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A.C. STERN, ed.; 1968; ACADEMIC PRESS, NEW YORK

Sect. 2 #11

ticles above about 5 μ in diameter since they may fail to adhere to the collecting slide. Samples collected by thermal precipitation are particularly desirable for direct microscopic examination. The disadvantage of most precipitators of this type is the low flow rate involved.

Several commercial versions of the thermal precipitator consist of a hot wire suspended near a glass microscope slide with the air flow directed between them. Low flow rates, of 10 or 20 cm^3/min, are provided by a vacuum pump or by water displacement.

Another type consists of an electrically heated plate suspended above a water-cooled plate on which a glass disk is placed (*36*). The air flow enters in the center of the heated disk and flows radially to the edges. The unit is self-contained with a cooling pump, air pump, and flowmeter. This model has a design flow of 500 cm^3/min. It may be used to collect viable bacteria or liquid aerosols by limiting the temperature gradient to about 320 °C/mm. All thermal precipitators have the advantage of a gentle precipitating force, thus preventing shattering or disaggregation of particles.

G. Centrifugal Methods

For the most part, samplers which fall into this category are midget cyclones (see also Chapter 43, Vol. III). The primary field of application is in sampling for large particles such as fly ash. They may be readily constructed, of metal or glass, in the laboratory or shop. Some commercial units are available. When properly designed, they have good efficiency for removal of particles of more than about 5 μ. Submicron particles are usually not captured at all.

Goetz (*37*) described an instrument for the quantitative separation and classification of airborne particulate matter. The unit consists of a rapidly rotating helical channel with a removable cone-shaped cover. Flow within the channel is provided by the motion of the helix and is kept in the laminar range. In operation, a high centrifugal acceleration (about 20,000 *g*) is imposed on the collected aerosol, and individual particles, following Stokes' law, are deposited on the inside of the cone. The position of their deposition is predictable. The device is effective for particle sizes down to 0.2 μ.

III. Sampling Gaseous Contaminants

A. General Considerations

A variety of gases and vapors may be involved in air pollution episodes. In general, gases and vapors behave alike when discharged into the air. The only significant difference between the two is that vapors are liquids at ordinary temperatures. The main reason for differentiating between the two is that different collection techniques may be used in sampling. A vapor may frequently be collected by simple condensation. Gases and vapors are readily diffused and mixed with the air upon discharge, and rapidly lose the identity of such physical properties as density. Their chemical properties, however, may produce undesirable conditions even when these compounds are present in very minute quantities. Several basic techniques are available for sampling gases and vapors. Not all of the techniques are suitable for all sampling conditions. Sampling devices which are very efficient for high concentrations of gases may not be suitable, without modifications, for sampling a contaminant such as hydrogen fluoride, which may cause undesirable effects in concentrations as low as 5 $\mu g/m^3$ of air. Some gases, such as carbon dioxide, aldehydes, and nitrogen oxides, are inefficiently collected in an absorber containing aqueous solutions when the gases are present in low concentration.

Many of the general considerations previously discussed are applicable here as well. Particular care must be taken if an aerosol sampler is used preceding a gas sampler. An apparently low gas concentration may result, owing to the presence of the aerosol sampler. It is also desireable when sampling for gases and vapors to observe the temperature and pressure conditions of the air mass from which the sample is collected.

B. Adsorption

Although probably less frequently used for collecting gases and vapors than other methods, adsorption has gained in application with the use of gas chromatography as an analytical tool (see also Chapter 47, Vol III). Gas adsorption is an operation in which a gas or vapor comes in contact with a solid so that its molecules adhere to the surface of the solid. The solid material is known as the adsorbent and the gas to be collected, the adsorbate. Since adsorption is largely a surface phenomenon, the amount of adsorbate which may be collected is dependent upon the specific surface or total surface per unit mass of the adsorbent. Other factors which control the removal capacity include the nature of the adsorbent and adsorbate, geometric state of the adsorbent, temperature, velocity of the airstream, concentration of the gas of interest as well as of the other gases in the stream, and how far adsorption has proceeded. An adsorption bed operates at high efficiency until just before the capacity of the bed is reached.

A variety of solids of an extremely porous nature have been de-

must therefore be taken to remove water vapor from the sampled airstream by condensation or other means. The method adopted for desiccation must not remove the gases of interest. A variety of coolants can be used to provide a wide range of temperatures, as indicated in Table VI. The precautions in the use of these coolants are mentioned in Section III,D.

C. Absorption

Absorption is one of the most frequently used methods for collecting gases (see also Chapter 46, Vol. III). Gas absorption is an operation in which a soluble component of a gas mixture is dissolved in a liquid or hygroscopic solid. The absorbent, which is the collecting agent, may change either physically or chemically or both during the absorption process. The absorbent may be either reactive or nonreactive.

Information on small gas absorbers has been reported by Calvert and Workman (*42*). They note the various factors which contribute to absorber efficiency and confirm that gas-phase diffusivity, liquid-phase diffusivity, residence time, reciprocal of bubble size, and solubility are of greatest importance. When the solubility of a gas in an absorbent is low, the efficiency of absorption tends to be low. This condition can be improved by using a chemically reactive absorbent. Although Calvert and Workman (*43*) describe a method for predicting the efficiency of bubbler-type absorbers, the prediction can only be considered an estimate. If very accurate knowledge of collector efficiency is required, the information must be obtained as indicated in Section I,A,4.

In the choice of absorbent, consideration is given to liquids with high solubilities for the solutes to be absorbed. The solubility of a gas in a liquid depends upon the partial pressure of the gas in the atmosphere, the temperature, and on the purity of the absorbent. The ideal solvent

TABLE VII
Solubility of Selected Gases in Distilled Water at 20 °C

Gas	Volume absorbed per volume of water[a]
Nitrogen	0.015
Oxygen	0.031
Nitric oxide	0.047
Carbon dioxide	0.878
Hydrogen sulfide	2.582
Sulfur dioxide	39.374

[a] Gas volumes reduced to 0 °C and 760 mm Hg.

is relatively nonvolatile, inexpensive, noncorrosive, stable, nonviscous, nonfoaming, and nonflammable. Distilled water fulfills many of the characteristics of an ideal solvent and frequently is used in collecting some gases. Its suitability for various common gases can be seen in Table VII. It can be seen that water will be quite suitable for hydrogen fluoride and sulfur dioxide but is not recommended for the others. Other solvents, such as alkaline solutions for acid gases and acid solutions for alkaline gases, may be used. In these cases, not only solubility but reactivity come into importance. Special chemical solutions may be used for special purposes or in anticipation of the use of a specific method of analysis. For example, straw oil may be used to collect hydrocarbons. An alkaline zinc acetate solution is used in one method of sampling for hydrogen sulfide in which the sulfide precipitates as the zinc salt. If the gas does not react chemically with the absorbent, its solubility is defined by Henry's law. If reaction does occur, the usual laws of chemical reaction apply.

As small a quantity of liquid absorbent as is necessary to cover the dispersion tube adequately should be used. Too much liquid dilutes the sample and may cause difficulties in the subsequent analysis. Losses by evaporation and by foam and mist carry-over must be considered. The effect of oxidation by the air being drawn through a reactive solution must be determined before sampling.

Devices used for sampling by absorption include the following: fritted glass scrubbers, impingers, packed columns, countercurrent scrubbers, and atomizing scrubbers.

1. *Fritted-Glass Scrubbers*

A great variety of sizes and shapes of these devices is available. A few are shown in Fig. 12. In general, units of this type provide the most efficient collection for gases. Fritted ware should not be used to sample for ozone and other oxidants. In addition to the readily available commercial devices, homemade units may be constructed using the gas dispersion tubes available from most glass supply houses. These units may be available in the form of a disk or a cylinder, and in a range of pore sizes. Coarse or extracoarse frits provide effective gas dispersion at relatively low head loss. The head-loss characteristics for a variety of scrubbing devices are shown in Fig. 13. It is to be emphasized that these data cover only the individual units tested. However, the shape of the curves probably applies to all similar units.

The efficiency of collection of gases will depend on a variety of factors previously described. Most fritted-glass scrubbers, however, under

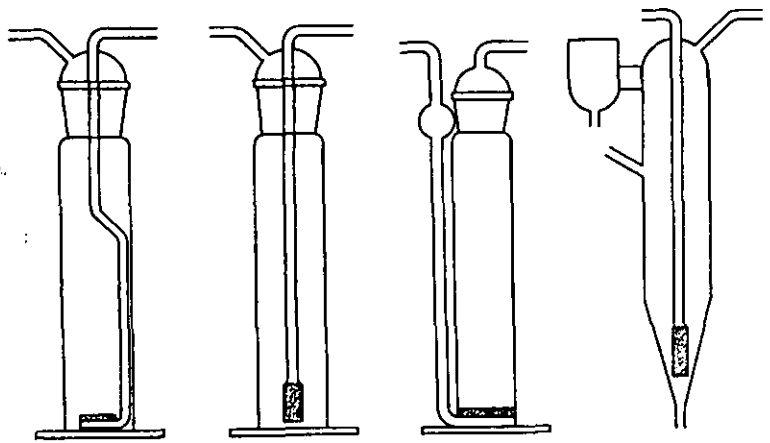

FIG. 12. Several types of fritted-glass scrubbers used in sampling for gases.

optimum conditions of flow rate and reagents, have an efficiency in excess of 90%. At the end of the sampling period the liquid reagent should be surged back and forth through the frit several times before a sample is withdrawn for analysis.

Since coarse-fritted ware has a pore size of about 50 μ, the units may gradually clog with use. They may be cleaned by surging the appropriate cleaning solution back and forth through the frit and then rinsing several times with distilled water in the same manner. Dirt can be removed with hot concentrated hydrochloric acid, fatty materials with carbon tetrachloride, and organic matter with hot concentrated sulfuric

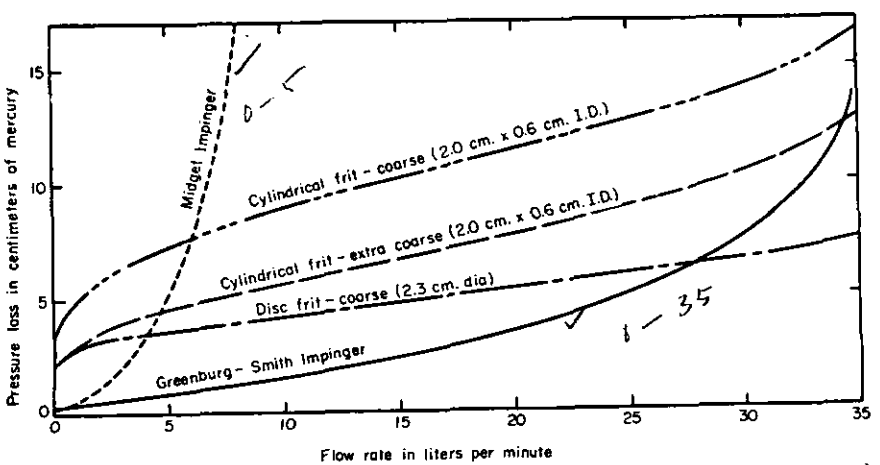

FIG. 13. Head-loss characteristics for several types of common gas scrubbers and impingers.

acid containing a few drops of sodium nitrite. Dichromate cleaning solution may permanently stain the frit and should not be used.

2. *Impingers*

Impingers frequently have been used for collecting samples of gases and vapors in the same manner as have fritted glass scrubbers. Several types of impingers are shown in Fig. 10. Work done in the laboratories at the University of Florida and at Southwest Research Institute (*44*) indicates that impingers may be somewhat less efficient for collection of gas samples than are fritted-glass scrubbers. In the low concentration commonly encountered in air pollution sampling, and when all types of collectors were operated at the optimum sampling rate, midget impingers were found to have an efficiency less than that of a fritted-glass scrubber. The threshold concentration level for the midget impinger was also found to be considerably higher than for several types of fritted-glass scrubbers. The lowest sulfur dioxide concentration at which the fritted-glass collectors exhibited reasonable efficiency was about one third of that necessary for the midget impinger. With highly soluble or reactive combinations of absorbent and absorbate, at moderate contaminant concentrations, the collection efficiency of both types of units approaches 100%.

3. *Packed Columns*

A number of homemade devices of this type have been described in the literature, in which glass beads or plastic saddles are used in the scrubber to break up the bubbles and increase the efficiency of absorption.

4. *Countercurrent Scrubbers*

Collection devices of this type are used in a number of recording instruments. The contactor usually consists of a long column containing a concentric helix or obstacles in the wall of the column which obstruct the flow of air and reagent. The reagent flows down the column in a thin layer and is brought into intimate contact with the turbulent flow of air coming in the opposite direction.

5. *Atomizing Scrubbers*

In collection devices of this type, the reagent is sprayed through the flowing column of sampled air. A fine spray is used; the reagent is collected in the bottom of the vessel and recirculated to the spray head. In general, drops of liquid falling through a gas provide a less efficient

absorption medium than do bubbles of the gas rising through the liquid. One device of this type is modeled after the venturi scrubber used in air cleaning (*45*).

D. Freezeout

This method is used where it is desirable to obtain a gross sample of all of the polluting constituents in the air. The technique involves drawing a sample of air through a series of collectors which are held at progressively lower temperatures. The coolants which might be used in a typical series are ice and water (0 °C), ice and salt (−21 °C), Dry Ice (−79 °C), liquid air (−149 °C), and liquid nitrogen (−196 °C). Liquid nitrogen is preferable to liquid oxygen (−183 °C) because of the safety factor, but it has the disadvantage of condensing oxygen from the air. A variety of low temperature coolants may be prepared and used as indicated in Table VI. The coolant should be contained in wide-mouthed Dewar vessels. If the vessel is unshielded, it should be covered completely on the outside surface by wrapping with plastic tape. The low temperature fluids must be handled with extreme care. Contact with the skin and inhalation of the vapors must be avoided. Some of the vapors are flammable and the gas released from liquid oxygen in high concentrations will cause nearly explosive combustion.

The common sampling rate for this technique is 1 dm^3/min. The collectors used are usually double-walled flasks immersed in the coolant. Both Shepherd (*46*) and Barnebey (*47*) traps have been used with success. Air flow takes place through the thin space between the walls. The Shepherd traps have been reputed to offer more severe icing problems with subsequent clogging. One of the problems which must be met is that of handling the large quantities of water which may condense out and freeze in the early stages. This water may contain some of the pollutants of interest and should thus be analyzed. A water-cooled condenser preceding the low temperature train may help solve the problem. A filter flask can serve as the receiver.

After collection, the samples must be sealed or held at the low temperature until ready for analysis. Analysis may require absorption after gasification, or some technique which permits analysis in the gaseous state. Examples of the latter are mass spectrometry, infrared spectrophotometry for organic materials, and gas chromatography.

E. Grab Sampling Techniques

In a number of instances it may be desirable to collect grab samples of polluted air. Several techniques presently are available for obtaining large and small grab samples. These include several types of evacuated bottles or flasks and several types of plastic envelopes or balloons. Also under investigation but not yet in use is a technique for compressing large volumes of air into cylinders.

In its most common form, the evacuated bottle consists of a flask which contains some reactive solution. A vacuum is drawn on the flask and the flask sealed. The volume of air which can be collected by this method may be calculated from the conditions of evacuation (*48*). In use, the flask is taken to the point of sampling, the seal broken, and the reactive solution shaken to absorb the maximum amount of impurities. The efficiency of this method approaches 100%. The solution containing the absorbed materials may then be analyzed by the usual chemical techniques. The major disadvantage of this procedure is the small amount of sample which can be collected. There is also a possibility of contaminating the sample if a greased stopcock is used as the seal.

