - 220 cm^3/min. Replace the flow control device if necessary. Start sampling only after obtaining an initial flow rate in this range.

6.3 Data forms should be filled in when the sample is changed. These data are extremely important in calculations used to determine daily pollutant concentrations. They include start and stop times in military units (e.g., 3:45 pm = 1545), start and stop flows in appropriate metric units, start and stop dates, as well as flowmeter number, pump serial number, filter number, orifice number, etc. Note any uncorrectible condition such as high winds, local construction (within 1/4 km), severe rains or other conditions that can affect the sample.

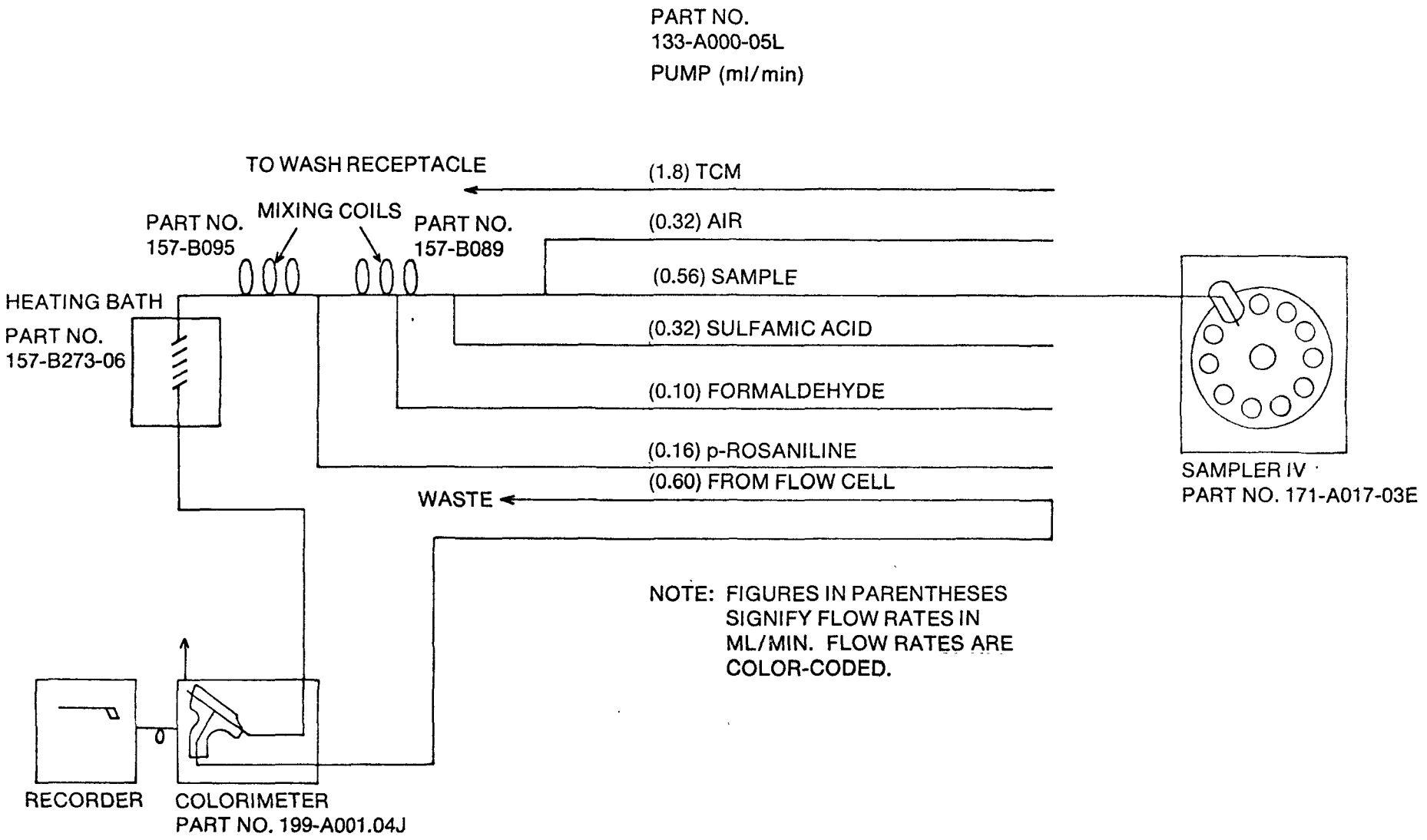
7. Analysis

7.1 Apparatus

7.1.1 Volumetric flasks, pipets, beakers to prepare solutions and standards. Use Class A glassware.

7.1.2 A Technicon II automated analysis system consisting of the components described below, is used for the analysis. Fig. 2 shows the arrangement.

Figure 2 - TECHNICON II AUTOMATED SULFUR DIOXIDE ANALYSIS SYSTEM



a. Sampler IV turntable: set for 40 samples/ hour and a 6:1 ratio of sample to wash time.

b. Proportioning pump III: capable of maintaining the flow rates indicated in Fig. 2. Pump tubing for the proportioning pump II must be poly (vinyl chloride) or other inert tubing for sample and reagent. Silicone tubing is used for air injection.

c. Sampler probe: made of Kel-F, poly (chlorotrifluoroethylene), or glass. Because of the corrosive properties of the TCM absorbing reagent, no metal should contact the sample solution.

d. Flow rates: sample and reagent flow rates are specified in Fig. 2. The different flow rates are obtained by selecting pump tubing of the proper inside diameter. Flow deviations are acceptable only to the extent that a proper calibration curve and quality control checks are maintained.

e. Mixing coils: 20 turn, 2 mm I.D. glass coils.

f. Heating bath: 45°C heated coil, total volume 5.4 ml.

g. Colorimeter and voltage stabilizer: Colorimeter with proper filters for measurement of absorbance at 560 nm. Interference filters should have a spectral bandwidth not greater

than 20 nm. The filters should be checked with an accurate spectrophotometer at least quarterly to assure maximum transmittance at the specified wavelength. The colorimeter contains a flow cell, 15 mm long with an I.D. of 2 mm.

7.1.3 Readout Device. A mv strip chart recorder or digital voltmeter of proper range.

7.2 Analysis Reagents

7.2.1 Sulfamic Acid (0.17 percent). Dissolve 1.7 g of sulfamic acid in distilled water and bring to mark in 1000 ml volumetric flask. Prepare fresh daily.

7.2.2 Formaldehyde (0.2 percent). Dilute 5 ml of formaldehyde solution (36-38 percent) to 1000 ml with distilled water. Prepare fresh daily.

7.2.3 Pararosaniline Dye (PRA). The dye must have a wavelength of maximum absorbance at 540 nm when assayed in 0.1 M sodium acetate-acetic acid (7.2.3.2).

7.2.3.1 Stock PRA Solution (0.20%). A specially purified (99-100%) solution of pararosaniline is commercially available in the required 0.20 percent concentration (Harleco Company, Gibbstown, New Jersey 08027), but must be assayed. Alternatively, PRA dye may be prepared from the crystalline

form, purified according to the procedure of Scaringelli, Saltzman and Frey, and assayed.

7.2.3.2 PRA assay procedure. One ml of the stock solution (0.20% is diluted to the mark in a 100 ml volumetric flask with distilled water. A 5 ml aliquot of that solution is then transferred to a 50 ml volumetric flask. Five ml of 1 M sodium acetate-acetic acid buffer (7.2.3.4) is added, and the mixture is then diluted to 50 ml volume with distilled water. After 1 hour the absorbance is determined at 540 nm with a spectrophotometer. The assay of the PRA is determined by the formula

Eq.1: $$\% \text{ PRA assay} = \frac{\text{Absorbance}}{\text{grams of dye taken*}} \times K$$

For 1-cm cells and spectral bandwidth of less than 11 nm, K = 21.3.

