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PART II

ENVIRONMENTAL PROTECTION AGENCY

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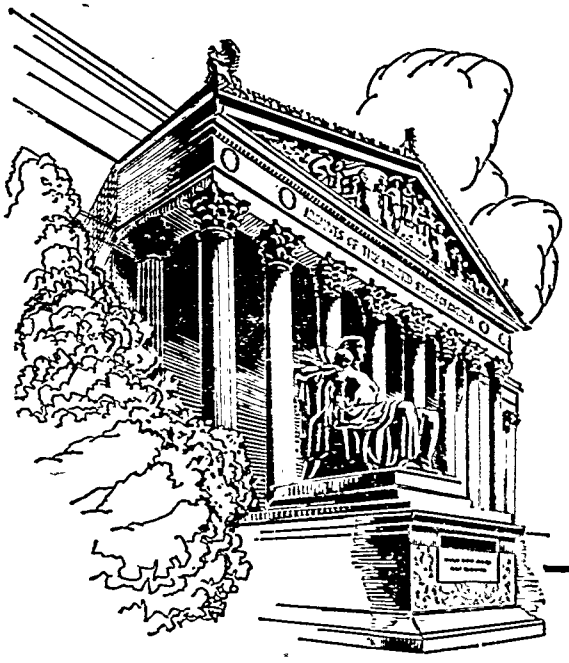
National Primary and Secondary Ambient Air Quality Standards



THE NATIONAL ARCHIVES OF THE UNITED STATES * 1934 *

Title 42—PUBLIC HEALTH

Chapter IV—Environmental Protection Agency

PART 410—NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS

Notices of proposed rule-making published in the FEDERAL REGISTER on January 30, 1971 (36 F.R. 1502) and March 26, 1971 (36 F.R. 5867) set forth regulations prescribing national primary and secondary ambient air quality standards proposed for adoption as Part 410 of 42 CFR. Interested persons were afforded an opportunity to participate in the rule-making by submitting comments. Following review of the proposed standards and consideration of the comments, the standards have been revised as described below and are being promulgated today.

National primary ambient air quality standards are those which, in the judgment of the Administrator, based on the air quality criteria and allowing an adequate margin of safety, are requisite to protect the public health.

National secondary ambient air quality standards are those which, in the judgment of the Administrator, based on the air quality criteria, are requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of air pollutants in the ambient air.

The comments submitted to the Environmental Protection Agency reflect divergences of opinion among interested and informed persons as to the proper interpretation of available data on the public health and welfare effects of the six pollutants for which national ambient air quality standards are being established. A number of comments question the feasibility of implementing the proposed standards. Because the Clean Air Act, as amended, does not permit any factors other than health to be taken into account in setting the primary standards, no revisions were made on this basis. In reviewing the proposed standards, the Environmental Protection Agency limited its consideration to comments concerning the validity of the scientific basis of the standards.

Current scientific knowledge of the health and welfare hazards of these air pollutants is imperfect. To increase and improve this knowledge, the Environmental Protection Agency will continue to conduct and support relevant research. At the same time, the need for increased knowledge of the health and welfare effects of air pollution cannot justify failure to take action based on knowledge presently available. The Clean Air Act, as amended, requires promulgation at this time of national standards for six air pollutants on the basis of available data set forth in air quality criteria documents. Thus, the Administrator is required to make judgments as to the proper interpretation of presently available data and to establish national primary standards which include an adequate margin of safety to protect human health. Where the validity of available research data has been questioned, but not wholly refuted, the Administrator has in each case promulgated a national primary standard which includes a margin of safety adequate to protect the public health from adverse effects suggested by the available data.

The national primary standard for carbon monoxide, proposed on January 30, 1971, was based on evidence that low levels of carboxyhemoglobin in human blood may be associated with impairment of ability to discriminate time intervals. This evidence is reflected in "Air Quality Criteria for Carbon Monoxide" (35 F.R. 4768). In the comments, serious questions were raised about the soundness of this evidence. Extensive consideration was given to this matter. The conclusions reached were that the evidence regarding impaired time-interval discrimination had not been refuted and that a less restrictive national standard for carbon monoxide would therefore not provide the margin of safety which may be needed to protect the health of persons especially sensitive to the effects of elevated carboxyhemoglobin levels. The only change made in the national standards for carbon monoxide was a modification of the 1-hour value. The revised standard affords protection from the same low levels of blood carboxyhemoglobin as a result of short-term exposure. The national standards for carbon monoxide, as set forth below, are intended to protect against the occurrence of carboxyhemoglobin levels above 2 percent. It is the Administrator's judgment that attainment of the national standards for carbon monoxide will provide an adequate safety margin for protection of public health and will protect against known and anticipated adverse effects on public welfare.