Stainless steel evacuated flasks, either with or without plastic inserts, have been successfully used in grab sampling. Samples may usually thus be obtained that are larger than those obtained with the use of glass containers. The flasks may be evacuated and filled, as previously mentioned.

Several types of gas sampling tubes are available. In their most common form these are glass cylinders of 200 to 1000 cm^3 capacity, sealed at both ends with glass stopcocks. They are filled by displacement using a hand-operated pump to produce a vacuum. With both stopcocks open the pump is used to flush the container thoroughly with the air being sampled, then both stopcocks are closed.

Another collection device is the plastic bag or balloon which, when inflated, will hold 5–10 ft^3. This may be made of many types of satisfactory plastics including polyethylene, polychlorotrifluoroethylene, polytetrafluoroethylene, or polyethyleneterephthalate. In use, the bag is inflated by using a vacuum cleaner or some similar pressure device. Because the air must first pass through the pressure device, there is a possibility of alteration or contamination of the sample. The collected sample is returned to the laboratory and the desired constituent absorbed, or some technique is used which can perform analysis directly on the gas sample (*22*).

A loose plastic liner may be filled by evacuating the container around it. The container may be made of any material which will permit evacuation of air between it and the liner. Liquid displacement methods are suitable for all of the devices mentioned.

Another very handy sampling technique involves the use of impregnated granular adsorbents or papers. These devices are generally

hand-operated and are available for a wide variety of gases and vapors. In most of them, a color change or length of stain is a measure of the concentration. Most of the units are proprietary devices.

IV. Simplified Techniques

An approach which is satisfactory for many purposes is to obtain cumulative indications over a period of time by simplified techniques (*49*). No quantitative measure of the concentration of polluting material per unit volume of air may be obtained by such methods, but satisfactory information for many purposes may be secured. The unit cost of such techniques is practically insignificant when compared with more elaborate procedures and equipment. These techniques depend for their activity on having the natural movement of the air bring the pollutant in contact with the appropriate reagent. Results of most of these procedures are dependent upon wind velocity, atmospheric moisture, and air temperature. Although in some instances attempts have been made to refine and to elaborate upon the basic techniques, much of the benefit may thus be lost. Generally, results obtained by simplified techniques correlate quite well with results obtained by other procedures. Simplified techniques may help to provide preliminary information on which to base decisions concerning a more elaborate sampling program, or they may be an end in themselves. Such techniques are available for sulfur dioxide, gaseous fluorides, hydrogen sulfide, ozone, and others. Undoubtedly, other reactants described in the literature could be applied in simplified techniques. More are needed for a variety of contaminants.

A. Sulfur Dioxide

The earliest of the dosimeter methods is applicable to one of the most common air pollutants. This is the lead peroxide candle method for estimating sulfur dioxide of Wilsdon and McConnell (*50*) described in Chapter 17, Section II,G,6.

A modification of the procedure, developed at the University of Florida, has proved quite satisfactory and labor saving. A glass specimen jar, 4.4 cm in diameter and 15 cm in length, is used as the form. These jars have Bakelite screw caps and are commonly known as "olive jars, 5 oz."

It is essential that preparation and storage of the materials take place in a location which is not exposed to sulfur dioxide or sulfates. Each

jar should be numbered near the cap end with a scriber, preferably the number of a sampling station. Each jar should be marked wi scriber at a distance from the closed end such that the total area b the mark, including the bottom surface, is equal to 100 cm². For jars recommended, this distance is 6.1 cm. Cut pieces of 2.5 cm (flatte diameter) tubular gauze about 20 cm in length, and staple through gauze perpendicular to the long axis about 0.5 cm from one end. T gauze inside out and slip smoothly over the closed end of the jar. top edge should be even with the scribed mark.

Prepare mucilage by dispersing 2 gm of gum tragacanth in 10 m absolute ethanol and adding, with one action while stirring, 190 m distilled water. Prepare a thin smooth paste by mixing the lead salt mucilage in the ratio of about 7 gm of lead dioxide to 5 ml of mucil Mix thoroughly at frequent intervals during use. If the mixture beco too thick during use, additional 5% ethanol in distilled water ma added to balance the solvent losses. The prepared forms are dippe the scribed mark, with the gauze serving as a reinforcement. A dipping, they are allowed to drain for a few seconds and the surfa smoothed with a 1-inch brush. Dry the cylinder slowly in the ai completed cylinder should have a reactive surface of 100 cm². coating should be thick enough to hide the texture of the gauze but enough to dry without crazing. The consistency of the paste and me of application may be varied to produce the desired result by experie At least one prepared cylinder should be stored in an airtight jar for as a control when the analysis is run. All cylinders to be exposed si taneously should be prepared at the same time. Exposure takes p in a standard shelter which protects the reactive surface from rain. A exposure for 1 month or longer, the candle is removed from the sh and the area of the reactive surface measured. The coated fabr stripped from the form by slitting with a razor, and the amount of sul determined. A similar candle containing the gauze reinforcement, which has not been exposed, is used as a control. The results of ob vations are reported as milligrams of sulfate per day per 100 cm lead peroxide.

ASTM has a standard method covering this application which scribes the method of fabrication and procedures in a general (ASTM D2010-65).

More recent work at the University of Florida confirms the importa of the lead dioxide particle size, cites methods of standardizing particle size among various batches of reagent, and establishes a rati basis of design for the lead dioxide cylinders (*51*).

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I. Introduction

Inorganic gaseous pollutants represent an important class of substances in analysis of samples for air pollution control purposes and for the assessment of ambient air quality. In general, these compounds are highly toxic to vegetation or to health of animals and man. They occur in the urban atmosphere in low concentrations, usually in the range of less than a part per million of air by volume and may be reported in terms of parts per hundred million, parts per thousand million or micrograms per cubic meter. Consequently, methods for the detection of short period average and maximum concentrations in the ambient air must be sensitive and accurate in the microchemical or ultramicrochemical range. Other desirable features of a method should include a high degree of specificity, ease of calibration, and minimum interference from other contaminant gases present in the air sample.

Reagents employed for absorption of the gas sample and the resultant reaction products should be stable and insensitive to oxidation, temperature, and light. Factors affecting the sensitivity and accuracy of a method, such as collection efficiency, stability of reagents and products, speed of reaction, temperature coefficient, and influence of interfering substances should be known or capable of control. The effect of interferences may be eliminated by absorption or chemical reaction with selective or specific reagents. Unfortunately, only a limited number of the large variety of methods available for air pollution analysis may be designated as specific. Most of the methods in common use are essentially nonspecific and depend upon oxidation-reduction, acid-base reactions, measurements of electrical conductivity, colorimetric procedures or other general techniques that yield a measure of the algebraic sum of absorbed pollutants having similar chemical properties.

Methods that have a high degree of specificity for substances are limited to some measurement of the intrinsic properties of the molecule, to the formation of unique reaction products or complexing agents, or to the prior removal of interfering substances by precipitation, distillation, filtration, dialysis, or reaction. Where it is not possible to employ a specific method, owing to the present state of knowledge, an empirical, nonspecific method may be used if the calibration and analytical procedure is rigidly standardized. An empirical method of analysis that depends upon the common chemical properties of a group of compounds can be very useful if the results may be correlated with one or more specific effects.

Many methods, both manual and instrumental, have been proposed for the determination of inorganic gaseous pollutants and the literature in this field has expanded rapidly. However, only a limited number of these has been subjected to collaborative testing to determine their reliability, precision, and accuracy.

II. Sulfur Dioxide

Of the available methods for sulfur dioxide analysis, those commonly employed in ambient air sampling are conductimetric (*1, 2*), titrimetric (*3, 4*), colorimetric (*5–7*), turbidimetric (*8–10*), and iodimetric (*11–14*). These methods may be used as manual laboratory precedures or incorporated into automatic monitoring instruments. Conductimetric and colorimetric monitoring instruments are in widespread use for the continuous measurement of ambient air concentrations of sulfur dioxide. A simple, cumulative method based on the rate of sulfation of exposed lead peroxide candles (*15, 16*) is employed extensively in a number of countries.

A. West-Gaeke Method (*5–7, 17*)—Colorimetric

The West-Gaeke method is applicable to the determination of SO_2 in ambient air in the concentration range from about 0.005 to 5 ppm. Sulfur dioxide in the air sample is absorbed in 0.1 *M* sodium tetrachloromercurate. Nonvolatile dichlorosulfitomercurate ion is formed in this process. Addition of acid-bleached pararosaniline and formaldehyde to the complex ion produces red-purple pararosaniline methylsulfonic acid, which is determined spectrophotometrically. The system obeys Beer's law up to about 0.6 μl of SO_2 per milliliter of absorbing solution. This method is not subject to interference from other acidic or basic gases or solids such as SO_3, H_2SO_4, NH_3 or CaO; the analysis should, however, be completed within 1 week after sample collection, and the concentrations of ozone and NO_2 should be less than that of the SO_2.

1. *Reagents*

All chemicals used must be of analytical-reagent grade.

a. Absorbing Reagent, 0.1 M Sodium Tetrachloromercurate. Dissolve 27.2 gm (0.1 mole) mercuric chloride and 11.7 gm (0.2 mole) sodium chloride in 1 liter of distilled water. (CAUTION: Highly poisonous; if spilled on skin, flush off with water immediately.) This solution can be stored at room temperature for several months.

b. Pararosaniline Hydrochloride (0.04%), Acid Bleached. Dissolve 0.20 gm of pararosaniline hydrochloride in 100 ml of distilled water and filter the solution after 48 hours. This solution is stable for at least 3 months if stored in the dark and kept cool. The pararosaniline used should have an assay of better than 95% and an absorbance maximum at 543 or 544 mμ. Pipet 20 ml of this into a 100-ml volumetric flask. Add 6 ml of concentrated HCl. Allow to stand 5 minutes, then dilute to mark with distilled water. This solution should be pale yellow with a greenish tint. It can be stored at room temperature in an amber bottle for a week or for about 2 weeks if refrigerated.

c. Formaldehyde, 0.2%. Dilute 5 ml of 40% formaldehyde to 1000 ml with distilled water. Prepare weekly.

d. Standard Sulfite Solution. Dissolve 640 mg sodium metabisulfite (assay 65.6% as SO_2) in 1.0 liter of water. This yields a solution of approximately 0.40 mg/ml as SO_2. The solution should be standardized by titration with standard 0.01 *N* I_2 with starch as indicator, and should be adjusted to 0.0123 *N*. Then 1 ml = 150 μl SO_2 (25 °C, 760 mm Hg). Prepare and standardize freshly.

e. Starch Solution (Iodine Indicator), 0.25%. Make a thin paste of 1.25 gm of soluble starch in cold water and pour into 500 ml of boiling water while stirring. Boil for a few minutes. Keep in glass-stoppered bottle.

f. Standard Iodine Solution, 0.01 N. Dissolve 12.69 gm of resublimed iodine in 25 ml of a solution containing 15 gm of iodate-free KI; dilute to the 1000-ml mark in a volumetric flask. Pipet exactly 100 ml of this 0.1 *N* solution and dilute to 1000 ml in a volumetric flask with 1.5% KI. This solution can be used as a primary standard if the weighing is carefully done, or it can be checked against a standard thiosulfate solution. This solution should be stored in an amber bottle, refrigerated, and then standardized on the day of use.

2. *Apparatus*

a. Absorber. An all-glass midget impinger or other collection device capable of removing SO_2 from an air sample using 10 ml of absorbing reagent should be used.

b. Air Pump. The air pump should be capable of drawing 2.5 liters/min through the sampling assembly.

c. Air Metering and Flow Control Devices. Metering and control devices should be capable of controlling and measuring flows with an accuracy of ±2%. The flowmeter should be calibrated for variations in reading with temperature and pressure of the airstream so that the appropriate corrections can be applied.

d. Spectrophotometer or Colorimeter. Color-measuring devices should be capable of measuring color intensity at 560 mμ, in absorbance cells 1 cm or larger.

3. *Analytical Procedure*

a. Collection of Samples. Set up a sampling train consisting of, in order, absorber, trap to protect flow device, flow control and metering devices, temperature and vacuum gage, and air pump. All probes and tubing upstream from the bubbler should be Pyrex glass, stainless steel, or Teflon. Butt-to-butt connections may be made with Tygon tubing. The downstream flow metering device can be empirically corrected to atmospheric conditions by conducting a dummy run with an upstream flowmeter in line that is open to the atmosphere.

Pipet exactly 10 ml of absorbing reagent into the absorber. Aspirate the air sample through the absorber at a rate of 0.2–2.5 liters per minute (depending upon the concentration of SO_2 in the atmosphere and the sampling time desired). The sampling time may vary from a few minutes to 24-hours. For 24-hour sampling the absorber selected should be capable of containing 20 ml or more of absorbing reagent. For best results, the sampling time and rate should be chosen to provide a concentration of approximately 2–4 μl of SO_2 in 10 ml of the absorbing reagent. The dichlorosulfitomercurate formed may be stored for 3 days with only a slight decrease in strength (about 1% per day). The sample may be stored in the collection device or transferred to a stoppered glass or polyethylene container.

b. Analysis. If a mercury precipitate is present owing to the presence in the air sample of inorganic sulfides, thiols, or thiosulfates, it may be removed by filtration or centrifugation. To the clear sample, adjusted to 10 ml with distilled water to compensate for evaporative losses, add 1.0 ml of acid-bleached pararosaniline solution and 1.0 ml of the 0.2% formaldehyde solution and mix.

Treat a 10-ml portion of unexposed sodium tetrachloromercurate solution in the same manner for use as the blank. If the collecting reagent remains exposed to the atmosphere during the interval between

sampling and analysis, the blank should be exposed in the same manner.

Allow 20 minutes for maximum color development and read the absorbance at 560 mμ in a spectrophotometer with the blank as reference.

4. *Calibration*

Pipet exactly 2 ml of standard sulfite solution into a 100-ml volumetric flask and dilute to mark with absorbing reagent. This final solution contains 3.0 μl SO_2 per milliliter.

Add accurately 0.5-, 1.0-, 1.5- and 2.0-ml portions of the dilute standard sulfite solution to a series of 10-ml volumetric flasks and dilute to the marks with absorbing reagent. Continue with the analysis procedure given above.

Plot the absorbance (optical density) as the ordinate against the microliters of SO_2 per 10 ml of absorbing solution on rectangular coordinate paper. Compute slope of straight line best fitting the data.

5. *Calculation*

Convert the volume of air sampled to the volume at standard temperature and pressure. Compute the microliters of SO_2 in the sample by multiplying the absorbance by the slope of the calibration plot. Then the concentration by volume is:

$$SO_2 \text{ ppm} = \frac{\text{microliters of } SO_2 \text{ in sample}}{\text{volume of air sampled in liters, STP}} \qquad (1)$$

B. Hydrogen Peroxide Method (3, 4)—Titrimetric

This method is applicable to the determination of SO_2 in ambient air in the concentration range from about 0.01 to 10.0 ppm. Sulfur dioxide in the air sample is absorbed in 0.03 *N* hydrogen peroxide (H_2O_2) reagent (adjusted to about pH 5). The stable and nonvolatile sulfuric acid formed in this process is titrated with standard alkali. The method requires only simple equipment and can be performed by analysts having lesser skills; it is preferable to the West-Gaeke method if SO_2 is the principal acid atmospheric gaseous pollutant and if long storage of samples (greater than 1 week) prior to analysis is required.