*Assume 0.1 gram of dye taken when assaying the Harleco solution.

7.2.3.3 PRA Working Reagent.

CAUTION: Always use extreme care in handling concentrated acid. Add it slowly. Protect eyes from splatters.

To a 200 ml volumetric flask, add 16 ml stock pararosaniline solution. Add an additional 0.2 ml stock solution for

each percent the stock assays below 100% as calculated by Equation 1. Then add 25 ml of concentrated (85%) phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7.2.3.4 Buffer (Acetate-Acetic acid, 1 M). In a 100 ml volumetric flask, dissolve 13.61 grams of sodium acetate trihydrate in approximately 50 ml of distilled water. Then add 5.7 ml of glacial acetic acid and dilute to volume with distilled water. (This buffer should have a pH of 4.7.)

7.3 Calibration Standards

7.3.1 Preparation of Sulfite-TCM Standards.

7.3.1.1 Stock Iodine solution (0.1 N). Place 12.7 g iodine, 40 g potassium iodide, and 25 ml distilled water in a 1000 ml volumetric flask. Stir until dissolved, then dilute to volume with distilled water.

7.3.1.2 Iodine Solution (0.01 N). Transfer 50 ml of 0.1 N Stock Iodine Solution to a 500 ml volumetric flask and dilute to mark with distilled water.

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

7.3.1.4 Stock Sodium Thiosulfate Solution (0.1 N). Dissolve 25 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 500 ml of distilled water, add 0.1 g sodium carbonate to the solution, and dilute to 1000 ml with distilled water. Allow the solution to stand one day before standardizing. To standardize, accurately weigh to the nearest 0.1 mg, 1.5 g primary standard (or best available grade with an assay of 99+ percent) potassium iodate previously dried at 180°C for 3 hours. Dilute to volume in a 500 ml volumetric flask. To a 500 ml iodine flask, pipet 50 ml of potassium iodate solution. Add 2 g potassium iodide and 10 ml of 1 N hydrochloric acid. Stopper the flask, and after 5 minutes, titrate with stock sodium thiosulfate solution to a pale yellow. Add 5 ml of starch indicator solution and continue the titration until

the blue color disappears. Calculate the normality (N_s) of the stock solution:

Eq. 2:
$$N_s = \frac{W}{V} \times 2.80$$

where N_s = Normality of stock sodium thiosulfate solution

V = Volume of sodium thiosulfate required, ml

W = Weight of potassium iodate, grams

$$2.80 = \frac{(1000 \text{ mg/g}) \quad (0.1 \text{ dilution factor})}{\dfrac{214 \text{ g } KIO_3\text{/mole}}{6 \text{ equivalents/mole}}}$$

7.3.1.5 Sodium Thiosulfate Titrant (~0.01 N). Pipet 100 ml of the stock sodium thiosulfate solution into 1000 ml volumetric flask and dilute to the mark with freshly boiled distilled H_2O. The normality (N_t) of the sodium thiosulfate titrant is:

Eq. 3:
$$N_t = 0.100\ N_s$$

where N_t = Normality of the sodium thiosulfate titrant

0.100 = Dilution factor

N_s = Normality of stock sodium thiosulfate solution (from Equation 2).

7.3.1.6 Stock Sulfite Solution. Dissolve sufficient anhydrous Na_2SO_3 or $Na_2S_2O_5$ in 1000 ml of recently boiled, cooled distilled water to give a solution containing approximately 50 µg SO_2/ml. The required amount of either compound can be calculated as follows:

Eq. 4: grams of $Na_2SO_3 = \frac{0.98}{\text{assay}}$

or

Eq. 5: grams of $Na_2S_2O_5 = \frac{0.74}{\text{assay}}$

Note: The assay of the reagent used should be 0.97 or greater. Have reagents ready to analyze this solution immediately.

7.3.1.7 Analysis of Stock Sulfite Solution. 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 minutes. Prepare the working sulfite-TCM solution (7.3.1.8) at the same time iodine solution is added to the flasks. By means of a buret containing

standardized 0.01 N sodium thiosulfate, titrate each solution in turn to a pale yellow. Then add 5 ml starch solution and continue the titration until the blue color disappears. Record the volumes of sodium thiosulfate used to titrate the blank (A) and the sample (B).

7.3.1.8 **Working Sulfite-TCM Calibration Standard.** Pipet 20 ml of the standardized sulfite solution into a 500 ml volumetric flask and dilute to the mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution:

Eq. 6: $$\mu g\ SO_2/ml = \frac{(A - B)\ (N_t)\ (32{,}000)}{25} \times 0.04$$

where A = Volume sodium thiosulfate for blank, ml

B = Volume sodium thiosulfate for sample, ml

N_t = Normality of sodium thiosulfate titrant from Eq. 3

32,000 = Milliequivalent wt. of SO_2, µg

25 = Volume standard sulfite solution, ml

0.04 = Dilution factor

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

7.3.2 Prepare calibration standards by dilution of the working sulfite-TCM standard (7.3.1.8) and subsequent dilution of the 1.0 μg SO_2/ml standards as indicated below. Use absorbing reagent for all dilutions.

Standard (μg SO_2/ml)	Volume of Standard (ml)	Diluted to (ml)	Concentration (μg SO_2/ml)
20	7.0	100	1.4
20	5.0	100	1.0
20	2.0	100	0.4
1.0	10.0	100	0.10
1.0	4.0	100	0.04
1.0	2.0	100	0.02

8. Analysis Procedures

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

Bring sample back to 50 ml with distilled water. (This assumes loss of volume due only to water evaporation.) Delay analysis for 20 minutes to allow any ozone to decompose.

8.2 Sample Analysis

8.2.1 Start reagents flowing through the analyzer system. The flow cell must be free of bubbles during operation. Refer to manufacturer's instructions for operating procedures. The sample and reagent flow rates listed in Fig. 2 are measured values, and are intended as a guide to maximize sensitivity.

8.2.2 Set the electronic zero by turning the display rotary switch to the zero position and adjusting the zero control for zero percent of scale with a screwdriver.

8.2.3 Set the electronic span by turning the display rotary switch to the full scale position and adjusting the full scale control with a screwdriver for 100 percent of scale.

8.2.4 Set the display rotary switch to the normal operation mode. With unreacted absorbing reagent in the flow cell, adjust the baseline to zero.

8.2.5 Once a stable baseline is obtained, span the colorimeter by introducing a 1.0 μg SO_2/ml calibration standard and adjusting the standard calibration control to 71.4% of recorder full scale. Use the specified range of 0 to 1.4 μg SO_2/ml. Repeat several times to verify the setting. If the calibration standard concentration is not exactly 1.0, the recorder response should be adjusted proportionately.

8.2.6 Fill the test cups with samples and place on turntable. One quality control sample, a 1.0 μg SO_2/ml calibration standard (7.3.2) is included after every 10 samples. Follow this by enough test cups filled with unreacted absorbing reagent to provide a baseline check. The quality control sample must produce a response within ±3.9 scale percent of the value indicated by the day's calibration curve for valid analyses.