National standards for photochemical oxidants have also been revised. The revised national primary standard of 160 μg./m.^{3} (0.08 p.p.m.) is based on evidence of increased frequency of asthma attacks in some asthmatic subjects on days when estimated hourly average concentrations of photochemical oxidant reached 200 μg./m.^{3} (0.10 p.p.m.). A number of comments raised serious questions about the validity of data used to suggest impairment of athletic performance at lower oxidant concentrations. The revised primary standard includes a margin of safety which is substantially below the most likely threshold level suggested by this data. It is the Administrator's judgment that a primary standard of 160 μg./m.^{3} (0.08 p.p.m.) as a 1-hour average will provide an adequate safety margin for protection of public health and will protect against known and anticipated adverse effects on public welfare.

National standards for hydrocarbons have been revised to make these standards consistent with the above modifications of the national standard for photochemical oxidants. Hydrocarbons are a precursor of photochemical oxidants. The sole purpose of prescribing a hydrocarbon standard is to control photochemical oxidants. Accordingly, the above-described revisions of the national standards for photochemical oxidants necessitated a corresponding revision of the hydrocarbon standards.

National standards for nitrogen dioxide have been revised to eliminate the proposed 24-hour average value. No adverse effects on public health or welfare have been associated with short-term exposure to nitrogen dioxide at levels which have been observed to occur in the ambient air. Attainment of the annual average will, in the Administrator's judgment, provide an adequate safety margin for protection of public health and will protect against known and anticipated adverse effects on public welfare.

Appendices A through F, which describe measurement methods, have been revised to clarify many technical points. As revised, each appendix describes a complete reference method for evaluating the ambient concentration of a pollutant for which national ambient air quality standards are being established.

Nine months after the date of publication of this notice, the States are required to submit to the Administrator, in accordance with section 110 of the Act, implementation plans for the attainment and maintenance of the national primary and secondary standards specified in this part. Requirements for the preparation, adoption, and submittal of implementation plans were published by the Administrator, as proposed rule-making, in the FEDERAL REGISTER on April 7, 1971 (36 F.R. 6680).

In consideration of the foregoing and in accordance with the statements in the notice of proposed rule-making, the national primary and secondary ambient air quality standards, Part 410, are hereby promulgated effective upon publication.

Dated: April 28, 1971.

WILLIAM D. RUCKELSHAUS,
Administrator.

A new Part 410 is added to Chapter IV, Title 42, Code of Federal Regulations as follows:

Sec.

410.1 Definitions.
410.2 Scope.
410.3 Reference conditions.
410.4 National primary ambient air quality standards for sulfur oxides (sulfur dioxide).
410.5 National secondary ambient air quality standards for sulfur oxides (sulfur dioxide).
410.6 National primary ambient air quality standards for particulate matter.
410.7 National secondary ambient air quality standards for particulate matter.
410.8 National primary and secondary ambient air quality standards for carbon monoxide.
410.9 National primary and secondary ambient air quality standard for photochemical oxidants.
410.10 National primary and secondary ambient air quality standard for hydrocarbons.
410.11 National primary and secondary ambient air quality standard for nitrogen dioxide.

Appendix A—Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method).
Appendix B—Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method).
Appendix C—Reference Method for the Continuous Measurement of Carbon monoxide in the Atmosphere (Nondispersive Infrared Spectrometry).
Appendix D—Reference Method for the Measurement of Photochemical Oxidants Corrected for Interferences Due to Nitrogen Oxide and Sulfur Dioxide.
Appendix E—Reference Method for the Determination of Hydrocarbons Corrected for Methane.
Appendix F—Reference Method for the Determination of Nitrogen Dioxide (24-Hour Sampling Method).