1. *Reagents*

a. Absorbing Solution, Hydrogen Peroxide, 0.03 N, pH 5. Dilute 3.4 ml of 30% H_2O_2 solution to 2 liters with distilled water. Determine the alkalinity of the solution by taking a 75-ml portion, adding 3 drops of mixed indicator, and adding approximately 0.002 *N* HCl or HNO_3 from a buret until the indicator turns pink (pH 5). Calculate the amount of acid necessary to adjust the acidity of the bulk of the absorbent and add the required amount. The zero blank, obtained by titrating 75 ml of the adjusted reagent with 0.002 *N* NaOH to the indicator equivalence point (green), should be not more than 2 drops. The reagent is stable at room temperature for at least 1 month.

b. Mixed Indicator, 0.1%. Dissolve 0.06 gm bromocresol green and 0.04 gm methyl red in 100 ml of methanol. When stored in an amber bottle at room temperature the reagent is stable for at least 6 months.

c. Standard Sulfuric Acid Solution, 0.002 N. Prepare this solution by appropriate dilution of concentrated sulfuric acid. Standardize by the gravimetric barium sulfate method with a 200-ml portion or with a primary standard such as $Na_2B_4O_7 \cdot 10H_2O$. This reagent may be stored indefinitely without change in strength.

d. Standard Sodium Hydroxide Solution, 0.002 N. Prepare 2 liters of this solution by dilution of 1 *N* sodium hydroxide with freshly boiled (CO_2-free) distilled water. Standardize as follows: Pipet 25 ml of standard sulfuric acid solution into an Erlenmeyer flask, add 3 drops of mixed indicator solution, and titrate with the sodium hydroxide reagent contained in a buret to the green equivalence point. Store the reagent in a polyethylene or other alkali-resistant bottle and restandardize bimonthly.

$$\begin{aligned} 1 \text{ ml of } 0.002\ N \text{ NaOH} &= 64\ \mu g\ SO_2 \\ &= 24.47\ \mu l\ SO_2 \text{ (25 °C, 760 mm Hg)} \\ &\quad \text{or } 22.4\ \mu l\ SO_2 \text{ (0 °C, 760 mm Hg)} \end{aligned} \qquad (2)$$

2. *Apparatus*

a. Absorber. A standard all-glass, impinger, multijet, or fritted bubbler may be used (capacity about 300 ml).

b. Air Pump. The pump should be capable of drawing 1 cfm through the sampling assembly.

c. Air Metering Devices. Metering devices should be capable of controlling and measuring flows with an accuracy of ±2%. The flowmeter should be calibrated for variation in reading with temperature and pressure so that the appropriate corrections can be applied.

d. Buret. A buret of 25- or 50-ml capacity graduated in 0.1-ml subdivisions, preferably with Teflon plug, should be capable of measuring volume with an accuracy of 0.05 ml.

3. *Analytical Procedure*

a. Collection of Samples. Set up a sampling train consisting of, in order, impinger, trap to protect flow device, flow control device, flow metering device, temperature and vacuum gage, and air pump. Measure 75 ml

of absorbing reagent into the large impinger. Aspirate air through the bubbler at a rate of 1 cfm for 30 minutes. Note the readings of the vacuum gage and thermometer. The downstream flowmetering device can be empirically corrected to atmospheric conditions by conducting a dummy run with an upstream flowmeter inline that is open to the atmosphere. If an integrated 24-hour air sample is desired, the sampling rate may be reduced to 1 liter per minute. For SO_2 concentrations of 0.3 ppm and greater, the strength of the standard alkali may be increased or the sampling time shortened. For concentrations greater than 0.8 ppm a second impinger should be connected in series so that a recovery efficiency of 98% is maintained. All probes and tubing upstream from the impinger should be Pyrex glass, stainless steel, or Teflon. Butt-to-butt connections may be made with short lengths of Tygon tubing. The collected sample will not decompose on standing; consequently, the solution may be titrated long after sample collection. The sample may be stored in the impinger, which has been stoppered or transferred to a stoppered glass or polyethylene container.

b. Titration. Add three drops of mixed indicator solution and titrate the solution with standard 0.002 *N* sodium hydroxide until the color changes from red to green. A reagent blank is titrated in the same manner, and this result (which should be less than 0.1 ml) is subtracted from the sample titer.

Results are computed on the basis of the following reaction:

$$SO_2 + H_2O_2 = H_2SO_4 \qquad (3)$$

Thus the net titer of 0.002 *N* NaOH (in milliliters) multiplied by 24.47 or 22.4 gives the microliters of sulfur dioxide. Concentration is computed as in Section II,A,5.

C. Conductimetric Method

The conductivity method (*1, 2*) is readily adaptable to either manual or continuous, automatic analysis of sulfur dioxide in the atmosphere on a nonspecific basis. Since conductivity is a property of all ionic solutions, soluble gases that form strong electrolytes in solution and soluble salts, if present, may cause interference by the resultant change in conductivity. The sulfur dioxide in the air sample is absorbed in a slightly acid solution of distilled water containing hydrogen peroxide and the change in conductivity of the resultant sulfuric acid is measured manually or recorded continuously. The method is applicable to the analysis of SO_2 concentrations in the range of 0.01–2 ppm or greater, depending upon air flow rates and volume of absorbing solution.

1. *Reagent—Absorbing*

A good grade of distilled water must be employed. Sufficient sulfuric acid is added to make this water equivalent to 2×10^{-5} *N* and enough hydrogen peroxide (3% solution) is added also to bring the absorbent to a strength of 3×10^{-3} *M* with respect to the peroxide. Carbon dioxide present in the normal atmosphere is not absorbed by this solution and causes no interference.

2. *Apparatus*

The apparatus for continuous monitoring should consist of a suitable assembly of sampling probe, absorber, regulating and recording device for air flow, regulating and recording device for liquid flow, air pump liquid-metering pump or constant-head device with capillary tube for dispensing the absorbent at a constant rate, thermostatted cabinet, conductivity electrodes, and conductivity recorder.

a. Sampling Probe. The sampling probe should be made of Pyrex glass, 316 stainless steel or Teflon tube with intake end turned down, and a loose glass wool filter to remove insects or large particulate matter. An inline prefilter should be mounted indoors, exterior to the instrument, or if necessary, inside the thermostatted cabinet, to prevent condensation of water vapor, which would absorb SO_2 and result in serious losses.

b. Absorber. A venturi scrubber or any reagent-air-contacting system capable of a scrubbing efficiency of 98% or more is acceptable. A suitable system consists of a glass tube, 8 mm inside diameter and 75 cm long, containing a spiral Nichrome wire, in which the liquid absorbent flows downward, countercurrent to the air sample introduced at the bottom of the tube.

c. Measuring, Regulating, and Recording Device for Air Flow. A flowmeter, needle valve, gas meter (wet test), or other flow measuring, flow regulating device capable of measuring flows with an accuracy of ±2% should be used. The air flow rate should be monitored continuously by means of suitable mechanical and electronic circuitry to cause characteristic markings to appear on the conductivity recorder chart.

d. Measuring, Regulating, and Recording Device for Liquid Flow. A metering pump, flowmeter, and needle valve or device capable of measuring flows with an accuracy of ±2% is acceptable. The liquid flow rate should be monitored continuously by means of suitable mechanical and electronic circuitry to cause characteristic markings to appear on the conductivity recorder chart.

e. Air and Liquid Pumps. Any air pump and liquid pump or combination air-liquid pump is acceptable that is capable of drawing air at a rate

of 5–15 liters per minute and liquid at a rate up to 30 ml per minute through the absorption-analyzing system under conditions of continuous operation. To assure satisfactory performance, the pump should have a much greater capacity, about 30-liters-per-minute air flow under the conditions of operation.

f. Thermostatted Cabinet. The reagent feed lines, absorption column, and conductivity cells should be enclosed in an insulated compartment thermostatically maintained at a temperature a few degrees higher than the highest ambient temperature expected. The temperature of the reagent in the conductivity cells should be continuously monitored by means of suitable electronic circuitry to cause characteristic markings to appear on the conductivity recorder chart.

g. Conductivity Electrodes. Two sets of platinum dip electrodes of suitable dimensions, one pair to measure the conductivity of the unreacted reagent and the other that of the reacted reagent, should be provided. (Cell constant 0.067 cm^{-1} approximately.)

h. Conductivity Recorder. A zero-to-10 mv, potentiometric, strip chart recorder with 30-day chart and scale graduated from zero to 100 and chart speed of 1 or 2 inches per hour, or any instrument capable of recording the differential output of the conductivity cells corresponding to an SO_2 concentration range of zero to 2 ppm with an accuracy of ±1% of full scale should be provided. A convenient range for a conductivity recorder is 50,000–125 ohms.

i. Reagent Reservoir and Delivery Bottle. Any bottle with sufficient volume to contain a 1 week's supply of reagent can be used; the reagent should be protected from air pollutants by the insertion of a soda-lime charcoal column on the air inlet line.

j. Switch-Controlled Electronic Check. A switch-controlled manual check containing the proper resistance to cause a deflection of the recorder corresponding to a concentration of 1 ppm SO_2 should be used.

k. Switch-Controlled Electronic Zero Check. A check should be used to simulate a differential conductivity between the reference cell and a known resistance equivalent to zero ppm SO_2. This also serves as a check on the purity of the unreacted reagent.

3. *Calibration*

a. Static Calibration, Standard Solutions. The instrument may be calibrated by sulfuric acid solutions of known composition corresponding to definite atmospheric SO_2 concentration in the range zero to 2 ppm. Solutions corresponding to 0.5, 1.0, 1.5, and 2.0 ppm SO_2 are prepared by the addition of calculated amounts of 0.1 *N* H_2SO_4 to the absorbing

reagent. The static methods described below may be used when the absorption efficiency is known to be greater than 98%.

1. Establish instrument zero by introducing the unexposed absorbing reagent in both the reference and sample conductivity cells; then the standard solutions are substituted for the absorbing reagent in the sample conductivity cell only. The instrument reading is checked against the standard reagent, and, if necessary, the instrument is adjusted by means of the span control to indicate the correct concentration.

2. The standard solution is substituted for the absorbing reagent and is introduced directly into the system as in normal operation. Sulfur dioxide-free air, obtained by passage of air through a drying tower containing ascarite or soda lime, is admitted to the analyzer under the same conditions as in actual sampling. The instrument reading is checked against the standard reagent, and the necessary corrections are made. Absorbing reagent is maintained in the reference cell.

b. Dynamic Calibration, Standard Gas Mixture. The dynamic calibration methods described below should be employed to take into account the scrubbing efficiency of the absorbing column under flow conditions. Standard air-SO_2 mixtures may be prepared in a rigid test chamber, compressed gas cylinder, or collapsible Mylar or other inert plastic bag and then introduced into the analyzer. The mixtures are prepared by diluting a measured quantity of pure SO_2 gas with a known volume of SO_2-free air. A measured quantity of SO_2 gas may be introduced into the test chamber through a rubber diaphragm by means of a hypodermic syringe and needle. In the compressed-gas-cylinder technique, the dilution of SO_2 is accomplished by introducing a measured amount of SO_2 by a hypodermic syringe into a partially evacuated, stainless steel cylinder and compressing the mixture by addition of air contained in a compressed-air cylinder at high pressure until the desired pressure is reached. When a rigid test chamber is employed, corrections should be applied for the diminution of gas concentration resulting from the dilution of the test gas by influent air during sampling, or a flexible plastic bag can be put inside the chamber to receive replacement air. The concentration of SO_2 in the gas streams prepared by the above methods should be calibrated by the West-Gaeke or hydrogen peroxide methods. A gas dilution apparatus and method for preparing reproducible dynamic mixtures in any desired concentration has been described by Thomas and Amtower (*18*).

c. Other. The instrument may also be calibrated against a manual method such as the West-Gaeke or the hydrogen peroxide method. Atmospheric air or synthetically produced air-SO_2 mixtures are introduced simultaneously into the analyzer and the manual absorber. The

instrument record is adjusted to read SO_2 concentrations as determined by the manual method.

D. Iodimetric Method

Several modifications of this method (*13, 14*) have been described for manual laboratory estimation or for continuous monitoring of atmospheric sulfur dioxide. A sensitive, automatic method is described by Katz (*14*). The optical absorbance of a series of dilute starch-iodine solutions in the range of 1×10^{-5} to 7×10^{-5} N is determined with a spectrophotometer at 450 mμ, using a reference blank containing equivalent quantities of starch, potassium iodide, and dilute sulfuric acid in distilled water. The optical absorbance of these blue solutions follows Beer's law and the spectrophotometer measurements may be employed to determine the concentration of SO_2 in an air sample after passage through a midget impinger, multijet, or other type of efficient absorber system.

1. *Reagents*

Blue starch-iodine solution. Mix 1–2 gm of high grade, soluble starch into a thin paste with a small amount of cold, distilled water and pour this into 500 ml of boiling water, with stirring. After boiling for a few minutes, cool the mixture and transfer to a 1-liter volumetric flask. To this flask are added 2 gm of potassium iodide (iodate-free), dissolved by shaking, followed by additions of 2 ml of 0.01 N sulfuric acid and 7.0 ml of the standard 0.01 N iodine solution. The mixture is made up to 1 liter volume with distilled water. This reagent is stable for several days when kept in stoppered polyethylene bottles. Stock solutions are stable for about 1 week when stored in a dark, cool room in clean sterile vessels. This absorbent is made up to an initial concentration of 7 or 8×10^{-5} N iodine. Standardization may be accomplished by titration with 0.01 N sodium thiosulfate (previously checked against an accurately prepared potassium dichromate solution), using 0.25% starch indicator solution.

1 ml of 10^{-5} N iodine solution = 0.112 μl of SO_2 at 0 °C and 760 mm Hg.

2. *Apparatus*

This iodimetric or colorimetric method may be employed in a continuous monitoring instrument equipped with photoelectric cells, a constant voltage light source, a suitable optical system, and a recording potentiometer to indicate the increase in light transmission of the blue solutions after aspiration with a measured volume of air. The range of sensitivity of this type of instrument is from 0.01 to 1.0 ppm or more, depending upon the volume and concentration of absorbent solution and the volume of the air sample. For example, a change in light transmission equivalent to reaction with 1×10^{-5} N iodine represents a concentration of 0.125 ppm of SO_2 for 25 ml of absorbent solution and 22.4 liters of air sample. Upwards of 300 liters of air may be passed through a multijet absorber containing this reagent, at 10 liters per minute, without any loss of iodine by volatilization. A countercurrent absorption column may also be employed without change in stability of the solution due to aspiration with pure air. A portable SO_2 meter based on the above reagent, and a measurement circuit consisting of photoelectric cells connected to a galvanometer has been developed by Cummings and Redfearn (*19*). According to Adams *et al.* (*20*), the addition of small quantities of *N*-acetyl-*p*-aminophenol and mannitol to a starch-iodine reagent contributes to improved stability so that it may be aspirated at approximately 0.1 cfm for periods of more than 12 hours.

E. Barium Sulfate Method—Turbidimetric

The basis of the barium sulfate method (*8–10*) is the absorption of sulfur dioxide in the air sample by aspiration in the acid hydrogen peroxide reagent (described in Section II, B) and subsequent determination of the sulfuric acid formed as barium sulfate by measurement of the turbidity of the precipitated suspension in a spectrophotometer at 500 mμ. The sulfate is precipitated by solid barium chloride in the presence of glycerol-alcohol solution to stabilize the suspension.

1. *Analytical Procedure*

A recommended analytical procedure (*10*) is to place a 20-ml aliquot of the absorbent hydrogen peroxide reagent, after aspiration with the air sample, in a 1-inch cuvette. Add 1 ml of 10 N HCl, and mix with 4 ml of glycerol-alcohol solution (1 volume of glycerol to 2 volumes of absolute ethyl alcohol). The absorbance of this solution is determined at 500 mμ against a reference cuvette containing distilled water. This reading is subtracted from the final reading. Add approximately 0.25 gm of barium chloride crystals and shake until dissolved. After standing for 40 minutes at room temperature (20°–30 °C), the absorbance of the turbid mixture is measured at 500 mμ against the reference cuvette containing distilled water.