Sample analysis, net μg SO_2/ml, is determined directly from the calibration curve (8.2.8). Samples exceeding the highest calibration standard are diluted up to 5:1 with absorbing solution until the

sample falls within the range. Rerun a randomly selected 5-10% of the samples for quality assurance.

8.2.7 Introduce the calibration standards at the beginning, near the middle, and at the end of each day's analyses. Record the percent response for each peak and subtract the baseline.

8.2.8 Plot net response in percent of full scale for all three calibrations (y-axis) vs. the corresponding concentration in μg SO_2/ml (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve. Determine a new calibration curve for each day's analyses.

8.2.9 Maintenance. Clean the apparatus after each use to prevent contamination of subsequent analyses. Consult manufacturer's instructions for cleaning procedures. Alkaline materials should not be used because of the formation of a precipitate with TCM.

8.2.10 Waste Disposal. Since the absorbing solution contains mercury, waste solution from the analysis should be treated prior to disposal or shipment for reclamation. The following procedure will remove greater than 99% of the mercury from the absorbing solution:[12]

a. To each liter of waste solution, add 10 g sodium carbonate until neutral and 10 g of granular zinc or magnesium.

b. Sodium hydroxide may have to be added if a neutral solution is not obtained with sodium carbonate.

c. Stir the solution for 24 hours in a hood.

CAUTION: Hydrogen gas will be released during this process.

d. After 24 hours, the solid material (mercury amalgam) will separate. Decant and discard the supernatant liquid.

e. Quantitatively transfer the solid material to a convenient container and dry.

8.2.11 Potential Sources of Error. Sulfur dioxide present in the air surrounding the Technicon analysis system can cause errors in the automated analysis. When using the small, 2 cm^3 Technicon IV sample cups, an error may result from the diffusion of SO_2 into the filled sample cup on the turntable. The error can be minimized by using larger sample cups such as disposable culture tubes in place of the small sample cups, by setting the sample probe so that it nearly touches the bottom of the culture tube, and by filling the tubes to the top. This technique increases the time required for the SO_2 to diffuse to the point of sampling.

Also, because room air segments the sample stream, contamination due to SO_2 could cause a shift in the baseline and a false increase due to absorption of SO_2 into the sample. If such contamination is suspected, purify the air by passing it through a TCM solution.

8.3 Calculations

8.3.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

where V = Volume of air sampled, m^3

F_1 = Measured flow rate before sampling, $cm^3/min.$

F_2 = Measured flow rate after sampling, $cm^3/min.$

T = Time of sampling, min.

10^{-6} = Conversion of cm^3 to m^3. $1\ m^3 = 10^6\ cm^3$

8.3.2 Uncorrected volume. The volume of air sampled is not corrected to S.T.P. because of uncertainty associated with 24-hour average temperature and pressure values.

8.3.3 Calculate the concentration of sulfur dioxide as $\mu g\ SO_2/m^3$ using:

$$\mu g\ SO_2/m^3 = \frac{(\mu g\ SO_2/ml) \times 50}{V} \times D$$

where 50 = Volume of absorbing reagent used in sampling, ml

V = Volume of air sampled, m^3

D = Dilution factor = 1 if not diluted.

8.3.4 Equation 1 is determined from the standard run in Sect. 8.2.7.

$$(\mu g/ml)\ SO_2 = ax + b$$

The slope (a) and intercept (b) are used to calculate SO_2 concentration.

8.3.5 If desired, concentration of sulfur dioxide may be calculated as ppm SO_2 using

$$m\ SO_2 = (\mu g\ SO_2/ml^3) \times 3.82 \times 10^{-4}$$

9. Calibration Apparatus

9.1 Sampling

9.1.1 Mass flowmeter equipped with a transducer, capable of reading a range of 0 to 10,000 cc/min or 0 to 10 liters/min. (should be periodically calibrated with a Brooks calibrator). A calibrated wet test-meter may also be used.

9.1.2 Complete bubbler setup as used in actual sampling in the field.

9.1.3 27 gauge needles, 3/8" long.

9.1.4 Red serum stoppers.

9.1.5 Vacuum pump capable of 5 to 20 liters/min and maintaining 0.7 atmospheres of vacuum.

9.1.6 Needle adapter used in the bubbler train in the field.

9.1.7 Vacuum tubing.

9.2 Analysis Calibration Apparatus and Reagents

9.2.1 Stopwatch capable of measuring 0.1 sec.

9.2.2 Graduated cylinder capable of measuring 0.1 cc.

9.2.3 Other apparatus and reagents discussed in Sections 7.1 and 7.3.

10. Calibration Procedure

10.1 Needle Calibration

10.1.1 Set up materials as in Figure 3.

10.1.2 Use distilled water in place of the sampling solution used in the field.

10.1.3 Allow 30-minute warmup for the mass flowmeter.

10.1.4 Start up the vacuum pump. Adjust the pressure gauge to 20" Hg of vacuum or better to keep from overtaxing the pump.

10.1.5 Place the needle in the train with the needle pointing away from the vacuum source. Take care not to bend the needle. Place it directly in the center of the serum stopper.

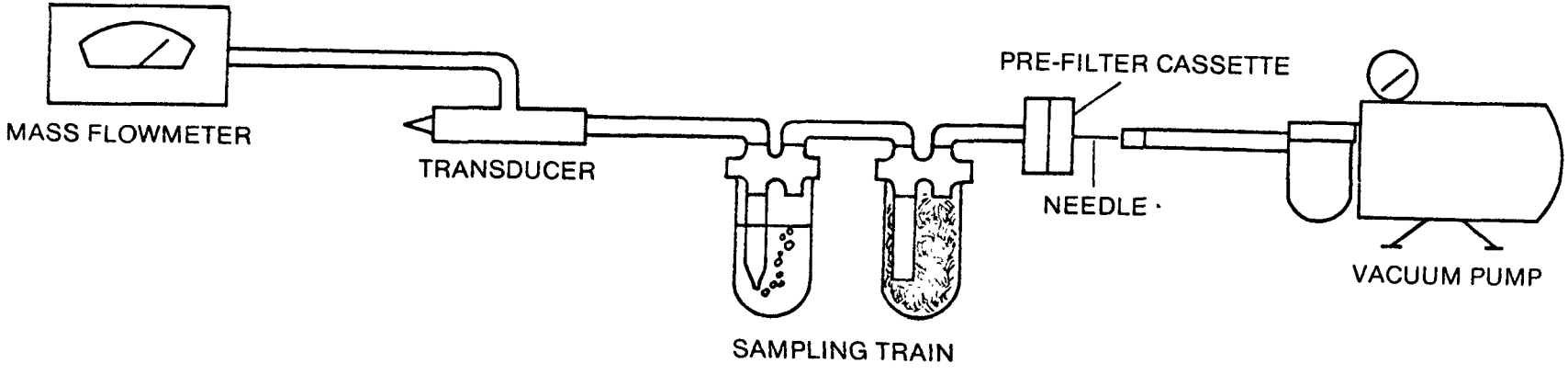
10.1.6 Observe the reading on the mass flowmeter. The flow should be no less than 180 cc/min or no greater than 220 cc/min. If this is not the case, discard the needle.

10.1.7 Follow this procedure for all needles to be checked, screening good needles from defective needles.

10.2 Analysis Calibrations

10.2.1 Calibrate the pump tubes using the stopwatch and graduated cylinder.

Figure 3 - NEEDLE CALIBRATION



$$\text{Flow} = \frac{\text{amount of solution pumped}}{\text{time solution pumped}}$$

10.2.2. The analyzer calibration is discussed in Sect. 8.2.

REFERENCES

1. Scarengelli, F. P., B. E. Saltzman, .and S. A. Frey, "Spectrophotometric Determination of Atmospheric Sulfur Dioxide," Anal. Chem. 39, 1709 (1967).