AUTHORITY: The provisions of this Part 410 issued under sec. 4, Public Law 91-604, Stat. 1679.

§ 410.1 Definitions.

(a) As used in this part, all terms not defined herein shall have the meaning given them by the Act.

(b) "Act" means the Clean Air Act, as amended (Public Law-91-604; 84 Stat. 1676).

(c) "Agency" means the Environmental Protection Agency.

(d) "Administrator" means the Administrator of the Environmental Protection Agency.

(e) "Ambient air" means that portion of the atmosphere, external to buildings, to which the general public has access.

(f) "Reference method" means a method of sampling and analyzing for an air pollutant, as described in an appendix to this part.

(g) "Equivalent method" means any method of sampling and analyzing for an air pollutant which can be demonstrated to the Administrator's satisfaction to have a consistent relationship to the reference method.

§ 410.2 Scope.

(a) National primary and secondary ambient air quality standards under section 109 of the Act are set forth in this part.

(b) National primary ambient air quality standards define levels of air quality which the Administrator judges are necessary, with an adequate margin of safety, to protect the public health. National secondary ambient air quality standards define levels of air quality which the Administrator judges necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant. Such standards are subject to revision, and additional primary and secondary standards may be promulgated as the Administrator deems necessary to protect the public health and welfare.

(c) The promulgation of national primary and secondary ambient air quality standards shall not be considered in any manner to allow significant deterioration of existing air quality in any portion of any State.

(d) The proposal, promulgation, or revision of national primary and secondary ambient air quality standards shall not prohibit any State from establishing ambient air quality standards for that State or any portion thereof which are more stringent than the national standards.

§ 410.3 Reference conditions.

All measurements of air quality are corrected to a reference temperature of 25° C. and to a reference pressure of 760 millimeters of mercury (1,013.2 millibars).

§ 410.4 National primary ambient air quality standards for sulfur oxides (sulfur dioxide).

The national primary ambient air quality standards for sulfur oxides, measured as sulfur dioxide by the reference method described in Appendix A to this part, or by an equivalent method, are:

(a) 80 micrograms per cubic meter (0.03 p.p.m.)—annual arithmetic mean.

(b) 365 micrograms per cubic meter (0.14 p.p.m.)—Maximum 24-hour concentration not to be exceeded more than once per year.

§ 410.5 National secondary ambient air quality standards for sulfur oxides (sulfur dioxide).

The national secondary ambient air quality standards for sulfur oxides, measured as sulfur dioxide by the reference method described in Appendix A to this part, or by an equivalent method, are:

(a) 60 micrograms per cubic meter (0.02 p.p.m.)—annual arithmetic mean.

(b) 260 micrograms per cubic meter (0.1. p.p.m.)—maximum 24-hour concentration not to be exceeded more than once per year, as a guide to be used in assessing implementation plans to achieve the annual standard.

(c) 1,300 micrograms per cubic meter (0.5 p.p.m.)—maximum 3-hour concentration not to be exceeded more than once per year.

§ 410.6 National primary ambient air quality standards for particulate matter.

The national primary ambient air quality standards for particulate matter, measured by the reference method described in Appendix B to this part, or by an equivalent method, are:

(a) 75 micrograms per cubic meter—annual geometric mean.

(b) 260 micrograms per cubic meter—maximum 24-hour concentration not to be exceeded more than once per year.

§ 410.7 National secondary ambient air quality standards for particulate matter.

The national secondary ambient air quality standards for particulate matter, measured by the reference method described in Appendix B to this part, or by an equivalent method, are:

(a) 60 micrograms per cubic meter—annual geometric mean, as a guide to be used in assessing implementation plans to achieve the 24-hour standard.

(b) 150 micrograms per cubic meter—maximum 24-hour concentration not to be exceeded more than once per year.

§ 410.8 National primary and secondary ambient air quality standards for carbon monoxide.

The national primary and secondary ambient air quality standards for carbon monoxide, measured by the reference method described in Appendix C to this part, or by an equivalent method, are:

(a) 10 milligrams per cubic meter (9 p.p.m.)—maximum 8-hour concentration not to be exceeded more than once per year.

(b) 40 milligrams per cubic meter (35 p.p.m.)—maximum 1-hour concentration not to be exceeded more than once per year.