2. *Calibration*

The concentration of sulfate corresponding to the measured absorbance is obtained by reference to a standard calibration curve prepared by analysis of a series of anhydrous sodium sulfate standards containing 2–60 μg of sulfate ion per milliliter of solution, in terms of measured absorbance of the corresponding barium sulfate suspensions in accordance with the above analytical procedure.

F. Discussion of Procedures

For all of the methods discussed in Sections II,A to E, inclusive, the error for the combined sampling and analytical technique is about ±10% in the concentration range below 0.10 ppm, with increasing accuracy with concentration in the range of 0.10–1 ppm. The West-Gaeke method is more specific, probably, than the other methods in the analysis of community atmospheres. Sulfuric acid or sulfates do not interfere. However, ozone and nitrogen dioxide interfere if present in the air sample at greater concentrations than SO_2. Interference of NO_2 can be eliminated by addition of 0.06% sulfamic acid in the absorbing reagent (*7*) or by addition of *o*-toluidine subsequent to sample collection (*21*). Interference from solid aerosols or particulate matter containing heavy metals can be prevented by use of a dry filter or impactor placed upstream. Much difficulty has been caused with the method by the use of impure pararosaniline hydrochloride. However, a commercial brand is now available that has been specially selected for this procedure (Fisher Scientific Co., catalog No. P-389). The purity of the reagent may be estimated by comparing the value obtained from the slope of the calibration plot with 0.15 absorbance unit per microliter, obtained with 1-cm cells in a Cary spectrophotometer, corresponding to a molar absorptivity of 36,700. The color produced is independent of temperature in the range of 11°–30 °C and is stable for 3 hours.

In the titrimetric hydrogen peroxide method, erroneously high results may be obtained by the presence of strong acidic gases, other than SO_2, in the air sample. Alkaline gases such as ammonia give erroneously low results. Ordinarily, sulfuric acid mist does not interfere since it is not appreciably separated from the air sample owing to its small particle size, except at high relative humidity (greater than 85%) when the mist particles may increase in size to particles greater than 1 μ. Carbon dioxide from the air is not absorbed in the acid hydrogen peroxide reagent. Solid aerosol impurities may be removed by a dry particulate filter or efficient impactor. Sulfate salts do not interfere.

Electroconductivity, which is measured in terms of the resistance of the solution between two electrodes immersed in it, is a property of all ionic solutions and is not specific for any particular compound. It is dependent upon the number and type of ions dissolved in solution. Soluble gases that yield electrolytes in solution cause the greatest interference. All hydrogen halides present would be measured. Except near special sources of contamination, these gases are, however, seldom present in air in appreciable amounts in comparison with SO_2. Weak acidic gases such as H_2S cause practically no interference because of their slight solubility and poor conductivity. If the water is free of bases, the carbon dioxide content of air causes no interference. Alkaline gases, such as ammonia, interfere by neutralizing the acid and yield comparatively low results because the transport number of the hydrogen ion is several times greater than that of other cations. Similarly, lime dusts or other basic solids, if absorbed, would cause comparatively low results for SO_2. Neutral and acidic aerosols such as sodium chloride or sulfuric acid give comparatively high results depending on their solubility, ionization, and the ability of the absorption system to remove them from the airstream, which, in this method, is very poor unless particle size is relatively large. Since the particle size of sulfuric acid mist is small (less than 1 μ) except perhaps when the relative humidity is greater than 85%, it is not measured appreciably in this method. A special absorber and different operating parameters are required for effective collection of sulfuric acid mist. A loose glass wool filter is used to minimize maintenance time requirements for cleaning of absorber and conductivity cells, and reducing the interference of particulate matter. Instrument response is a function of gas concentration, air flow and liquid flow rate, and conductivity cell constants. Response time is a function of liquid flow rate and the distance and volume between the absorber and the conductivity cells.

A change in temperature of 2 °F will alter the conductivity of a strong electrolyte by approximately 2%; consequently, for accurate operation, the absorption column and conductivity cells should be enclosed in an insulated compartment thermostatically maintained at a temperature a few degrees higher than the maximum ambient temperature expected.

In the iodimetric method, sulfuric acid mist or sulfates and unsaturated hydrocarbons do not interfere. However, there is interference from oxidizing and reducing substances such as nitrogen dioxide, ozone, or oxidants and hydrogen sulfide. Appreciable errors may therefore be encountered in sampling atmospheres where such gases are likely to be present in appreciable concentrations in relation to the sulfur dioxide.

Interferences in the turbidimetric barium sulfate method for sulfur dioxide may be caused by soluble sulfates, hydrogen sulfide, and sulfuric

acid mist trapped during the air sampling. Particulate sulfates and sulfuric acid may be removed by an appropriate filter or aerosol collector placed upstream while sampling. Factors that must be controlled in this method are the stability of the colloidal barium sulfate suspension, sulfate concentration, barium ion concentration, pH, and aging of the barium chloride solution.

Thomas and Amtower (*18*) compared the results obtained by analysis of a considerable number of dynamically prepared synthetic mixtures of dilute sulfur dioxide in air; employing the (1) conductimetric, (2) titrimetric hydrogen peroxide, (3) West-Gaeke colorimetric and (4) turbidimetric barium sulfate procedures. When an efficient absorber is employed in gas sampling, such as a multijet absorber or midget impinger, excellent analytical agreement was obtained with all of these four methods in the analysis of prepared gas mixtures by the gas dilution apparatus over the concentration range of less than 0.10 to about 1 ppm. The addition of ozone at a concentration of 0.56 ppm had no significant effect on the results of the sulfur dioxide analyses. Addition of nitrogen dioxide in the concentration range of about 0.15–0.50 ppm to the SO_2-air mixtures also had no significant effect on the results, although the colorimetric SO_2 determinations tended to show a small decrease in concentration. Possibly, in this case, there was some slight interference with color formation of the diazotized pararosaniline methyl sulfonic acid by the nitrogen dioxide or ozone, even though sulfamic acid was added after the absorption and before the color reagents to overcome this effect. The maximum difference between "gas volume" concentration and "analytical" concentration seldom exceeded 0.01–0.02 ppm. (See also Section II,G,2.)

G. Miscellaneous Sulfur Dioxide Methods

1. *Fuchsin-Formaldehyde Method—Colorimetric*

In the fuchsin-formaldehyde method (*22*, *23*), SO_2 in the atmosphere is removed and concentrated by scrubbing through a sampling solution of 0.1 *N* sodium hydroxide and 5% glycerol. The subsequent determination of SO_2 is based on a color reaction first developed by Steigmann (*24*). The chromogenic reagent consists of a mixture of basic fuchsin, sulfuric acid, and formaldehyde, which develops a red-violet color in the presence of sulfurous acid.

The absorption maximum is at 570 mμ and the color is independent of temperature in the range 23°–26 °C. Above this range the effect of temperature on the absorbance of the sample gives increasingly erroneous results. A 30-minute color development thermostatted at 25 °C is suggested. The extent of color stability for longer periods was not reported.

Inorganic sulfides, thiols, and thiosulfates interfere with the determination and may be removed as a mercury precipitate by treatment with saturated mercuric chloride prior to the addition of the colorimetric reagent (*25*).

The method has a sensitivity of 0.01 ppm with a 40-liter air sample scrubbed through 10.0 ml of absorbing solution. The minimum amount detectable is 0.1 μg/ml solution. At a sampling rate of 20 liters/hour with a midget fritted bubbler, the collection efficiency is close to 100%. Stang *et al.* (*26*) using a Greenburg-Smith all-glass impinger containing 100 ml of 1% glycerol in 0.05 *N* sodium hydroxide and sampling at 1 ft^3/min, obtained results indicating from 93 to 99% efficiency based on the amount of SO_2 collected in two impingers in series.

Moore *et al.* (*23*) reported that NO_2, if present in the same concentration range as SO_2, produces a negative interference owing to the bleaching effect of NO_2 on the fuchsin-formaldehyde sulfite color. Corrections for the effect of NO_2 on the colorimetric SO_2 values were obtained by concurrent determination of SO_2 by the conductimetric and colorimetric methods and of NO_2 by the Saltzman method.

Paulus *et al.* (*27*) found it necessary to establish a new standard curve with each new batch of colorimetric reagent. They also reported on the effect of aging, light, and agitation on the collected sample. Solution strength was determined after the first, third, and sixth days of sample collection. Average losses of 6% were found after 6 days. The samples that showed losses after the first and third days were mostly in the lowest concentration range. No losses due to sunlight or artificial light were found. The effect of agitation is important when samples are shipped by mail. Losses due to agitation are comparable to those due to the aging experiments and are, therefore, not hastened by this condition.

The fuchsin-formaldehyde method for the determination of SO_2 in air is included in the ACGIH manual of recommended methods for the analysis of factory atmospheres (*28*). An average deviation of 8% was found. According to ACGIH, when concentrations of nitrogen oxides higher than those of SO_2 are anticipated, the polarographic method should be used. (See also Section II,G,3.)

2. *Stratmann Method—Colorimetric*

Atmospheric SO_2 is initially absorbed on silica gel and then reduced with hydrogen to H_2S on a platinum contact catalyst at 700°–900 °C.

The H_2S formed is passed into a bubbler containing 2% ammonium molybdate in 0.4 *N* sulfuric acid. The resulting blue-violet molybdenum complex is then determined colorimetrically with the aid of a Ziess Opton S57 filter. According to the amount of reagent used, 1–200 μg of SO_2 can be determined. Efficiency of removal of atmospheric SO_2 is higher than 90% at a sampling rate up to 5 liters per minute. If the quantity of air sampled contains more than 300 mg of water, it must be dried by passage through a preliminary drying tower containing phosphorus pentoxide. It was found that pressures up to 200 mm Hg and temperatures between 18° and 40 °C do not affect the collection efficiency. The method had a sensitivity of 0.01 ppm with a 40-liter air sample when the H_2S produced in the catalytic desorption process is absorbed in 10 ml of the ammonium molybdate reagent. The interference of SO_3 is eliminated by preceding the silica gel absorption equipment by a bubbler containing phosphoric acid.

The Stratmann method (*29*) suffers from interference by water vapor. The removal of this moisture may be accompanied by a loss of sulfur dioxide from the sample. In tests of this method for the Working Party on Atmospheric Pollution of the Organization for European Economic Cooperation by the United Kingdom delegation, on a routine basis in comparison with the West-Gaeke, hydrogen peroxide, and direct iodine methods at a city center site, it was found that the Stratmann method yielded erratic results (*30*). (Fair agreement was obtained between the West-Gaeke and hydrogen peroxide measurements. The direct iodine method showed a tendency to yield consistently high results, presumably because the iodine solution was not stabilized sufficiently to prevent the carry-over by the airstream of iodine from the solution.)

3. *Polarographic Method*

In the polarographic method (*27*), SO_2 in air is removed and concentrated by scrubbing through an absorbing solution, contained in a standard, all-glass, Greenburg-Smith impinger, consisting of 2% glycerol in 0.05 *N* sodium hydroxide at a rate of 24 liters/min for 30 minutes. Subsequently an acetate buffer (pH 4) is added, and the combined solution is deaerated by bubbling nitrogen through the sample contained in an air electrolysis vessel. The flow of nitrogen is then stopped, and a polarogram is made from −0.35 to −1.00 volt. A sensitivity of 0.006 μa/mm is used.

For a 30-minute air sample contained in 75 ml of absorbent, the sensitivity is 0.02 ppm. Smaller concentrations could be determined, depending largely on the ability to measure the inked lines on the polarogram.

Air samples can be determined with an accuracy of ±10% and a reproducibility of 3%.

According to Kolthoff and Miller (*31*) only one of the two tautomers of sulfurous acid is reducible at the dropping mercury electrode; and at pH 4, there is less of the reducible than of the nonreducible tautomer present. (The fuchsin-formaldehyde colorimetric determination involves a similar situation in that only one of the tautomers results in the formation of a red color. The same conditions of collection efficiency and reagent stability also apply, since the scrubbing media used in the methods are identical.)

Sulfur compounds generally do not interfere with the polarographic method. Cystine does not interfere with the analysis but reacts with the SO_2 while in the collecting medium. (The disulfide group is reduced to sulfhydryl by SO_2.) Nitrites are reduced at the dropping mercury electrode at a more negative potential than SO_2 and presumably would interfere only if present in very large concentration.

4. *Barium Chloranilate Method—Colorimetric*

This method (*32, 33*) is based on the reaction of solid barium chloranilate with sulfate ion at pH 4 in 50% ethyl alcohol to liberate highly colored acid-chloranilate ion. The concentration is determined spectrophotometrically with the absorption peak at 530 mμ. Atmospheric SO_2 is removed, concentrated, and oxidized to sulfate by scrubbing through 0.5% aqueous H_2O_2 solution. A buffer solution, 95% ethyl alcohol and 0.1 gm barium chloranilate, is added and the mixture is shaken for 10 minutes. The excess barium chloranilate and the precipitated barium sulfate are removed by filtration. The method has a sensitivity of 0.05 ppm with a 1000-liter air sample scrubbed through 25 ml of absorbing solution. Kanno (*32*) reported a collection efficiency of close to 100% at a sampling rate of 5 liters/min. The residual presence of H_2O_2 and CO_2 did not interfere with the colorimetric method. The accuracy and the effect of interfering materials were not reported. Phosphates, fluorides and chlorides are known to interfere in the chloranilate procedure, and a preliminary separation would be required. A method for the conversion of the gravimetric lead peroxide method to colorimetric with the use of barium chloranilate is also described by the author.

5. *Electrolytic Method—Potentiometric*

This method (*34–36*) involves the absorption of sulfur dioxide from a flow-controlled airstream in an acidified bromide solution. A continuous reaction is established between the absorbed SO_2 and bromine generated

electrically. A continuous, automatic analyzer (Titrilog) has been manufactured on this principle.

The apparatus consists of a sampling probe, flow control device, absorption-titration cell, current-generating electrodes, oxidation-reduction-sensing electrode system, amplifier, milliampere recorder, and gas pump. Air is drawn continuously through the titration cell at a fixed rate of approximately 1 liter/min. The zero level is automatically recorded periodically by passage of the air sample through a charcoal-soda lime filter. Sulfur dioxide in the measured airstream is absorbed in an acidified bromide solution contained in the titration cell. The instrument is initially adjusted to generate continuously a comparatively low level of bromine in the acid-bromide reagent. A pair of electrolyzing electrodes is used in which bromine is generated at one electrode and hydrogen is evolved in the second electrode. Any compound in the airstream that is oxidized by bromine will proportionately reduce the initially selected bromine concentration. This reduction in bromine concentration changes the oxidation-reduction potential of the reagent, which is immediately sensed by the appropriate sensor electrode system. This, in turn, electronically calls for generation of sufficient additional bromine to maintain the original bromine concentration. The electric current required to generate this additional bromine is a measure of the reducing gas in the atmosphere.