2. Logsdon, O. J. II and M. J. Carter, "Comparison of Manual and Automated Analysis Methods for Sulfur Dioxide in Manually Impinged Ambient Air Samples." EPA-Region V, 1819 West Pershing Road, Chicago, Illinois 60609.

3. Op. Cit., Scaringelli, Saltzman, Frey.

4. Pate, J. B., B. E. Ammons, G. A. Swanson, J. P. Lodge, Jr., "Nitrite Interference in Spectrophotometric Determination of Atmospheric Sulfur Dioxide," Anal. Chem. 37, 942 (1965)

5. Zurlo, N. and A. M. Griffini, "Measurement of the SO_2 Content of Air in the Presence of Oxides of Nitrogen and Heavy Metals," Med. Lavoro, 53, 830 (1962).

6. Op. Cit., Scaringelli, Saltzman, Frey.

7. Op. Cit., Zurlo and Griffini.

8. Scaringelli, F. P., L. Elfers, D. Norris, and S. Hochheiser, "Enhanced Stability of Sulfur Dioxide in Solution," Anal. Chem. 42, 1818 (1970).

9. Urone, P., J. B. Evans, and C. M. Noyes, "Tracer Techniques in Sulfur Dioxide Colorimetric and Conductimetric Methods," Anal. Chem. 37, 1104 (1965).

10. Bostrom, C. E., "The Absorption of Sulfur Dioxide at Low Concentrations (pphm) Studies by an Isotopic Tracer Method," Intern J. Air Water Poll. 9, 333 (1965).

11. Lodge, J. P., et al., "The Use of Hypodermic Needles as Critical Orifices in Air Sampling," J. Air Pollut. Contr. Assn. 16, 197-200 (1966).

12. Thompson, R. J., J. Air Pollut. Contr. Assn., 21, 428 (1971).

IV. NITROGEN DIOXIDE BUBBLERS (NO_2)

IV. NITROGEN DIOXIDE BUBBLERS (NO_2)

Automated Sodium Arsenite Method

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling air through a sodium hydroxide arsenite solution to form a stable solution of sodium nitrite.[1] The nitrite ion produced during sampling is reacted with phosphoric acid, sulfanilamide, and N-1-(naphthyl)ethylenediamine dihydrochloride to form an azo dye. The amount od dye produced is proportional to the nitrogen dioxide concentration. This dye is measured colorimetrically and the concentration is obtained from these measurements.

1.2 The method applies to 24-hour field samples and their laboratory analysis.

2. Range and Sensitivity

2.1 The analysis range is .01 to 1.4 μg NO_2^-/ml. Beer's Law is followed through this range. The range of the method is 20 to 750 $\mu g/m^3$ (0.01 to 0.4 ppm) nitrogen dioxide.[2] This range requires 50 ml absorbing reagent and a sampling rate of 200 cm^3/min. for 24 hours. The method is 82-87% efficient.

2.2 Minimum detectable limits have not been established for the Technicon II analysis.

3. Interferences[3]

3.1 Nitric oxide is a positive interferent.[4] Carbon dioxide is a negative interferent. These interferences were combined with ambient concentrations of NO_2. At varying ambient levels, this method has an average positive bias of 9.9 µg NO_2/m^3. The 95% confidence interval for this bias is 7.5 to 12.2 µg NO_2/m^3.

3.2 Sulfur dioxide interferences are eliminated by converting it to sulfate ion with hydrogen perioxide before analysis.[5]

4. Precision, Accuracy and Stability

4.1 The relative standard deviations for sampling NO_2 concentrations of 78, 105 and 329 µg/m^3 are 3, 4 and 2%.

4.2 Accuracy data is not available.

4.3 Collected samples are stable for at least 6 weeks.

5. Sampling

5.1 Apparatus

5.1.1 Sampling Train. A sampling apparatus diagram is shown in Figure 1. The apparatus section, or sampling train, between the glass intake manifold and the copper vacuum manifold is generally supported in a "bubbler box," Figure 1-a.

5.1.3 Absorption Tube. Polypropylene tube 164 x 32 mm, equipped with a polypropylene two-port cap. Do not use rubber stoppers as they cause high and