§ 410.9 National primary and secondary ambient air quality standards for photochemical oxidants.

The national primary and secondary ambient air quality standard for photochemical oxidants, measured and corrected for interferences due to nitrogen oxides and sulfur dioxide by the reference method described in Appendix D to this part, or by an equivalent method, is: 160 micrograms per cubic meter (0.08 p.p.m.)—maximum 1-hour concentration not to be exceeded more than once per year.

§ 410.10 National primary and secondary ambient air quality standard for hydrocarbons.

The hydrocarbons standard is for use as a guide in devising implementation plans to achieve oxidant standards.

The national primary and secondary ambient air quality standard for hydrocarbons, measured and corrected for methane by the reference method described in Appendix E to this part, or by an equivalent method, is: 160 micrograms per cubic meter (0.24 p.p.m.)—maximum 3-hour concentration (6 to 9 a.m.) not to be exceeded more than once per year.

§ 410.11 National primary and secondary ambient air quality standard for nitrogen dioxide.

The national primary and secondary ambient air quality standard for nitrogen dioxide, measured by the reference method described in Appendix F to this part, or by an equivalent method, is: 100 micrograms per cubic meter (0.05 p.p.m.)—annual arithmetic mean.

APPENDIX A.—REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1. *Principle and Applicability.* 1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachloromercurate (TCM). A dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air, is formed (*1, 2*). Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen). The complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid (*3*). The absorbance of the solution is measured spectrophotometrically.

1.2 The method is applicable to the measurement of sulfur dioxide in ambient air using sampling periods up to 24 hours.

2. *Range and Sensitivity.* 2.1 Concentrations of sulfur dioxide in the range of 25 to 1,050 $\mu g/m.^3$ (0.01 to 0.40 p.p.m.) can be measured under the conditions given. One can measure concentrations below 25 $\mu g./m.^3$ by sampling larger volumes of air, but only if the absorption efficiency of the particular system is first determined. Higher concentrations can be analyzed by using smaller gas samples, a larger collection volume, or a suitable aliquot of the collected sample. Beer's Law is followed through the working range from 0.03 to 1.0 absorbance units (0.8 to 27 $\mu g.$ of sulfite ion in 25 ml. final solution computed as SO_3).

2.2 The lower limit of detection of sulfur dioxide in 10 ml. TCM is 0.75 $\mu g_{.3}$ (based on twice the standard deviation) representing a concentration of 25 $\mu g./m.^3 SO_2$ (0.01 p.p.m.) in an air sample of 30 liters.

3. *Interferences.* 3.1 The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulfamic acid (*4, 5*), ozone by time-delay (*6*), and heavy metals by EDTA (ethylenediaminetetroacetic acid, disodium salt) and phosphoric acid (*4, 6,*). At least 60 $\mu g.$ Fe (III), 10 $\mu g.$ Mn(II), and 10 $\mu g.$ Cr(III) in 10 ml. absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 $\mu g.$ CU. (II) and 22 $\mu g.$ V(V).

4. *Precision, Accuracy, and Stability.* 4.1 Relative standard deviation at the 95 percent confidence level is 4.6 percent for the analytical procedure using standard samples. (*5*)

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

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *Absorber.* Absorbers normally used in air pollution sampling are acceptable for concentrations above 25 $\mu g./m.^3$ (0.01 p.p.m.). An all-glass midget impinger, as shown in Figure A1, is recommended for 30-minute and 1-hour samples.

For 24-hour sampling, assemble an absorber from the following parts:

Polypropylene 2-port tube closures, special manufacture (available from Bel-Art Products, Pequannock, N.J.).

Glass impingers, 6 mm. tubing, 6 inches long, one end drawn to small diameter such that No. 79 jewelers will pass through, but No. 78 jewelers will not. (Other end fire polished.)

Polypropylene tubes, 164 by 32 mm. Nalgene or equal).

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

5.1.3 *Air Flowmeter or Critical Orifice.* A calibrated rotameter or critical orifice capable of measuring air flow within ±2 percent. For 30-minute sampling, a 22-gauge hypodermic needle 1 inch long may be used as a critical orifice to give a flow of about 1 liter/minute. For 1-hour sampling, a 23-gauge hypodermic needle five-eighths of an inch long may be used as a critical orifice to give a flow of about 0.5 liter/minute. For 24-hour sampling, a 27-gauge hypodermic needle three-eighths of an inch long may be used to give a flow of about 0.2 liter/minute. Use a membrane filter to protect the needle (Figure A1a).