Oxidizable sulfur compounds other than SO_2 such as H_2S, mercaptans, organic sulfides, and disulfides are recorded by the analyzer. Some gases such as olefins, diolefins, and phenolic compounds would be titrated to a limited degree. The presence of these interferences would yield relatively high results for SO_2. Chlorine, bromine, chlorine dioxide, nitrogen dioxide, or ozone would reduce the bromine demand and would be manifested by comparatively low results for SO_2. It is possible to conduct a prior separation of an atmospheric mixture of sulfur-containing compounds before passing the sample into the analyzer (*37*). An automatic multiple-selector valve operating on a timed sequence can pass the air sample sequentially through various filters and scrubbers as follows:

1. Bismuth subcarbonate-H_2SO_4 solution to remove H_2S;
2. Potassium dichromate solution to remove H_2S and SO_2;
3. Alkaline $CdSO_4$ solution to remove H_2S, SO_2, and RSH;
4. Activated charcoal-soda lime to remove all reactive constituents.

The range of SO_2 detectable by the instrument is 0.1–10 ppm with a sensitivity of 0.1 ppm and a reproducibility of 0.2 ppm. A 90% response to a change in concentration is effected in 30 seconds.

Nader and Dolphin (*38*) have developed a circuit modification that increases instrument sensitivity by a factor of 10. This however, results in excessive background noise level and zero drift. McKee and Rollwitz (*39*) pursued a similar modification and increased instrument sensitivity to one scale division per 0.01 ppm SO_2; full-scale deflection corresponded to 0.75 ppm. A potentiometric recorder was substituted for the recording milliameter. The noise level was reduced to a satisfactory level by an electronic filter. Zero drift was still the greatest difficulty encountered, and occasionally no record was obtained when the zero point drifted off the scale.

6. *Lead Peroxide Candle Method*

The lead peroxide (PbO_2) method (*15, 16;* see also Chapter 16) of measuring the extent of atmospheric pollution by SO_2 was developed in England by the Department of Scientific and Industrial Research (DSIR) in 1932. The object was to provide an index of the activity of SO_2 in the atmosphere as a measure of its effect on fabrics, buildings and metals. The method is based on measuring the sulfation caused by gaseous SO_2 in ambient air by exposing PbO_2 paste. It is a cumulative method similar to the usual measurement of dustfall. The candle used in England consists of a porcelain cylinder about 10 cm in circumference. A 10 × 10-cm piece of cotton gauze is wrapped around the porcelain form as reinforcement and the active reagent is applied. The active reagent is applied in the form of a paste consisting of 8 gm of PbO_2 in about 5 ml of a gum tragacanth solution prepared by dissolving the gum in ethyl alcohol and diluting with distilled water. The candle is exposed in a shelter, which protects the reactive surface from rain, for a period of 1 month; shorter or longer exposure periods may be used, depending upon the SO_2 activity of the atmosphere. After exposure, the material is stripped from the candle with sodium carbonate, and the amount of sulfate is determined by the standard gravimetric procedure. The results are reported as milligrams of SO_3 per 100 cm^2 of PbO_2 per day.

Wilsdon and McConnell (*40*) indicated that the rate of sulfate formation is proportional to SO_2 concentration in the atmosphere, at least up to 15% conversion of the reactive material. From experiments in a wind tunnel, the rate of reaction was found to vary inversely as the fourth root of the wind velocity. An increase in temperature of 1 °C increased the reaction rate about 0.4%. The reaction rate also increased considerably when the surface was wet. Conversion to $PbSO_4$ was found to be a function of PbO_2 particle size. The authors noted a change in reaction rate with different batches of PbO_2. In the work done in England, a large batch of PbO_2 sufficient to last for several years was obtained. The re-

sults obtained by this method correlated very well with data secured by other methods (volumetric) when the results were corrected for wind velocity and temperature. These experiments were conducted at SO_2 concentrations (30–300 ppm) much larger than those in the atmosphere.

Parker and Richards (*41*) estimated that errors of sampling and analysis are about 10%. Eight PbO_2 cylinders were exposed simultaneously for a period of 6 months during 1948–1949. The mean rate of sulfation was 2.6 mg of SO_3 per 100 cm^2/day and the standard deviation of one observation was 7% of the mean.

Thomas and Davidson (*42*) employed PbO_2 cylinders to obtain relative sulfation values at selected sites in the vicinity of large, coal-burning steam plants. No deterioration in the rate of reactivity of PbO_2 with SO_2 was noted in periods of exposure as long as 4 months. A relatively low degree of correlation was obtained for sulfation rates and SO_2 dosage as measured by the Thomas Autometer. This was attributed principally to the typically low average SO_2 dosage at most sites near a single source. At the site of maximum exposure, the average SO_2 concentration was 0.02 ppm. Rather than compare field values with a sealed laboratory control, control cylinders were operated at remote sites 60–70 miles distant from a sulfur dioxide source. Sulfation rates varied from 0.02 to 0.04 mg of SO_3/100 cm^2/day. This value of about 0.03 mg of SO_3 per 100 cm^2/day is considered to be a realistic value for clean air, which is an order of magnitude greater than that established from sealed-source laboratory controls. The basic cylinder employed at Tennessee Valley Authority consists of an ordinary 8-ounce, short-form glass jar. Eight grams of PbO_2 paste are painted on a 100-cm^2 band of cotton gauze stapled around the glass jar. Freshly coated cylinders are dried overnight in a desiccator and screwed into the smaller of two concentric, brazed and soldered-metal jar tops. This assembly is screwed into a wide-mouthed, 32-ounce glass jar, which serves as a convenient carrier for shipment and storage. At the site of the field station, the inner small jar with PbO_2 coating is inverted and screwed into a jar top permanently mounted on the base of a louvered shelter. The shelter is mounted on a 4-foot post. Supports such as utility poles may be used.

A further modification of the original procedure, developed at the University of Florida is described in Chapter 16. Section IV,A.

Foran *et al.* (*43*) found that measurement of SO_2 activity by means of PbO_2 candles was well suited to measuring relative concentrations of SO_2 in conjunction with metal corrosion. Thus Severity of corrosion of zinc and stainless steel panels closely correlated with SO_2 dosage as measured by the PbO_2 candle method. Wilkins (*44*) compared

relative values of SO_2 concentrations determined by the H_2O_2 and the PbO_2 candle methods. A close correlation of sulfation rate with SO_2 concentration was obtained. The conversion factor from parts per million to sulfation rate was milligrams per 100 cm^2 per day $\times$ 0.04 = SO_2, ppm. It was found that the factor by which the PbO_2 reading must be multiplied to give the concentration of SO_2 varied from month to month at any given site and from site to site for any given month. Yearly means for each of seven sites in and around London were obtained by dividing the concentration of SO_2 in micrograms per cubic meter by the rate of sulfation of PbO_2 in milligrams SO_3 per 100 cm^2 per day by the H_2O_2 method. The yearly means of the sites varied from 63 to 172, with an average value of 112. These results show no simple connection between concentrations of SO_2 and PbO_2 readings. The author concluded that PbO_2 readings at any one site should not be used to give an indication of change in concentration from one month to another. Comparisons between one year and another are also not very precise, though they may be used in defining areas of gross pollution. Nevertheless, if trends over a number of years are considered, for example, by a comparison of one 5-year average with the next or of 5-year running averages, the variation due to wind, weather, etc., tends to become small and the measurement of SO_2 more precise; the 5-year average has long been recommended by the DSIR for this purpose.

In any district of limited size, for example, the area surrounding a particular source such as a power station, it is a reasonable assumption that the cylinders would be exposed to the same weather conditions—wind, humidity, temperature—so that the rate of sulfation should bear the same relation to concentrations of SO_2 for each. The pattern of concentration so obtained should, therefore, be valid, even though the absolute value for each month can be obtained only by comparison with data obtained from other SO_2 apparatus.

Hickey and Hendrickson (*45*) investigated some of the critical parameters of the lead dioxide exposure method. The behavior of the system in the region of the critical loading percentages for sulfur dioxide was determined as well as the effects of particle size of the lead dioxide, the presence of reduced sulfur compounds, and the use of different types of binders for the paste. It was found that a marked increase in gas absorptive capacity can be realized by using lead dioxide of particle size equal to or less than about 0.36 μ, or of a specific surface equal to or greater than about 9 m^2/gm. A definite relationship was found to exist between allowable exposure times and atmospheric concentrations of sulfur dioxide, with particle size as a major parameter.

III. Sulfuric Acid Mist

A. Mader, Hamming, and Bellin Method

Small amounts of sulfuric acid mist in the ambient atmosphere have been determined by Mader, Hamming, and Bellin (*46*) by filtration of the sample through specially washed Whatman No. 4 filter paper. The acid collected may be measured by titration with alkali or by turbidimetric or nephelometric techniques. There is no interference from sulfur dioxide in this method.

1. *Apparatus*

The apparatus consists of a holder in which the washed and dried filter paper can be clamped, with appropriate inlet and outlet connections to the sampling point, air metering device, and pump. Filter paper disks are prepared by leaching, with successive washings of distilled water, a number of Whatman filter papers, 18.5-cm in diameter, until soluble impurities have been removed. The washed filter papers are dried in an oven at 100 °C and a number of 1-inch disks are cut out by means of a sharp cutting tool. These disks are stored in a desiccator. Several disks, selected at random from each batch of filter paper are tested for pH by mascerating with 20 ml of carbon dioxide-free distilled water of known pH. The pH of this paper slurry should not deviate appreciably from that of the distilled water.

2. *Analytical Procedure*

For air analysis, two of the dry filter paper disks are placed in the holder and the air sample is drawn through the filters at a measured rate of about 1 cfm for 1 hour or more, with recording of the pressure drop through the filter, air temperature, and pressure. The filter disks then are removed and placed in a clean, dry jar.

The filter disks are analyzed by maceration in 20 ml of distilled water. The pH is measured with an accurate meter and the slurry is titrated with 0.002 *N* sodium hydroxide solution, using the pH meter for determination of the end point. This is considered to be the pH of carbon dioxide-free distilled water, corrected for filter paper batch acidity or alkalinity.

The titratable acidity may be expressed as parts per million sulfuric acid by volume, as follows:

$$H_2SO_4 \text{ ppm} = \frac{(\text{ml base} \times N \times 0.049 \times 22.41 \times 10^6)}{98 \times 28.32 \times \text{ft}^3 \text{ air sample at STP}} \qquad (4)$$

B. Commins Method (*47*)

Commins (*47*) has found the following method to be suitable for the determination of particulate acid in town air. The acid aerosol is collected by filtration through 1-inch circles of Whatman No. 1 filter paper at flow rates up to 30 liters/min over periods of 1–6 hours, depending upon the severity of the existing air pollution. The method of analysis involves titration of the filter papers to pH 7. A solution of bromothymol blue in de-ionized water is prepared by adding 4 ml of a 0.1% solution of the indicator in alcohol to 100 ml of de-ionized water. To this solution, sufficient 0.01 *N* sodium tetraborate is added to produce a stable apple-green color (approx. pH 7). The sample filter paper is cut into two exactly equal portions, one portion being added to 1–2 ml of this solution and titrated with the standard tetraborate to the original green color. A similar beaker containing the same volume of the solution is kept as a control. During titration, the solution is agitated by vigorous swirling and the end point is reached after about 5 minutes. This end point is shown by a stable green color identical to that of the control solution.

The amount of acid indicated by this procedure has to be corrected for water-insoluble bases present in the sample, since some of the acid will react with these bases. The true amount of acid is found by adding a known excess of 0.01 *N* sodium tetraborate (at least 0.1 ml more than the amount indicated above) to the 1–2 ml of pH 7 solution and then immersing the second portion of the filter paper in it and titrating the excess with 0.01 *N* sulfuric acid. The concentration of acid, calculated as sulfuric acid in micrograms per cubic meter of air, is as follows:

$$\mu g/m^3 = \frac{98{,}000 \times N \times ml}{V} \qquad (5)$$

N = normality of sodium tetraborate (0.01 *N*)
ml = equivalent volume in milliliters of tetraborate solution to neutralize acid during back titration of half the filter paper sample
V = volume of air sampled (m^3)

Acidic gases such as sulfur dioxide, nitrogen dioxide, and carbon dioxide do not interfere in this method of filtration of acid aerosol. Basic gases, such as ammonia, may interfere and should be removed prior to filtration of the sample, if present in appreciable concentration. Particulate acids such as hydrochloric, phosphoric, and nitric acid may be present in urban air and collected on filter paper. Usually however, the amounts of these acids in the atmosphere that can be collected from several cubic meters of air are extremely small. Interference by in-

soluble bases is overcome by use of the back titration procedure described above, since it allows the sodium tetraborate to neutralize the acid before the insoluble base can do so. Commins found only negligible amounts of soluble bases in his samples collected from the air in the city of London, England. His findings suggest that the predominant acid present in the air is sulfuric acid.

C. Sulfate Aerosol Measurement

In an investigation of the size distribution of sulfate aerosols in the ambient air of Cincinnati, Ohio and Chicago, Illinois, Roesler *et al.* (*48*), employed a cascade impactor of six stages of separation on stainless steel or glass plates followed by a filter stage (Andersen Sampler) to collect the samples. The sulfate was extracted from the plates with hot water. Portions of the filters were extracted by boiling with water under reflux for 30 minutes. The filtered solutions were analyzed by the turbidimetric barium sulfate technique in the manner previously described, employing powdered barium chloride in the presence of alcohol, glycerol, and hydrochloric acid. Low concentrations or smaller samples were analyzed by a nephelometric technique (*49*).

IV. Hydrogen Sulfide—Methylene Blue Method

Although a number of methods have been described for the determination of hydrogen sulfide, only the most sensitive procedure can be applied to ambient air analysis. This gas is usually present in the community atmosphere in the parts per hundred million or lower concentration range, rather than in the parts per million range. It can create an odor nuisance at 0.10 ppm or less. The best procedure for air pollution survey and control purposes is absorption in a solution of zinc acetate or some cadmium salt, with subsequent colorimetric estimation as methylene blue. This method has been studied by Budd and Bewick (*50*), applied to air analysis by the Los Angeles Air Pollution Control District (*51*) and reported by Jacobs *et al.* (*52*).

In this method the hydrogen sulfide is absorbed by passing the air sample through an absorption mixture of an alkaline suspension of cadmium hydroxide contained in a standard impinger at a sampling rate up to 1 cfm or in a midget impinger at 0.1 cfm. The sulfide ion is reacted with a mixture of *p*-aminodimethylaniline, ferric chloride, and chloride ion to yield methylene blue. The concentration of hydrogen sulfide is determined by measurement of the optical absorbance of the colored sample in comparison with that of standard solutions of hydrogen sulfide equivalent, by reference to a calibration curve. Spectrophotometric measurements are made at a wavelength of 670 mμ.

A. Reagents

Keep in refrigerated condition.

1. *Amine-Sulfuric Acid Stock Solution*

To 30 ml of distilled water add 50 ml of concentrated sulfuric acid. This mixture is cooled and mixed with addition of 12 gm of *N, N*-dimethyl-*p*-phenylenediamine until complete solution.

2. *Amine-Sulfuric Acid Test Solution*

Dilute 25 ml of above stock solution with 1:1 sulfuric acid to a total volume of 1 liter.

3. *Ferric Chloride Solution.*

Dissolve 100 gm of $FeCl_3 \cdot 6H_2O$ in distilled water to make up to 100 ml of solution.

4. *Absorption Mixture*

Dissolved 4.3 gm of cadmium sulfate, $Cd\ SO_4 \cdot 8H_2O$ in distilled water. Mix with a solution containing 0.3 gm sodium hydroxide in water and dilute to 1 liter. This mixture must be stirred well before using.

B. Analytical Procedure

After adding 50 ml of the absorption mixture in a standard impinger, the air sample is passed at a measured rate of about 1 cfm for 30 minutes or longer. Add 0.6 ml of amine-sulfuric acid test solution and 1 drop of ferric chloride solution to the impinger and shake after each addition. This mixture is transferred to a 50-ml volumetric flask, made up to volume, and allowed to stand for 30 minutes. A reference reagent blank is prepared by adding the above amounts of test reagent and ferric chloride solution to 45 ml of absorption mixture in a 50-ml volumetric flask, making up to volume, and allowing the mixture to stand for 30 minutes.