Figure 1 - SAMPLING SYSTEM

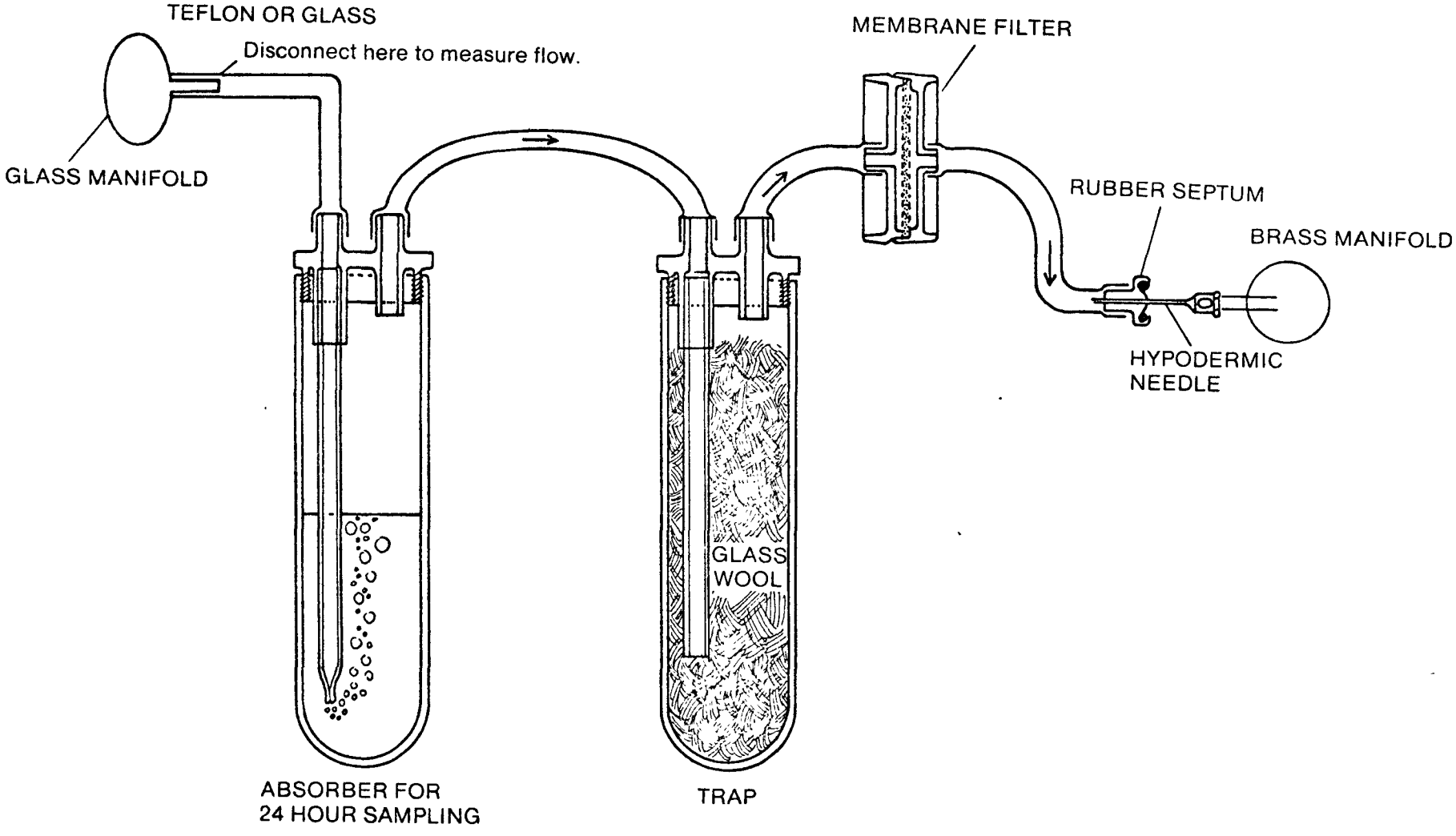
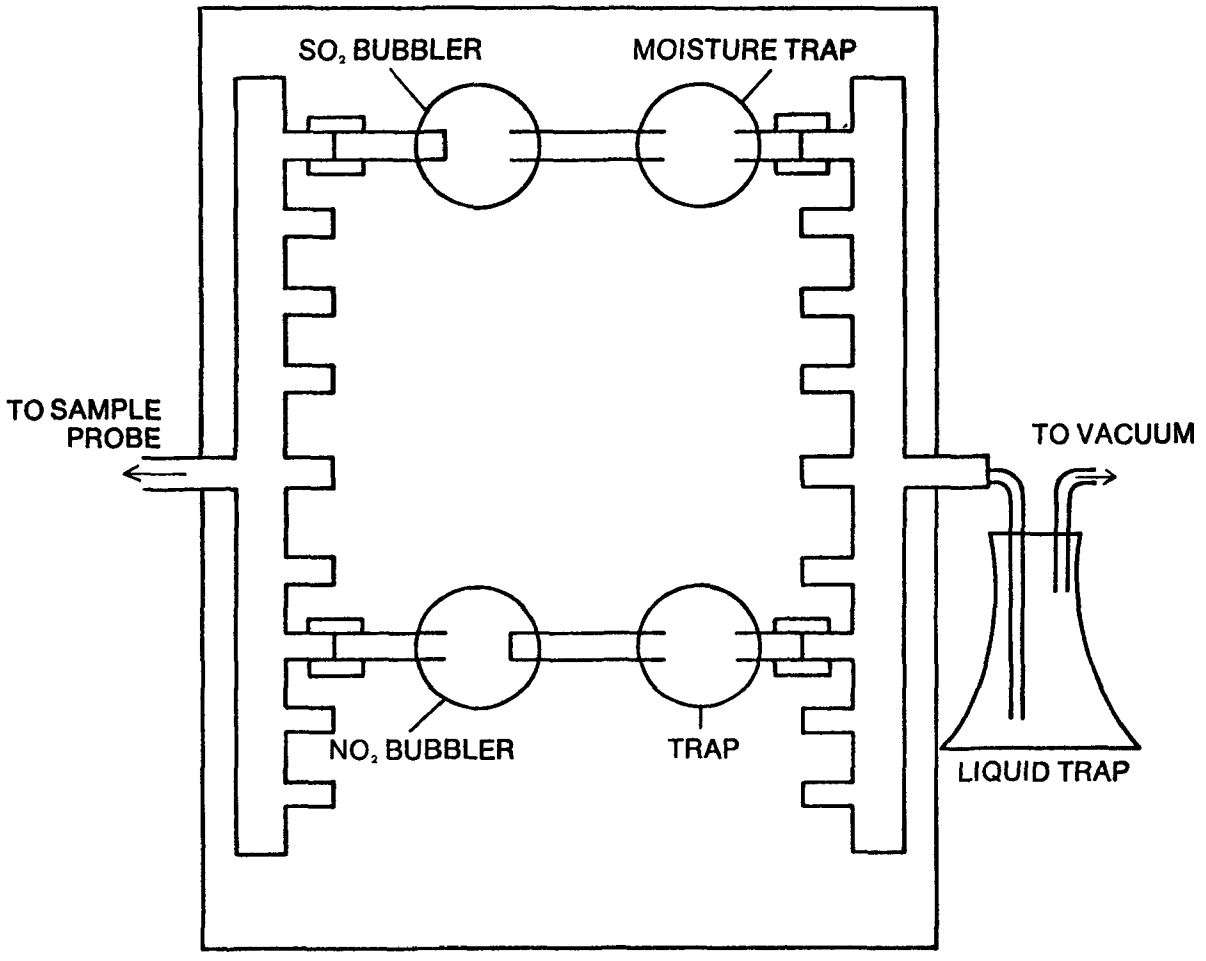


Figure 1-a - BUBBLER BOX



varying blank values. A restricted orifice glass tube is used to disperse gas. The 152 mm tube, 8 mm O. D. - 6 mm I.D., should have the end drawn to 0.3 - 0.8 mm I.D. Position the tube to allow a 6 mm clearance from the absorber bottom.

5.1.4 Moisture Trap. Polypropylene tube equipped with two-port cap. The entrance port of the cap is fitted with tubing that extends to the bottom of the trap. Loosely pack the unit with glass wool to prevent moisture entrainment.

5.1.5 Membrane Filter. Porosity of 0.8 - 2.0 microns. Used to protect flow control device from particulate matter and moisture. Change the membrane filter after 10 samples.

5.1.6 Flow Control Device. Any device capable of maintaining a constant flow (±2% for 24 hours) through the sampling solution between 180-220 cm^3/min. A typical flow control device is a 27-gauge 3/8" hypodermic needle.[6]

5.1.7 Flowmeter. Used to check the flows at the beginning and end of a 24-hour sample. Must be capable of measuring 180-220 cm^3/min to within 5%.

5.1.8 Bubbler Box. Designed to hold the above apparatus, the box contains a glass inlet and copper exhaust manifold, each with six sampling ports.

Place a liquid trap on the common exhaust vacuum line to prevent pump contamination.

Other bubbler samplers may be used at the same time when this box arrangement is employed.

5.1.9 Pump. Capable of maintaining the minimum vacuum and flows required for the 24-hour sample. A vacuum of 0.7 atmosphere or greater is necessary.

5.2 Reagents

5.2.1 Sodium Hydroxide. ACS Reagent Grade.

5.2.2 Sodium Arsenite. ACS Reagent Grade.

5.2.3 Absorbing Reagent. Dissolve 4.0 g sodium hydroxide in distilled water, add 1.0 g of sodium arsenite and dilute to 1000 ml with distilled water.

6. Sampling Procedure

6.1 Assemble the sampling apparatus as shown in Figure 1. Connect components upstream from the absorption tube with teflon tubing. Connect glass tubing with dry ball joints, or with butt-to-butt joints of tygon, teflon, or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated mark on the absorption tube.

6.2 Insert the flowmeter into the sample line between the glass manifold and the sample bubbler to measure the flow. Note this flow and remove the flowmeter from the system. This process is done immediately after inserting a new unexposed bubbler tube and just before it is taken off line 24 hours later.

Check the system for leaks if the flow rate before sampling is not between 180-220 cm^3/min. Replace the flow control device if necessary. Start sampling only after obtaining an initial flow rate in this range.