6.2 *Analysis.*

5.2.1 *Spectrophotometer.* Suitable for measurement of absorbance at 548 nm. with an effective spectral band width of less than 16 nm. Reagent blank problems may occur with spectrophotometers having greater spectral band width. The wavelength calibration of the instrument should be verified. If transmittance is measured, this can be converted to absorbance:

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

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Distilled water.* Must be free from oxidants.

6.1.2 *Absorbing Reagent [0.04 M Potassium Tetrachloromercurate (TCM)].* Dissolve 10.86 g. mercuric chloride, 0.066 g. EDTA (thylenediaminetetraacetic acid, disodoum salt), and 6.0 g. potassium chloride in water and bring to mark in a 1,000-ml. volumetric flask. (Caution: highly poisonous. If spilled on skin, flush off with water immediately). The pH of this reagent should be approximately 4.0, but it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3.(*7*) The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

5.2 *Analysis.*

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

6.2.2 *Formaldehyde (0.2 percent).* Dilute 5 ml. formaldehyde solution (36–38 percent) to 1,000 ml. with distilled water. Prepare daily.

6.2.3 *Stock Iodine Solution (0.1 N).* Place 12.7 g. iodine in a 250-ml. beaker; add 40 g. potassium iodide and 25 ml. water. Stir until all is dissolved, then dilute to 1,000 ml. with distilled water.

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

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

6.2.6 *Stock Sodium Thiosulfate Solution (0.1 N).* Prepare a stock solution by dissolving 25 g. sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1,000 ml. freshly boiled, cooled, distilled water and add 0.1 g. sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh, to the nearest 0.1 mg., 1.5 g. primary standard potassium iodate dried at 180° C. and dilute to volume in a 500-ml. volumetric flask. To a 500-ml. iodine flask, pipet 50 ml. of iodate solution. Add 2 g. potassium iodide and 10 ml. of 1 N hydrochloric acid. Stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml. starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution:

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

N=Normality of stock thiosulfate solution.

M=Volume of thiosulfate required, ml.

W=Weight of potassium iodate, grams.

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

6.2.7 *Sodium Thiosulfate Titrant (0.01 N).* Dilute 100 ml. of the stock thiosulfate solution to 1,000 ml. with freshly boiled distilled water.

Normality=Normality of stock solution ×0.100.

6.2.8 *Standardize Sulfite Solution for Preparation of Working Sulfite-TCM Solution.* Dissolve 0.3 g. sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g. sodium sulfite (Na_2SO_3) in 500 ml. of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 $\mu g./ml.$ of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 ml. of the 0.01 N iodine into each of two 500-ml. iodine flasks (A and B). To flask A (blank) add 25 ml. distilled water, and to flask B (sample) pipet 25 ml. sulfite solution. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulfite-TCM Solution (6.2.9) at the same time iodine solution is added to the flasks. By means of a buret containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml. starch solution and continue the titration until the blue color disappears.

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

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

A=Volume thiosulfate for blank, ml.

B=Volume thiosulfate for sample, ml.

N=Normality of thiosulfate titrant.

32,000=Milliequivalent wt. of SO_2, $\mu g.$

25=Volume standard sulfite solution, ml.

0.02=Dilution factor.

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

6.2.10 *Purified Pararosaniline Stock Solution (0.2 percent nominal).*

6.2.10.1 *Dye Specifications.* The pararosaniline dye must meet the following performance specifications: (1) the dye must have a wavelength of maximum absorbance at 540 nm. when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid; (2) the absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), should not exceed 0.170 absorbance unit at 22° C. with a 1-cm. optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye; (3) the calibration curve (Section 6.2.1) should have a slope of 0.030±0.002 absorbance units/$\mu g.$ SO_2 at this path length when the dye is pure and the sulfite solution is properly standardized.