The spectrophotometer is set to zero optical absorbance with 25 ml of the reference blank at 670 mμ and the absorbance of 25 ml of the sample is then determined. By reference to a standard calibration curve, the concentration of hydrogen sulfide in the sample is measured.

C. Calibration

Calibration is carried out by adding 0, 1, 2, 3, 4 and 5 μg of hydrogen sulfide equivalent in the form of pure reagent to 20 ml of absorption mixtures contained in 25-ml flasks. After addition of 0.6 ml of test solution and 1 drop of ferric chloride solution, with stirring to each flask, the mixtures are diluted to 25 ml and allowed to stand for 30 minutes. The solution without hydrogen sulfide is used as a reference reagent blank for setting the spectrophotometer at zero absorbance at 670 mμ. Plot the optical absorbance against H_2S concentration in micrograms per 25 ml of sample.

D. Calculation

The results on the air sample may be calculated in parts per thousand million (billion), by volume, as follows:

$$H_2S\ (\text{ppb}) = \frac{\mu\text{g } H_2S \times 2 \times 719}{\text{vol. of air sample in liters at 25 °C and 760 mm}} \quad (6)$$

V. Nitrogen Dioxide and Nitric Oxide

These oxides are produced in varying amounts during the combustion of all types of fuels. Wohlers (*53*) has calculated emission of nitrogen oxides, in tons per day from various cities.

The most sensitive method for the determination of nitrogen dioxide in the atmosphere is based on the Griess-Ilosvay reaction by means of which a pink-colored dye complex is formed between sulfanilic acid, nitrite ion, and α-naphthylamine in an acid medium. Various modifications of this method have been proposed, but the one that is employed most widely is that introduced by Saltzman (*54*).

A. Nitrogen Dioxide—Saltzman Method

This method (*54, 55*) is sensitive over a range of from a few parts per billion (ppb) to about 5 ppm. The air sample is aspirated in fritted glass bubblers. The method is also applicable to the analysis of nitric oxide after it is oxidized to an equivalent amount of nitrogen dioxide by passage through a bubbler containing potassium permanganate solution (*55*). The presence of other gases in the sample causes only a slight interference.

1. *Reagents*

All reagents are made from analytical-grade chemicals in nitrite-free water, prepared, if necessary, by redistilling distilled water in an all-glass still after adding a crystal each of potassium permanganate and of barium hydroxide. They are stable for several months if kept well stoppered in brown bottles in the refrigerator. The absorbing reagent should be allowed to warm to room temperature before use.

a. N-(1-Naphthyl)-ethylenediamine Dihydrochloride, 0.1%. Dissolved 0.1 gm of the reagent in 100 ml of water. This is a stock solution.

b. Absorbing Reagent. Dissolve 5 gm of sulfanilic acid in almost a liter of water containing 140 ml of glacial acetic acid. Gentle heating is permissible, if desired, to speed up the process. To the cooled mixture, add 20 ml of the 0.1% stock solution of *N*-(1-naphthyl)-ethylenediamine dihydrochloride, and dilute to 1 liter. Avoid lengthy contact with air during both preparation and use, since this will result in discoloration of reagent because of absorption of nitrogen dioxide.

c. Standard Sodium Nitrite Solution, 0.0203 gm per liter. One milliliter of this working solution produces a color equivalent to that of 10 μl of nitrogen dioxide (10 ppm in 1 liter of air at 760 mm Hg and 25 °C). Prepare fresh just before use by dilution from a stronger stock solution containing 2.03 gm of the reagent grade granular solid (drying is unnecessary) per liter. The stock solution should be stable for 90 days.

d. Acid Permanganate Solution. Dissolve 2.5 gm of potassium permanganate in about 90 ml water, add 2.5 gm of concentrated sulfuric acid (or 5.2 ml of 1:3 H_2SO_4) and dilute to 100 ml with distilled water. Prepare at frequent intervals, since the keeping quality is not good; discard when an appreciable precipitate of brown manganese dioxide is noted.

2. *Apparatus*

a. Absorber. A special all-glass bubbler with a 60-μ maximum pore diameter frit is used.

b. Acid Permanganate Bubblers. A midget impinger with a nozzle about 1 mm in diameter and ground glass joints may be used. Accumulated deposits of manganese dioxide may be readily cleaned out by warming with a solution of hydroxylamine hydrochloride or oxalic acid.

c. Air Metering Device. A glass rotameter capable of accurately measuring a flow of 0.4 liter per minute is recommended.

d. Air Pump. An appropriate suction pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. It is desirable to have a tee connection at the intake. The inlet connected to

the sampling train should have an appropriate trap and needle valve (preferably of stainless steel). The second inlet should have a valve for bleeding in a large excess flow of clean air to prevent condensation of acetic acid vapors from the absorbing reagent, with consequent corrosion of the pump.

e. Spectrophotometer or Colorimeter. A laboratory instrument suitable for measuring the pink color at 550 mμ, with stoppered tubes or cuvettes, is recommended.

3. *Analytical Procedure*

a. Sampling Train. Assemble, in order, a fritted absorber, rotameter, and pump. Use ground-glass connections upstream from the absorber. Butt-to-butt glass connections with slightly greased Tygon or pure gum rubber tubing may also be used for connections without losses if lengths are kept minimal. Since the rotameter operates at an appreciable vacuum, make one dummy run to calibrate it against another rotameter or wet test meter installed upstream from the bubbler and operating at atmospheric pressure. If preferred, the sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no nitrogen dioxide is lost. In either case, for accurate measurements, the rotameter must be kept free from spray or dust.

b. Sampling Procedure. Pipet exactly 10 ml of absorbing reagent into the fritted bubbler. Draw an air sample through it at the rate of 0.4 liter (or less) per minute until sufficient color has developed (about 10 minutes). Note the total air volume sampled. If the sample air temperature and pressure deviate greatly from 25 °C and 760 mm Hg, measure and record the values.

c. Determination. After collection or absorption of the sample, a direct red-violet color appears. Color development is complete within 15 minutes at ordinary temperatures. Compare with standards visually or transfer to stoppered cuvettes and read in a spectrophotometer at 550 mμ, using unexposed reagent as a reference. Colors may be preserved, if well stoppered, with only 3–4% loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the nitrogen dioxide, the colors should be determined as soon as possible to minimize any loss.

4. *Calibration*

Add graduated amounts of standard sodium nitrite solution up to 1 ml (measured accurately in a graduated pipet or small buret) to a series of 25-ml volumetric flasks, and dilute to marks with absorbing reagent. Mix, allow 15 minutes for complete color development, and read the colors. Good results can be obtained with these small volumes of standard solution if they are carefully measured. If preferred, however, larger volumes may be used with correspondingly larger volumetric flasks. The 1-ml standard is equivalent to 4 μl of nitrogen dioxide per 10 ml of absorbing reagent.

Plot the absorbances of the standard colors (corrected for the blank) against the milliliters of standard solutions. Beer's law is followed. Draw the straight line giving the best fit and determine the slope (the value in milliliters of sodium nitrite intercepted at absorbance of exactly 1). This value multiplied by 4 gives the standardization factor, M, defined as the number of microliters of nitrogen dioxide required by 10 ml of absorbing reagent to give an absorbance of 1. For 2-cm cells the value was 3.65.

5. *Calculation*

Correct the volume of air sampled to standard temperature and pressure. Quantities of nitrogen dioxide may be expressed as microliters, sampled volume in liters times parts per million nitrogen dioxide. It has been determined empirically (*54*) that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide; hence, 2.03 μg of sodium nitrite is equivalent to 1 μl of nitrogen dioxide.

molar volume (760 mm Hg, 25 °C) = 24.47 liters.
molecular weight $NaNO_2 = 69.00$

hence:

$$1\ \mu l\ NO_2 = \frac{10^{-6}}{24.47}\ \text{moles}\ NO_2 = \frac{10^{-6}}{24.47} \times 0.72 \times 69 \qquad (7)$$

$$= 2.03 \times 10^{-6}\ \text{gm}\ NaNO_2$$

Results for samples are computed as follows:

$$NO_2\ \text{ppm} = \text{corrected absorbance} \times \frac{M}{V} \qquad (8)$$

If the volume of the air sample, V, is a simple multiple of M, calculations are simplified. Thus, for the M value of 3.65 previously cited, if exactly 3.65 liters of air are sampled through a bubbler, the corrected absorbance is also parts per million directly. If other volumes of absorbing reagent are used, V is taken as the volume of air sample per 10 ml of reagent.

B. Nitric Oxide—Concentrations of 10 ppm or Less

Assemble a sampling train composed of, in order, rotameter, fritted absorber, acid permanganate bubbler (with a nozzle rather than fritted inlet), fritted absorber, and pump. Pipet exactly 10 ml of absorbing reagent into each fritted absorber (first and third in the train). The second bubbler in the train should contain 10 ml of the acid permanganate solution (see above), which may be reused several times. Draw an air sample through at a rate of 0.04 liter per minute (or less) until sufficient color has developed (about 10 minutes). After allowing an additional 15 minutes for full color development, the solution from the third bubbler may be read in the spectrophotometer and the nitric oxide computed. Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. If a simultaneous determination of nitrogen dioxide is desired it may be obtained by reading the colored solution from the first bubbler in a similar manner.

C. Discussion of Procedures

1. *Frit Porosity*

The porosity of the fritted bubbler is important. An efficiency of 95% may be expected with a flow rate of 0.4 liter/min and a maximum pore diameter of 60 μ. Considerably lower efficiencies are obtained with coarser frits, but these may be utilized if the flow rate is reduced. Since quality control by some manufacturers is rather poor, it is desirable to measure the porosity of a new absorber experimentally as follows: Carefully clean the apparatus as described in Chapter 16, Section III,C,1, and rinse thoroughly with distilled water. Assemble the bubbler, add sufficient distilled water to cover the fritted portion, and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. The following equation is then used:

$$\text{maximum pore diameter } (\mu) = \frac{30\ s}{P} \qquad (9)$$

where s is the surface tension of water at the test temperature in dynes per cm (73 at 18 °C, 72 at 25 °C, and 71 at 31 °C), and P is the measured vacuum in mm of Hg.

2. *Nitrite Equivalent of Nitrogen Dioxide*

Standardization is based upon the empirical observation (*54*) that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide. Using sodium nitrite is much more convenient than preparing accurately known gas samples of standardizing.

3. *Efficiency of Nitric Oxide Conversion*

Conversion efficiency of nitric oxide to nitrogen dioxide by the permanganate bubbler may be commonly as low as 70%. This depends somewhat upon the quality of the permanganate solution and the design of the bubbler.

Conversion efficiencies of 95–100% have been reported (*56*) for an alternative method using a 17-mm outside diameter glass **U**-tube, containing one sheet of impregnated glass fiber paper cut into 1/4-inch strips, at a flow rate of 290 ml/min. (A stack of 25 sheets of 7-cm-diameter paper is impregnated with 25 ml of 2.5% $Na_2Cr_2O_7$, 2.5% H_2SO_4, and dried in a vacuum oven at 160 °F, or on a hot plate at 200 °F. Discard top and bottom sheets, store in closed bottle.) The useful life of the paper is limited, and it deteriorates rapidly when exposed to reagent vapors downstream from a bubbler. Hence a different sampling train, composed of rotameter, paper, fritted absorber, and pump, is used. The analysis yields the total of nitric oxide and nitrogen dioxide. A separate analysis of the latter gas must be made and deducted to give the concentration of nitric oxide.

4. *Effects of Interfering Gases*

A 5-fold ratio of ozone to nitrogen dioxide will cause a small interference, the maximal effect occurring in 3 hours. The reagent assumes a slightly orange tint.

A 10-fold ratio of sulfur dioxide produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1% acetone to the reagent before use retards the fading by forming a temporary addition product with sulfur dioxide. This permits reading within 4–5 hours (instead of the 45 minutes required without the acetone) without appreciable interferences.

The interferences from other nitrogen oxides and other gases that might be found in polluted air are negligible.

Thomas *et al.* (*55*) have devised an automatic apparatus for the continuous determination of nitric oxide and nitrogen dioxide in the atmosphere, employing a potassium permanganate solution for oxidation of the nitric oxide and the Saltzman reagent for colorimetric estimation.

Lyshkow (*57*) has modified the Griess-Saltzman reagent by the addition of R-salt as a promoter for more rapid color development and

by optimizing the concentrations of diazotizing and coupling agents. This improved and enhanced the response of a rapid-sensing, monitoring instrument for the colorimetric determination of nitrogen dioxide in air.

The composition of this absorbing reagent, per liter of deionized water is:

0.050 gm *N*-(1-naphthyl) ethylenediamine dihydrochloride
0.050 gm R-salt, (2-naphthol-3, 6-disulfonic acid, disodium salt)
1.50 gm sulfanilamide
1.50 gm tartaric acid
0.25 ml Kodak Photoflow (as a wetting agent)

In contrast to the Griess-Saltzman reagent which has an absorption efficiency of approximately 72% at a nitrogen dioxide level of 1 ppm, with air and reagent flow rates of 1 liter/min and 1 ml/min, respectively, the absorption efficiency of Lyshkow's modified reagent was found to be in excess of 90%.

VI. Ozone and Oxidants

The results of analyses for oxidant and ozone content of the atmosphere have been found to constitute an index of the degree of eye-irritating and plant-damaging pollution present in an oxidizing or photochemical type of smog atmosphere.

Two general methods have been recommended for the determination of oxidants (including ozone). One is based on the use of a neutral, buffered potassium iodide solution as absorbent for the air sample. Thorp (*58*) found that the sensitivity of the potassium iodide method could be increased by means of a buffer solution consisting of aluminum chloride and ammonium chloride. The second method involves the absorption of the sample in an alkaline solution of potassium iodide in which the interference due to sulfur dioxide is eliminated by treatment with hydrogen peroxide in accordance with the work of Smith and Diamond (*59*). Both of these methods have been studied and improved by Saltzman *et al.* (*60–62*). The following details of procedure are given in accordance with the recommendations of Saltzman.

A. Neutral Buffered Potassium Iodide Method

This method is intended for the manual determination of oxidants (including ozone) in the range of a few parts per hundred million to about 10 ppm. Ozone, chlorine, hydrogen peroxide, organic peroxides, and various other oxidants will liberate iodine by this method. A positive response of about 10% of the parts per million nitrogen dioxide occurs. It is customary for convenience to express the results as ozone. The advantages of this procedure over the alkaline iodide procedure are simplicity, accuracy, and precision. The analysis must, however, be completed during the period of 30 minutes to 1 hour after sampling. Sampling is conducted in midget impingers containing 1% potassium iodide in a neutral (pH 6.8) buffer composed of 0.1 *M* disodium hydrogen phosphate and 0.1 *M* potassium dihydrogen phosphate. Iodine is liberated in the absorbing reagent and measured in an appropriate instrument. Serious interfering effects occur from reducing gases and dusts.