6.3 Data forms should be filled in when the sample is changed. These data are extremely important in calculations used to determine daily pollutant concentrations. They include start and stop times in military units (e.g., 3:45 p.m. = 1545), start and stop flows in appropriate metric units, start and stop dates, as well as flowmeter number, pump serial number, filter number, orifice number, etc. Note any uncorrectible condition such as high winds, local construction (within 1/4 km), severe rains or other conditions that can affect the sample.

7. Analysis

7.1 Apparatus

7.1.1 Volumetric flasks, pipets, and beakers to prepare standards. Use Class A glassware.

7.1.2 Instrument. Technicon Autoanalyzer II as listed below:

a. Sample turntable with variable sample rate and variable sample to wash ratio.

b. Proportioning pump: flow rates are varied using flexible tubing of varying diameters.

c. Mixing coils: use 3 (20 turn) standard mixing coils.

d. 40 ft. time delay coil.

e. 15 mm flow cell colorimeter: a phototube colorimeter operated at 558 nm with an auxiliary power supply, amplifier, and a tubular

flow cell. (The interference filters should be checked before use and at quarterly intervals for wavelength of maximum transmission.)

f. Recorder: 10 mv strip chart recorder.

7.1.3 Flows in the automated system may be other than those indicated by Figure 2, but should give corresponding results to the manual method of analysis.

7.2 Analysis Reagents

7.2.1 Sulfanilamide. Melting point, 165-167°C.

7.2.2 N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). Best grade available.

7.2.3 Hydrogen Peroxide. ACS Reagent Grade, 30%.

7.2.4 Sodium Nitrite. Assay of 97% $NaNO_2$ or greater.

7.2.5 Phosphoric Acid. ACS Reagent Grade, 85%.

7.2.6 Sulfanilamide Solution. Dissolve 20 g sulfanilamide in 700 ml distilled water. Add, with mixing, 100 ml concentrated phosphoric acid and dilute to 1000 ml. This refrigerated solution is stable for one month.

7.2.7 NEDA Solution. Dissolve 0.5 g of NEDA in 500 ml of distilled water. Refrigerated and protected from light, this solution is stable for one month.

7.2.8 Hydrogen Perioxide Solution. Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution, protected from light and refrigerated, can be used for one month.

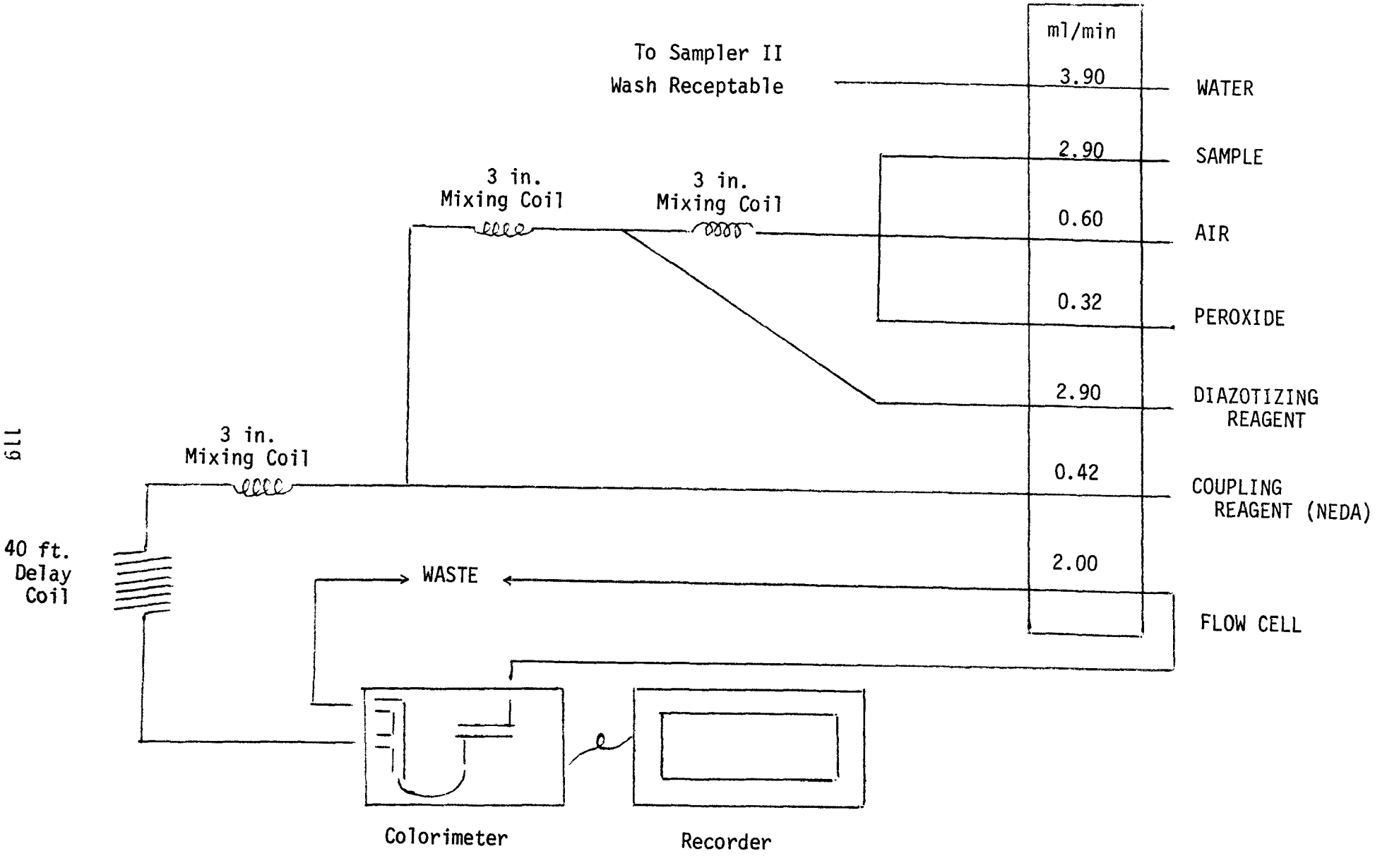


Figure 2 - Nitrogen Dioxide Automated Flow Diagram

7.2.9 Standard Nitrite Solution. Dissolve sufficient dessicated sodium nitrite and dilute with distilled water to 1000 ml to make a solution containing 1000 µg NO_2^-/ml. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100$$

where G = Amount of $NaNO_2$ grams

1.500 = Gravimetric factor in converting NO_2 into $NaNO_2$

A = Assay, percent.

Store this solution in the refrigerator.

7.2.10 Working Standards. Dilute 10 ml of the standard nitrite solution to 500 ml with absorbing reagent. This intermediate stock solution contains 20.0 µg NO_2^-/ml. Using this intermediate solution and absorbing reagent as the dilutent, prepare the following set of working standards:

Working Standard (µg NO_2^-/ml)	Volume of Intermediate Standard (To be diluted)	Final Volume
1.4	7.0 ml	100
1.2	6.0 ml	100
1.0	10.0 ml	200
0.8	4.0 ml	100
0.5	5.0 ml	200
0.2	5.0 ml	500
0.1	10.0 ml of 1 µg NO_2^-/ml	100
0.05	5.0 ml of 1 "	100
0.01	2.0 ml of 1 "	200

The .5 µg NO_2^-/ml standard is run every tenth sample to check the stability of the analytical procedure.

8. Analysis Procedure

8.1 Sample Preparation

8.1.1 Replace water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorption tube. Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot (less than 10 ml) of the collected sample with unexposed absorbing reagent.