6.2.10.2 *Preparation of Stock Solution.* A specially purified (99–100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco*). Alternatively, the dye may be purified, a stock solution prepared and then assayed according to the procedure of Scaringelli, et al. (*4*)

6.2.11 *Pararosaniline Reagent.* To a 250-ml. volumetric flask, add 20 ml. stock pararosaniline solution. Add an additional 0.3 ml. stock solution for each percent the stock

*Hartmen-Leddon, 60th and Woodland Avenue, Philadelphia, PA 19143.

assays below 100 percent. Then add 25 ml. 3 M phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7. *Procedure.*

7.1 *Sampling.* Procedures are described for short-term (30 minutes and 1 hour) and for long-term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the dynamic range.

7.1.1 *30-Minute and 1-Hour Samplings.* Insert a midget impinger into the sampling system, Figure A1. Add 10 ml. TCM solution to the impinger. Collect sample at 1 liter/minute for 30 minutes, or at 0.5 liter/minute for 1 hour, using either a rotameter, as shown in Figure A1, or a critical orifice, as shown in Figure A1a, to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Determine the volume of air sampled by multiplying the flow rate by the time in minutes and record the atmospheric pressure and temperature. Remove and stopper the impinger. If the sample must be stored for more than a day before analysis, keep it at 5° C. in a refrigerator (see 4.2).

7.1.2 *24-Hour Sampling.* Place 50 ml. TCM solution in a large absorber and collect the sample at 0.2 liter/minute for 24 hours from midnight to midnight. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Determine the total air volume by multiplying the air flow rate by the time in minutes. The correction of 24-hour measurements for temperature and pressure is extremely difficult and is not ordinarily done. However, the accuracy of the measurement will be improved if meaningful corrections can be applied. If storage is necessary, refrigerate at 5° C. (see 4.2).

7.2 *Analysis.*

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

7.2.1.1 *30-Minute and 1-Hour Samples.* Transfer the sample quantitatively to a 25-ml. volumetric flask; use about 5 ml. distilled water for rinsing. Delay analyses for 20 minutes to allow any ozone to decompose.

7.2.1.2 *24-Hour Sample.* Dilute the entire sample to 50 ml. with absorbing solution. Pipet 5 ml. of the sample into a 25-ml. volumetric flask for chemical analyses. Bring volume to 10 ml. with absorbing reagent. Delay analyses for 20 minutes to allow any ozone to decompose.

7.2.2 *Determination.* For each set of determinations prepare a reagent blank by adding 10 ml. unexposed TCM solution to a 25-ml. volumetric flask. Prepare a control solution by adding 2 ml. of working sulfite-TCM solution and 8 ml. TCM solution to a 25-ml. volumetric flask. To each flask containing either sample, control solution, or reagent blank, add 1 ml. 0.6 percent sulfamic acid and allow to react 10 minutes to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml. 0.2 percent formaldehyde solution, then 5 ml. pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 minutes and before 60 minutes, determine the absorbances of the sample (denote as A), reagent blank (denote as A_0) and the control solution at 548 nm. using 1-cm. optical path length cells. Use distilled water, not the reagent blank, as the reference. (NOTE! This is important because of the color sensitivity of the reagent blank to temperature changes which can be induced in the cell compartment of a spectrophotometer.) Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol after use. If the temperature of the determinations does not differ by more than 2° C. from the calibration temperature (8.2), the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve (8.2). If the reagent blank differs by more than 0.03 absorbance unit from that found in the calibration curve, prepare a new curve.

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

8. *Calibration and Efficiencies.*

8.1 *Flowmeters and Hypodermic Needle.* Calibrate flowmeters and hypodermic needle (3) against a calibrated wet test meter.