1. *Reagents*

All reagents are made from analytical-grade chemicals. Traces of reducing impurities cause very serious errors.

a. Double-Distilled Water, Used for All Reagents. Distill water in an all-glass still, add a crystal each of potassium permanganate and barium hydroxide, and redistill.

b. Absorbing Reagent. Dissolve 13.61 gm of potassium dihydrogen phosphate, 14.20 gm of anhydrous disodium hydrogen phosphate (or 35.82 gm of dodecahydrate salt), and 10.00 gm of potassium iodide successively and dilute the mixture to exactly 1 liter. Age at room temperature for at least 1 day before using. This solution may be stored for several weeks in a glass-stoppered brown bottle in the refrigerator, or for shorter periods at room temperature. Do not expose to sunlight.

c. Standard Iodine Solution, 0.05 N. Dissolve successively 16.0 gm of potassium iodide and 3.173 gm of iodine; make to a volume of exactly 500 ml. Age for at least 1 day before using. Standardization is unnecessary if the weighing is carefully done, although, if desired, the solution may be standardized by titration with sodium thiosulfate using starch indicator.

2. *Apparatus*

a. Absorber. All-glass midget impingers with a graduation mark at 10 ml, are used. Other bubblers with nozzle or open-end inlet tubes may be used. Fritted bubblers tend to give comparatively low results. Impingers must be kept scrupulously clean and dust free. All traces of grease must be removed by treatment with dichromate-concentrated sulfuric acid solution followed by tap and distilled water.

b. Air Metering Device. A glass rotameter capable of measuring a flow of 1–2 liters per minute with an accuracy of ±2% is recommended.

c. Air Pump. An appropriate suction pump capable of drawing the

cyanide in the test solution is measured in a fluorometer. To a cuvette are added 1.0 ml portions of 0.5 *N* potassium hydroxide, the test solution, the glycine solution, the palladium chelate solution, and 1% solution of magnesium chloride hexahydrate. After standing 8 minutes, the intensity of fluorescence is measured. Hanker *et al.* (*76*) used a Klett No. 5970 fluorometer with a primary filter, Corning No. 5970, and secondary filters, Corning Nos. 4308 and 3389. The concentration of cyanide in the sample is determined by reference to a calibration curve prepared by measuring, as above, the fluorescence of known concentrations of standard potassium cyanide solutions. This method may detect as little as 0.02 μg of cyanide per milliliter of test solution.

Another method for the fluorometric determination of free hydrogen cyanide has been devised by Hanker, Gamson, and Klapper (*77*). This is based on the reaction of chloramine-T with cyanide to form cyanogen chloride. The latter substance can react with nicotinamide to yield a product which exhibits strong fluorescence in alkaline media. This method is also applicable to the direct determination of cyanide.

X. Ammonia and Ammonium Compounds

Ammonia is a common air contaminant resulting from the combustion of fuels, decay of vegetation and animal matter, and many chemical process operations. It reacts readily with acid gases, particularly sulfur oxides, to form ammonium salts. The concentration of these substances in the air may be determined readily by passage of the air sample through a standard impinger containing dilute sulfuric acid or boric acid, followed by reaction with Nessler's reagent and colorimetric estimation. Nessler's reagent consists of an alkaline solution of the double compound of mercuric iodide and potassium iodide ($HgI_2 \cdot 2KI$). Although direct Nesslerization of the sample solution may be performed, it is more accurate to carry out a distillation step by making the acid sample solution slightly alkaline and distilling off the ammonia from the sample into a receiver containing boric acid solution, prior to Nesslerization.

The referee distillation method described in ASTM, D1426-58 (*78*), is a suitable method for the determination of ammonia in the air sample after absorption in 50 ml of 0.005 *N* sulfuric acid in a standard impinger at a sampling rate of 1 cfm for 30 minutes. The sample solution is buffered at a pH of 7.4 to inhibit hydrolysis of organic nitrogen compounds, and distilled into a solution of boric acid (20 gm per liter). The ammonia may be determined colorimetrically after Nesslerization or with a spectrophotometer at 460 mμ. The concentration is determined by reference to a calibration curve or by color comparison with standards of ammonium chloride solutions containing microgram quantities of ammonia (1 ml = 0.01 mg nitrogen).

Korenman (*79*) has employed both α- and β-naphthylamine in a sensitive test for the detection of as little as 18 μg of ammonia in 1 liter of air. The test is carried out by impregnating a strip of filter paper with a solution prepared by diazotizing the naphthylamine with sodium nitrite and hydrochloric acid. The prepared paper is a pale greenish-yellow color but changes to a dark orange-brown color in the presence of air containing ammonia.

XI. Carbon Monoxide

The exhaust gas from motor vehicles constitutes the largest source of carbon monoxide in an urban area. Although much smaller percentages of carbon monoxide are found in the combustion products of fuels used for power, steam, and heating purposes, nevertheless significantly large quantities of carbon monoxide are also discharged from these sources in an urban area.

A number of methods for the analysis of carbon monoxide in air have been described in detail by Jacobs (*3*: Chapter 11, Section 1, Vol. 1). The classical iodine pentoxide method has been investigated by Teague (*80*), Katz *et al.* (*81*), and others (*82–84*). Katz and his co-workers (*85, 86*) have studied the oxidation of carbon monoxide over solid silver permanganate reagents. The coulometric determination of the iodine vapor liberated by the action of carbon monoxide on iodine pentoxide may be accomplished by measurement of the current generated in a suitable detector cell, according to Levaggi and Feldstein (*87*) and Hersch and Sambucetti (*88*). The application of gas chromatography to the separation of carbon monoxide in air from other substances, followed by reduction of this gas with hydrogen to methane and subsequent analysis of the methane produced with a flame ionization detector, has been studied by several investigators (*89, 90*). A simple detector tube consisting of purified silica gel impregnated with a solution of ammonium molybdate and palladium sulfate which yields a color reaction from faint green to blue in the presence of carbon monoxide was developed by Shepherd (*91*) during World War II. This method is only roughly quantitative. A convenient, modern method for the continuous monitoring of carbon monoxide in air is by use of a nondispersive infrared spectrometer.

XII. Carbon Dioxide

The average concentration of carbon dioxide in the uncontaminated lower atmosphere is now about 315 ppm. However, the concentration is subject to considerable local variations with values as high as 400 to more than 550 ppm being reported by Cholak in industrial and residential areas of cities (*92*). In a rural or agricultural area the concentration at breathing level may fluctuate with the time of day in the growing season, falling below 300 ppm during the period of daytime photosynthesis and rising to about 350 ppm at night during respiration.

It is relatively simple to determine carbon dioxide in the air since this gas is the most abundant atmospheric pollutant and other acid gases likely to cause interference are usually present in concentrations less than 1 ppm. An accurate titrimetric estimation may be made by absorption of the sample in a standard solution of barium hydroxide containing barium chloride and titration of the excess baryta with a standard acid solution, such as oxalic acid.

The air sample at a measured rate of 300–500 ml/min is passed through a fritted glass bubbler containing 25.0 ml of 0.01 *N* barium hydroxide and 25 ml of barium chloride (60 gm/liter) solution. The absorption efficiency of the solution can be raised to nearly 100% by the addition of a small amount of *n*-butyl alcohol (0.25–0.40%) to decrease the surface tension and the size of the air bubbles. It is essential that the absorption reagent be protected from contact with air at all times prior to sampling and during the titration step by bulbs containing ascarite. All distilled water used in preparation of reagents must be freshly boiled to expel dissolved carbon dioxide. After sampling has been completed, the absorber is connected to a source of purified nitrogen, and a stream of nitrogen is passed through the solution during titration of the excess barium hydroxide with 0.01 *N* oxalic acid solution.

The titration is carried out in the presence of 5 drops of a mixed indicator consisting of 1 gm of phenolphthalein and 0.5 gm thymolphthalein in 100 ml alcohol. One milliliter of 0.01 *N* alkali or acid is equivalent to 0.22 mg of carbon dioxide. To convert milligrams of carbon dioxide per liter of air at 25 °C and 760 mm Hg pressure to concentration in parts per million multiply by 556.

In the early 1930's, Thomas devised a continuous monitoring method for carbon dioxide in air (*93*), based on absorption of the air sample in 0.0052 *N* sodium hydroxide solution (containing 0.25–0.40% *n*-butyl alcohol) in a fritted glass bubbler equipped with platinum electrodes. The change in conductivity of the absorbent solution corresponding to the degree of conversion of the sodium hydroxide to carbonate was measured automatically and continuously by means of a recording Wheatstone bridge galvanometer. The method was calibrated by a standard titrimetric procedure. During continuous monitoring the absorbers were maintained at constant temperature by being mounted in a constant temperature bath.

The determination of carbon dioxide in air may also be carried out by means of a nondispersive infrared spectrometer or continuous analyzer, in a manner analogous to that described for carbon monoxide (*94*).

XIII. Continuous Analysis

Probably the earliest application of continuous analysis was made by Thomas *et al.* (*1, 2, 93*) and by M. Katz *et al.* (*95*) in studies of the occurrence of sulfur dioxide in smelter areas and of the effects of this gas on plants, including continuous measurements of carbon dioxide in air to evaluate the photosynthesis and respiration of fumigated vs. untreated plants. (See also Chapter 26.)

Today there are continuous analyzers available as manufactured items for the determination of all the common inorganic gaseous pollutants, including sulfur dioxide, hydrogen sulfide, and oxidizable sulfur compounds, volatile fluorides, nitric oxide and nitrogen dioxide, ozone and oxidants, carbon monoxide and carbon dioxide. Various analytical principles are employed in the determination of these gases, such as electrical conductivity, coulometric or potentiometric estimation, colorimetric or photometric analysis, infrared absorption and other properties as already described. These instruments may be equipped with automatic zero correction and calibration features of both chemical and electronic nature. Sampling and analysis may be programmed for any given time cycle to provide average and maximum concentration levels.

A description of available Technicon Autoanalyzers has been given by Zaleiko (*96*). These instruments utilize wet chemical procedures in a system involving gas absorption and colorimetric analysis. The following procedural steps may be incorporated into the system: (1) programmed sampling valves, (2) a digester or bath, (3) mixing coils or mechanical mixer, (4) proportioning pumps with precalibrated flexible tubes for delivery of liquid reagent, (5) controlled air flow, (6) dialyzer for separation of suspended solids by diffusion or by filtration through paper, (7) heating bath and distillation column (if necessary), (8) temperature control, (9) dual beam colorimeter with narrow band inter-

ference filters, strip chart recorder, automatic standardization and compensation controls. Among substances that may be measured in this type of system are sulfur dioxide by a modified West-Gaeke method, nitrogen dioxide and nitric oxide, oxidants, chlorine and chlorides, fluorides and cyanides.

Chemical reagent analyzers called Acralizers (Beckman Instruments) are also available in portable and stationary models for the continuous analysis of sulfur dioxide, nitric oxide, and nitrogen dioxide, and oxidants. Recording analyzers for oxides of nitrogen have been developed by Thomas *et al.* (*55*) and by Saltzman and Mendenhall (*97*).

The application of electrolytic titrimetry or the coulometric principle has been utilized by Regener (*98*) in the construction of an atmospheric ozone monitor (Mast Development Co.) based on the liberation of iodine from potassium iodide solution. The system contains a pair of production electrodes through which a regulated current flows to produce a very low, fixed concentration of iodine. A pair of sensing electrodes is employed to control the addition of sodium thiosulfate and to provide for accurate amperometric titration of the end point. The instrument contains two reaction chambers, each of which receives one-half the air sample. One part of the sample is passed through an oven at 300 °C to destroy ozone whereas the other half is unheated. The difference that develops in the production current is directly proportional to the ozone concentration. Other instruments employing the coulometric principle include the Titrilog, mentioned in Section II,G,5, for the measurement of sulfur dioxide, hydrogen sulfide, and other oxidizable sulfur compounds.

Several automated methods have been developed for the continuous monitoring of volatile fluorides. The principle of fluorescence quenching by fluoride has been utilized by Chaiken *et al.* (*99*) and developed more fully by Thomas and St. John (*100*), employing filter paper strips impregnated with a methyl alcohol solution of magnesium oxinate When the tape is illuminated with ultraviolet radiation of 3650 Å, the resultant visible fluorescence may be detected by a photocell. Gaseous fluoride in the air sample passing through this illuminated tape markedly reduces the fluorescence. The instrument may be employed to monitor fluoride in air in the range of 0.2 to more than 10 ppb.

Adams and Koppe (*101*) have developed a fluoride analyzer of the dosimeter type that consists of an automatic flow colorimeter with an air-reagent contacting cell containing a solution of a zirconium salt-Eriochrome Cyanine R. Semiautomated methods for the determination of fluoride in air and plant tissues have been described by Weinstein *et al.* (*102*).

XIV. Conclusion

Considerable progress has been made in recent years in the development of more sensitive reagents and procedures for the analysis of air pollutants in the microgram and nanogram concentration range. But the number of truly specific methods is still limited to only a few of the common contaminants. This emphasizes the need for evaluation of interferences, reproducibility and accuracy, among other factors, and for standardization of procedures. Ambient air quality objectives or standards for various pollutants are being adopted by various states within the United States and in other countries. Such standards imply that the concentration levels of each pollutant can be determined with the required degree of accuracy, according to a specified and tested procedure.

However, within the urban and industrial environment, pollutants occur as complex mixtures capable of interfering seriously with a particular method that has been insufficiently tested. There is an urgent need for collaborative testing of available methods by expert groups to determine their reliability and limitations. Valuable work is being done in this respect by Committee D-22 of the American Society for Testing and Materials and the Intersociety Committee on Manual of Methods for Ambient Air Sampling and Analysis (*103*).

Although the older gravimetric and titrimetric laboratory methods are being replaced by more sophisticated instrumental techniques, such as coulometry, spectrophotometry, and gas chromatography, simple, inexpensive but specific methods are still required for their calibration, for preliminary assessment of air pollution problems, and for laboratory and field applications.

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The development of analytical procedures for organic gases and vapors has progressed rapidly in recent years, stimulated by research showing the importance of organic substances as both reactants and products in photochemical air pollution (*1, 2*). Almost all of these methods are available only as laboratory techniques; very few have yet been adapted for monitoring instruments. Most of these procedures are based on colorimetric and gas chromatographic techniques. Before the development of gas chromatography, infrared spectrophotometry and mass spectrometry were applied to both atmospheric and emission analysis. More recently however, these methods have been used mainly in labo-

B. Planning the Study

Testing and monitoring require a considerable amount of planning of equipment and procedures for sampling and subsequent analysis of samples in the laboratory. Timing must also be planned both because the industrial processes involved frequently undergo cyclic changes and because actual sampling time is but a small fraction of the total time involved in assembling equipment, calibration, and travel. Such details as power supply, scaffolding, and access to the sampling source must be arranged for in advance.

The amount of sample required for suitable laboratory analysis dictates the sampling procedure to be employed. For example, in sampling ammonium chloride in a stack, a membrane filter may plug within a few seconds. Such a sample would be too light to weigh and insufficient for other laboratory procedures. Despite the wide range of equipment available, it sometimes appears ironic that what should be a simple stack-sampling procedure often requires a detailed literature search and the development of specialized sampling equipment. Complete familiarity with the process involved is therefore necessary before undertaking a source-sampling study. Operations directly related to the source should be carefully reviewed to determine the peculiarities of the processing equipment used, the time cycles involved, and the peak loading which might cause effluent and temperature variations. A review of this type can uncover a wide variety of significant process idiosyncrasies which, if not known, could completely invalidate results. Errors can result because peak loading periods were missed, an insufficient number of samples were taken, or temperature variations and composition changes were not accounted for, so that the results are not representative of the process. For example, for a few minutes in every hour the gas flow characteristics and the particulate loading may double in the electric furnace melting of brass scrap where scrap containing large amounts of oil is loaded into the furnace, thereby producing high stack gas temperatures and the emission of incompletely burned oil. Similarly, in both the gray iron cupola and the open hearth, stack loading varies, depending upon the charging, melting, and pouring cycle. The sampling procedure must account for these variations.