8.1.2 A problem arises when using the 8.5 ml plastic cups in the sampling tray. The sample will deteriorate with time. The exact mechanism is as yet unknown. Run the samples so that the liquid does not remain in these cups for more than 30 minutes.

8.2 Analyzer Assembly and Use

8.2.1 The autoanalyzer is employed for this analysis. Interference filters of 558 mμ and a 15 mm tubular flow cell are used in the colorimeter. The sampler turntable is operated at 40 sample positions per hour with a 1:2 sample to wash time ratio. Eight minutes elapse between sample pickup and appearance of the corresponding peak on the recorder chart.

8.2.2 Assemble system with flows as shown in Fig. 2. Refer to Technicon II manual for specific assembly instructions.

8.2.3 After assembling the system, place all pump tubes in their respective solution containers and check the flows. Put the sample line in a container of distilled water. Allow the system to run 5 - 10 minutes. Check the debubbler to be sure that no bubbles are entering the colorimeter.

Run the analyzer until a stable baseline is obtained. Place the sample line in a container of unreacted absorbing reagent and pump the chemicals through the system to zero the instrument. Adjust the range with the standards to read out as desired on the strip chart recorder.

After running these standards and a blank of unreacted absorbing solution, plot the absorbance vs μg NO_2^-/ml. The system follows Beer's Law. A straight line passing through the origin should be obtained. The final curve is prepared for each batch of samples by averaging 3 sets of standards (one set at the beginning, one mid-way through the analysis, and one at the end). The .500 μg NO_2^-/ml standard is run every <u>tenth</u> sample to check the stability of the analytical procedure.

8.2.4 After plotting the standard curve, the system is ready to analyze samples. Peak height readings should be made by drawing a line connecting the baseline and measuring at the midpoint. Samples which exceed the absorbance of the highest standard

of the calibration curve are diluted until the concentration falls within the calibration range. A broadening of the colorimeter output with a corresponding loss in peak height usually indicates that the pump tubing should be replaced. Silicone rubber tubing is recommended in place of the standard pump tubing.

8.2.5 Rerun a random 5-10% of the samples to maintain internal quality assurance.

8.2.6 Purge this system daily with distilled water. Place all the reagent tubes in the water and pump for 15 - 30 minutes. Leave distilled water in the system until the next run.

8.2.7 Obtain alternate strip chart recorder ranges by using the Standard Calibration Dial on the colorimeter.

8.3 Calculations

8.3.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

where V = Volume of air sampled, m^3

F_1 = Measured flow rate before sampling, cm^3/min.

F_2 = Measured flow rate after sampling, cm^3/min.

T = Time of sampling, min.

10^{-6} = Conversion of cm^3 to m^3.

$1\ m^3 = 10^6\ cm^3$

8.3.2 Uncorrected Volume. The volume of air sampled is not corrected to S.T.P. because of uncertainty associated with 24-hour average temperature and pressure values.

8.3.3 Calculate the concentration of nitrogen dioxide as $\mu g\ NO_2/m^3$ using:

$$\mu g\ NO_2/m^3 = \frac{(\mu g\ NO_2^-/ml) \times 50}{V \times 0.82}$$

where 50 = Volume of absorbing reagent used in sampling, ml

V = Volume of air sampled, m^3

0.82 = Collection efficiency.

8.3.4 Equation 1 is determined from the standards run in Section 8.2.3

(1) $\mu g\ NO_2^-/ml = ax + b$

The slope (2) and intercept (b) are used to calculate NO_2^- concentration.

The final curve is prepared for each batch of samples by averaging 3 sets of standards (one set at the beginning, one set mid-way through the analysis, and one at the end).

8.3.5 If desired, concentration of nitrogen dioxide may be calculated as ppm NO_2 using

$$ppm\ NO_2 = (\mu g\ NO_2/m^3) \times 5.32 \times 10^{-4}$$

9. Calibration Apparatus

9.1 Sampling

9.1.1 Mass flowmeter equipped with a transducer capable of reading a range of 0 to 10,000 cc/min or 0 to 10 liters/min (should be periodically calibrated with a Brooks calibrator). A calibrated wet testmeter may also be used.

9.1.2 Complete bubbler setup as used in actual sampling in the field.

9.1.3 27 gauge needles, 3/8" long.

9.1.4 Red serum stoppers.

9.1.5 Vacuum pump capable of 5 to 20 liters/min and maintaining 0.7 atmospheres of vacuum.

9.1.6 Needle adapter used in the bubbler train in the field.

9.1.7 Vacuum tubing.

9.2 Analysis Calibration Apparatus and Reagents

9.2.1 Stopwatch capable of measuring 0.1 sec.

9.2.2 Graduated cylinder capable of measuring 0.1 cc.

9.2.3 Other apparatus and reagents discussed in Sections 7.1 and 7.2.10.

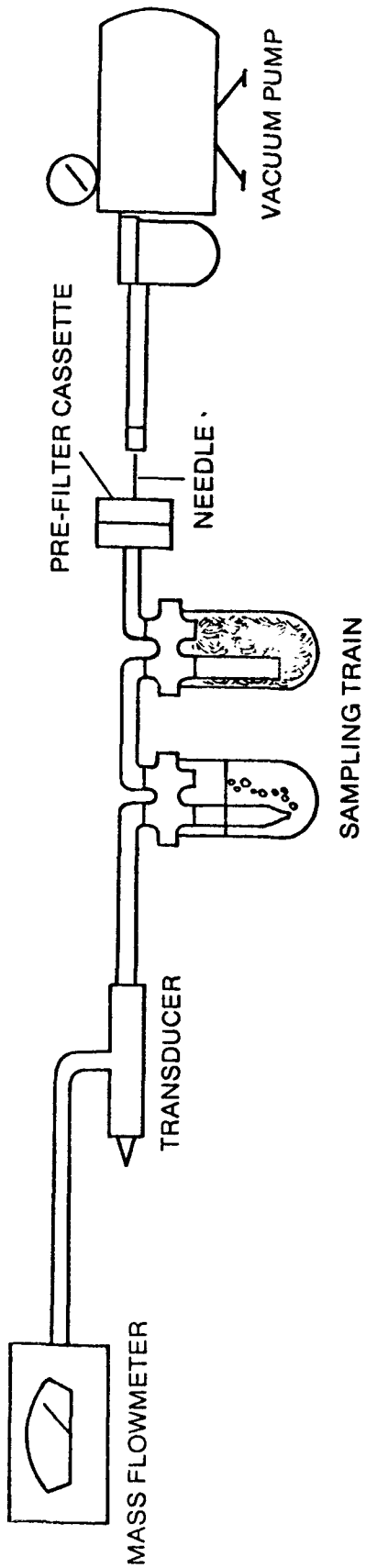
10. Calibration Procedure

10.1 Needle Calibration

10.1.1 Set up materials as in Figure 3.

10.1.2 Use distilled water in place of the sampling solution used in the field.

Figure 3 - NEEDLE CALIBRATION



10.1.3 Allow 30-minute warmup for the mass flowmeter.

10.1.4 Start up the vacuum pump. Adjust the pressure gauge to 20" Hg of vacuum or better to keep from overtaxing the pump.

10.1.5 Place the needle in the train with the needle pointing away from the vacuum source. Take care not to bend the needle. Place it directly in the center of the serum stopper.

10.1.6 Observe the reading on the mass flowmeter. The flow should be no less than 180 cc/min or no greater than 220 cc/min. If this is not the case, discard the needle.