Gases are usually collected by absorption, adsorption, freeze-out, or grab sampling. Particulate material sampling is more difficult than gas sampling because of particle size, mass agglomeration, charge, and shape. A satisfactory sample is one which is representative of the flow pattern in the duct or stack, is free of contamination, and has undergone no chemical or physical change.

II. Source Testing Procedures

A. Measurement of Gas Flow Rate

The first step in source sampling is always the measurement of the rate of flow of gas or air through the duct, stack, roof monitor, window, or other cross section at which pollutant concentration is to be sampled. In particulate sampling, the approximate range of stack or duct velocity must be known before sampling starts, to enable the use of most isokinetic sampling procedures, i.e., sampling in which the flow of gas into the sampling device has the same velocity and direction as the ambient atmosphere being sampled. A wide variety of instruments for measuring air velocity are available for this purpose (*1–4*). The standard pitot tube combination with a differential pressure gage is the most widely used and most satisfactory velocity-measuring instrument. As shown in Fig. 1, the pitot tube consists of two concentric tubes, one serving to measure impact pressure, and the other to measure static pressure. Since both taps are connected across a differential manometer the pressure reading indicates velocity pressure. Velocity can be determined by referring to a velocity pressure table or by calculating with the use of the following:

$$V = 1096.5\sqrt{\frac{p_v}{S}}$$

$$= 4005\sqrt{p_v} \text{ for air at 70 °F and 29.92 inches Hg}$$

$$= 953\sqrt{p_v \cdot \frac{1}{G} \cdot \frac{T}{P}} \qquad (1)$$

where V = velocity, feet per minute at duct conditions
p_v = velocity pressure, inches of water
S = gas density at duct conditions, pounds per cubic foot
G = specific gravity of gas (air = 1)
T = absolute temperature of gas in duct, °R
P = absolute static pressure of gas in duct, inches Hg

Jamison *et al.* (*5*) describe an electrically controlled pneumatic system designed for purging the standard pitot tube when flow rate is being determined in a duct heavily loaded with liquid droplets and/or solids. A three-position manual switch actuates solenoid valves so that in the "read" position the pitot tube is connected to the manometer; in the "vent" position to the atmosphere; and in the "purge" position to a compressed air supply.

Figure 2 illustrates a type of double pitot tube which consists of two

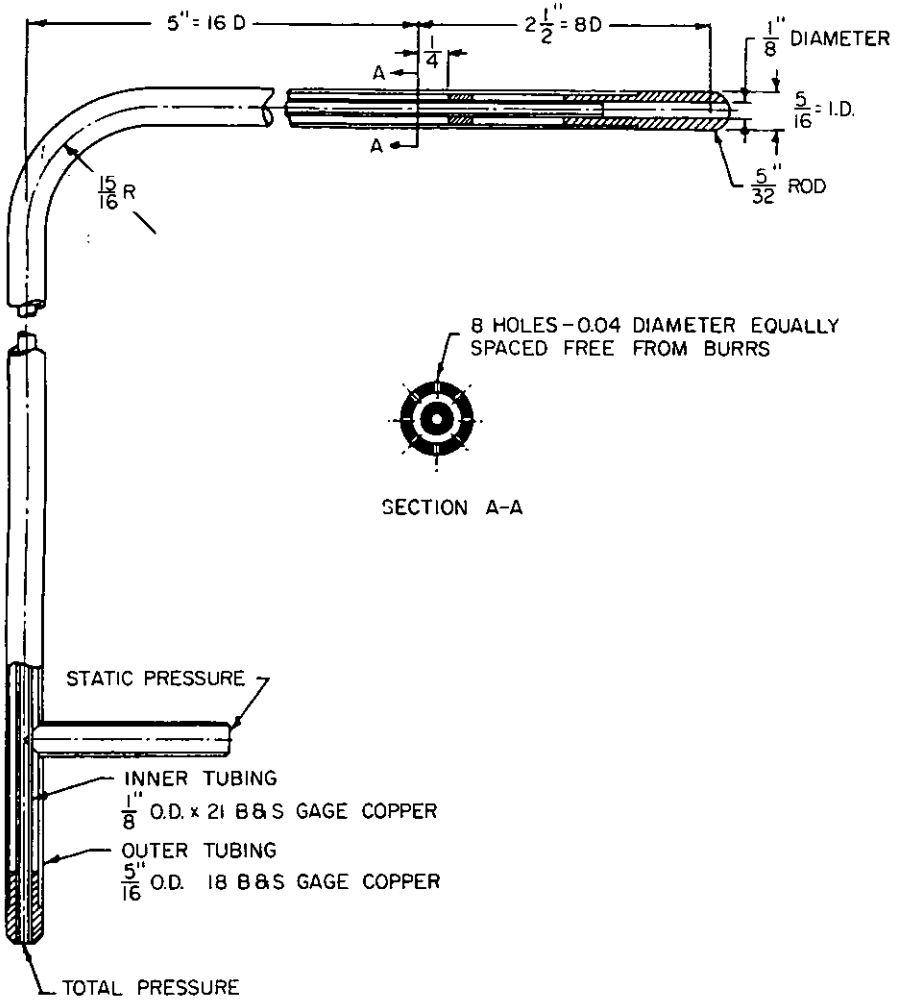

FIG. 1. Standard pitot tube. [From American Society of Heating, Refrigeration and Air Conditioning Engineers (*4*).]

opposing openings, one made to face upstream and the other facing downstream during velocity measurement. The instrument design serves to minimize the difficulties of plugging of the fine static pressure holes of the standard pitot tube when used in dirty gas streams and, by virtue of design, gives a higher manometer reading than the standard pitot tube. The main disadvantages are greater sensitivity to nonparallelism with flow and a variable calibration coefficient depending

upon flow conditions. It is necessary that double pitot tubes and similar, specially designed instruments be calibrated under flow conditions which are substantially similar to those at test locations.

The pitot tube traverse for determining the average gas velocity in a duct is made whenever possible at a section 5 to 10 diameters downstream from any major gas stream disturbance such as an elbow or branch entry, 3 to 5 diameters upstream from similar turbulent conditions, and in circular ducts should consist of two sets of readings, 90°

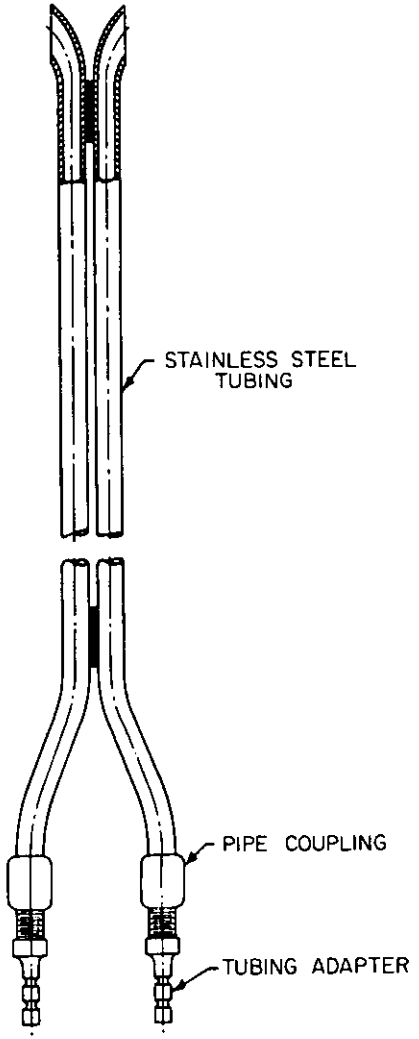

FIG. 2. Double pitot tube. [Courtesy Western Precipitation Corp., Los Angeles, Calif.]

apart. Each set of readings should be spaced so as to be at the center of annular rings of equal area in a circular duct, and at the centers of a minimum of nine hypothetical squares on at least three lines in a rectangular duct (Fig. 3). For approximate results in circular ducts, a center-line reading can be used provided the measurement location is preceded by at least 10 diameters of straight duct. It is necessary that the center-line velocity pressure be multiplied by 0.81 or the center-line velocity by 0.90 to obtain average duct velocity. Since accessible duct cross sections preceded by 7-1/2 diameters of duct are frequently not available (Fig. 4), it is generally necessary to select a measuring cross section which is a compromise between accessibility and aerodynamic conditions optimum for measurement. Further, since the ideal sampling location is often nonexistent, a series of pitot traverses are required to "feel out" the most suitable sampling location. Where necessary in excessively turbulent ducts, the number of pitot traverse points should be increased. Conditions of flow also serve to govern the number of sampling points and stack samples, to obtain representative results. Pitot traverse points are usually also used as sampling points. The differential manometer used with the pitot tube limits the minimum velocity measurement to about 800 ft/min (equivalent to about 0.04 inches of water). The Whalen gage (*6*) is more sensitive than the inclined manometer and can be used for measuring velocities as low as 200 ft/min. The gage utilizes two liquids of different specific gravities and is a null method instrument which must be carefully leveled and handled. Its delicate nature does not suit it to the usual field study.

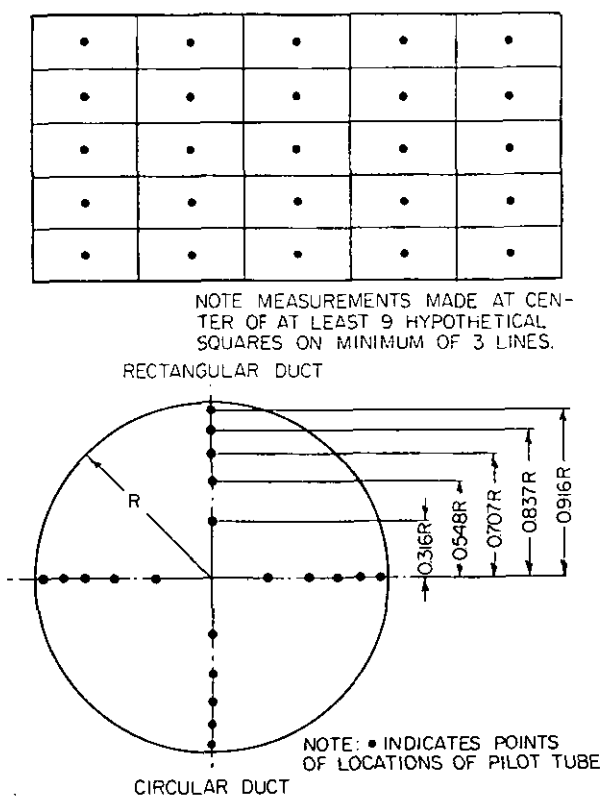

FIG. 3. Location of pitot traverse points.

FIG. 4. Ideal pitot traverse locations are seldom available.

Hama and Curley (*6a*) have described an electrical sensing manometer

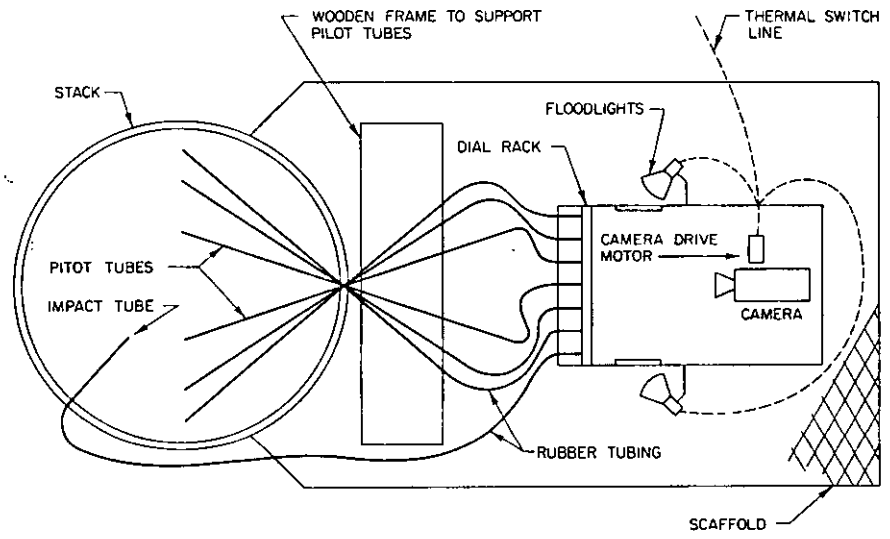

FIG. 5. Plan view of photo-pitot equipment positioned for measuring vent discharge. [Courtesy Air Pollution Control Assoc.]

which can be used with the standard pitot tube to measure velocities as low as 300 fpm. The instrument is essentially a vertical **U**-tube containing an electrolyte (water with a few grains of salt) and measurement is achieved through micrometer depth gages. A small battery is used as a source of current. It is necessary in use to isolate the instrument from vibrations and to maintain a constant liquid temperature.

Use of the pitot tube to evaluate intermittent nonsteady flow in a duct system is often difficult or impossible. Harding *et al.* (*7*) overcame this problem by devising a rack holding six pitot tubes at appropriate traverse point positions within the stack, thus obtaining an instantaneous traverse across the stack (Fig. 5). The pitot tubes were connected to dial-type differential pressure gages and a single-frame movie camera and floodlights were employed to photograph the dial array and a clock once every 20 seconds.

In using the pitot tube, it is important to recognize the fact that variations in temperature, pressure, and humidity affect density and, accordingly, enter into the determination of velocity pressure. The procedure for determining the flow rate of gas with a pitot tube traverse consists essentially of measuring the velocity pressure readings where required, converting them to equivalent velocities, averaging these velocity values (one does not average the velocity pressures) and, finally, multiplying average velocity by the cross-sectional area of the duct. This procedure will give the actual flow in cubic feet of gas per minute at the temperature, pressure, and humidity of the gas being measured.

Instruments such as the rotating vane anemometer, the swinging vane anemometer, the heated thermometer anemometer, and the thermal anemometer are also used for measuring velocity but are not well suited to stack-sampling procedures. They do find use in measuring gas flow through roof monitors, windows, and other building openings.

B. Collection of Samples from Stack

1. *Stack Sampling Equipment*

A series of stack sampling system components is illustrated in Fig. 6, which also indicates those points where temperature and pressure measurements are to be made. Depending upon stack conditions and the sampling system, relative humidity, where required, can be determined either by measuring dry and wet bulb temperature at the sampling location or by measuring the total condensate. As is apparent, relative humidity may significantly affect the gas density calculation and the flowmeter correction factor. Methods for determining relative humidity and specific gravity of gases are discussed in detail elsewhere (*3*, *4*). Figure 7 illustrates a procedure for measuring the dry and wet bulb temperatures of a gas at a temperature above 212 °F.

The stack-sampling components illustrated in Fig. 6 are indicative of the wide variety of sampling systems that can be used in a stack study, depending upon the source to be sampled, the contaminants involved, and the data desired. All incorporate combinations of probes to go into the stack and collection devices (Table I) for removing the contaminants being measured from the gas that is being sampled through the probe. Much of the probe equipment shown is not commercially available, so that this type of equipment must be constructed as needed. The major disadvantage in using probe type (a), in Fig. 6, is the length of pipe between the nozzle and the collecting device, in which material deposition can occur. Such probes are frequently jacketed and heated in order to prevent condensation. The error introduced by deposition of materials in the probe is eliminated with the use of nozzle assemblies (b) and (c), Fig 6, which are placed directly in the gas stream and which, by attaining gas stream temperature, also eliminate the condensation problem. One variation of nozzle assembly type (b), Fig. 6, is described by Dennis *et al.* (*8*) and is illustrated in detail in Fig. 8. Nozzle assembly type (c), Fig. 6, includes a miniature cyclone and, when required, a fabric filter system in series, all placed directly in the duct as shown. This arrangement has been developed by Hawksley *et al* (*9*). The assembly is shown in detail in Fig. 9.