10.1.7 Follow this procedure for all needles to be checked, screening good needles from defective needles.

10.2 Analysis Calibrations

10.2.1 Calibrate the pump tubes using the stopwatch and graduated cylinder.

$$\text{Flow} = \frac{\text{amount of solution pumped}}{\text{time solution pumped}}$$

10.2.2 The analyzer calibration is discussed in Section 8.2.3.

REFERENCES

1. Christie, A. A., et al. "Field Methods for the Determination of Nitrogen Dioxide in Air," Analyst 95, 519-524 (1970).

2. Ibid.

3. Beard, M. E., et al. "An Evaluation of the Effects of NO_1 CO_2 and Sampling Flow Rate on the Arsenite Procedure for Measurement of NO_2 in Ambient Air," Preliminary Draft.

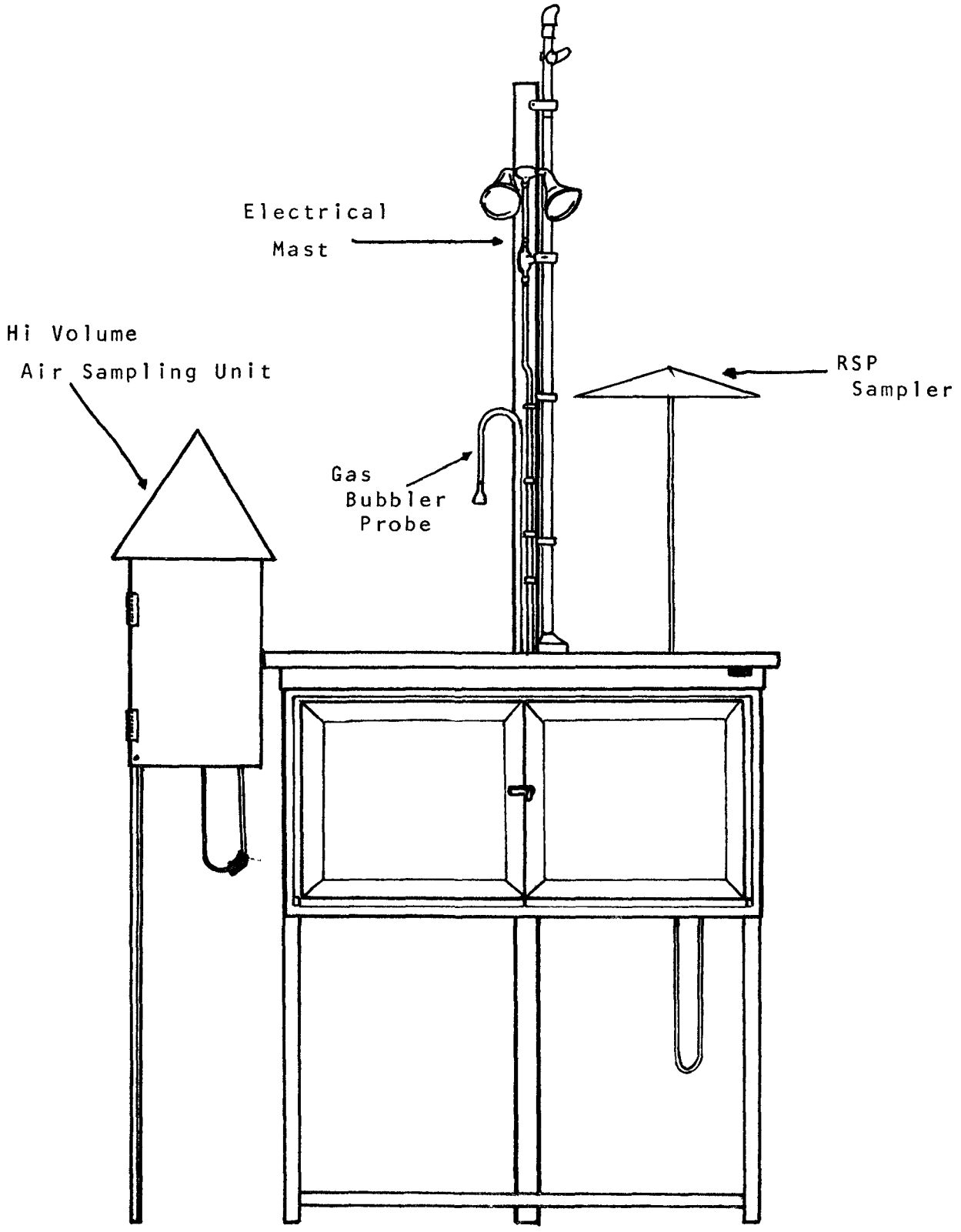
4. Merryman, E. L., et al. "Effects of NO CO_2, CH_4, H_2O and Sodium Arsenite on NO_2 Analysis," Presented at the Second Conference on Natural Gas Research and Technology in Atlanta, Ga., on June 5, 1972.

5. Jacobs, M. B. and S. Hochheiser, "Continuous Sampling and Ultramicrodetermination of Nitrogen Dioxide in Air," Anal. Chem. 30, 426, (1958).

6. Lodge, J. P., et al. "The Use of Hypodermic Needles as Critical Orifices in Air Sampling," J.A.P.C.A., 16, 197-200 (1966).

7. "Community Health Air Monitoring Program (CHAMP)", EPA Contract No. 68-02-0759.

CHESS AIR MONITORING SHELTER



Shelter specs: 4' x 3' x 2'

Mast approximately 12' above ground

APPENDIX

CHESS MONITORING SHELTER

The previously described CHESS sampling apparatus was centralized in a small aluminum shelter. This 4 x 3 x 2 foot prefabricated shelter was designed to be constructed on site. They were mounted on 3 ft. aluminum legs which could be bolted to aluminum angles driven into the ground for extra support. The shelters were painted white to provide for cooler summer operation. Locks were provided for the stuctures.

Attached to the shelter exterior were the hi-volume sampler shelter, the RSP sampling probe, the gas bubbler sampling probe and a 12-14 ft. electrical mast. The hi-volume sampler shelter was attached to the CHESS shelter with the air inlet approximately 6 feet above the ground. The inlet to the gas sampling probe and the RSP sampler probe was mounted approximately 3 feet above the roof of the CHESS shelter. The electrical mast was placed approximately 2-3 feet below ground for maximum support, in concrete if necessary. Housed in the shelter were the bubbler box, the vacuum pump, the heater and a temperature controlled exhaust fan. The fan and heater, the hi-volume sampler motor, and the vacuum pump were attached to separate 15 ampere-110 volt AC circuits.

The vacuum pump maintained the sample flows for the bubbler box and the RSP sampler. A spare pump was frequently maintained in the shelter.

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

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/1-76-011		

4. TITLE AND SUBTITLE	5. REPORT DATE
Community Health Environmental Surveillance Studies (CHESS) Air Pollution Monitoring Handbook: Manual Methods	January 1976
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
William F. Barnard	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Exposure Assessment Branch Population Studies Division Health Effects Research Laboratory	1AA601
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Health Effects Research Laboratory Office of Research & Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document is a methods manual handbook for the Community Health Environmental Surveillance Studies program. It covers Total Suspended Particulates (TSP), Total Suspended Nitrates (TSN), Total Suspended Sulfates (TSS), Respirable Suspended Particulate (RSP), Sulfur Dioxide, and Nitrogen Dioxide. This manual is to be used as a reference publication.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Environmental Surveys Toxicology Monitors	Community Health Environmental Surveillance Studies CHESS Health Effects Survey	14 B 06 F

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