8.2 *Calibration Curves.*

8.2.1 *Procedure with Sulfite Solution.* Accurately pipet graduated amounts of the working sulfite-TCM solution (6.2.9) (such as 0, 0.5, 1, 2, 3, and 4 ml.) into a series of 25-ml. volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in 7.2.2. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within ±1° C. and in the range of 20° to 30° C. The temperature of calibration and the temperature of analysis must be within 2 degrees. Plot the absorbance against the total concentration in μg. SO_2 for the corresponding solution. The total μg. SO_2 in solution equals the concentration of the standard (Section 6.2.9) in μg. SO_2/ml. times the ml. sulfite solution added (μg. SO_2= μg./ml. SO_2×ml. added). A linear relationship should be obtained, and the y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal and denote as B_s. B_s is the calibration factor. (See Section 6.2.10.1 for specifications on the slope of the calibration curve). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 *Procedure with SO_2 Permeation Tubes.*

8.2.2.1 *General Considerations.* Atmospheres containing accurately known amounts of sulfur dioxide at levels of interest can be prepared using permeation tubes. In the systems for generating these atmospheres, the permeation tube emits SO_2 gas at a known, low, constant rate, provided the temperature of the tube is held constant (±0.1° C.) and provided the tube has been accurately calibrated at the temperature of use. The SO_2 gas permeating from the tube is carried by a low flow of inert gas to a mixing chamber where it is accurately diluted with SO_2-free air to the level of interest and the sample taken. These systems are shown schematically in Figures A2 and A3 and have been described in detail by O'Keeffe and Ortman (9), Scaringelli, Frey, and Saltzman (10), and Scaringelli, O'Keeffe, Rosenberg, and Bell (11).

8.2.2.2 *Preparation of Standard Atmospheres.* Permeation tubes may be prepared or purchased. Scaringelli, O'Keeffe, Rosenberg, and Bell (11) give detailed, explicit directions for permeation tube calibration. Tubes with a certified permeation rate are available from the National Bureau of Standards. Tube permeation rates from 0.2 to 0.4 μg./minute inert gas flows of about 50 ml./minute and dilution air flow rates from 1.1 to 15 liters/minutes conveniently give standard atmospheres containing desired levels of SO_2 (25 to 330 μg./m.³; 0.01 to 0.15 p.p.m. SO_2). The concentration of SO_2 in any standard atmosphere can be calculated as follows:

$$C=\frac{P\times 10^3}{R_d+R_i}$$

Where:

C = Concentration of SO_2, μg./m.³ at reference conditions.
P = Tube permeation rate, μg./minute.
R_d = Flow rate of dilution air, liter/minute at reference conditions.
R_i = Flow rate of inert gas, liter/minute at reference conditions.

8.2.2.3 *Sampling and Preparation of Calibration Curve.* Prepare a series (usually six) of standard atmospheres containing SO_2 levels from 25 to 330 μg. SO_2/m.³. Sample each atmosphere using similar apparatus and taking exactly the same air volume as will be done in atmospheric sampling. Determine absorbances as directed in 7.2. Plot the concentration of SO_2 in μg./m.³ (x-axis) against $A-A_0$ values (y-axis), draw the straight line of best fit and determine the slope. Alternatively, regression analysis by the method of least squares may be used to calculate the slope. Calculate the reciprocal of the slope and denote as B_s.

8.3 *Sampling Efficiency.* Collection efficiency is above 93 percent; efficiency may fall off, however, at concentrations below 25 μg./m.³. (12, 13)

9. *Calculations.*

9.1 *Conversion of Volume.* Convert the volume of air sampled to the volume at reference conditions of 25° C. and 760 mm. Hg. (On 24-hour samples, this may not be possible.)

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

V_s = Volume of air at 25° C. and 760 mm. Hg, liters.
V = Volume of air sampled, liters.
P = Barometric pressure, mm. Hg.
t = Temperature of air sample, °C.

9.2 *Sulfur Dioxide Concentration.*

9.2.1 When sulfite solutions are used to prepare calibration curves, compute the concentration of sulfur dioxide in the sample:

$$\mu g.\ SO_2/m.^3=\frac{(A-A_0)\ (10^3)\ (B_s)}{V_s}\times D$$

A = Sample absorbance.
A_0 = Reagent blank absorbance.
10^3 = Conversion of liters to cubic meters.
V_s = The sample corrected to 25° C. and 760 mm. Hg, liters.
B_s = Calibration factor, μg./absorbance unit.
D = Dilution factor.
For 30-minute and 1-hour samples, D=1.
For 24-hour samples, D=10.

9.2.2 When SO_2 gas standard atmospheres are used to prepare calibration curves, compute the sulfur dioxide in the sample by the following formula:

$$SO_2,\ \mu g./m.^3=(A-A_0)\times B_s$$

A = Sample absorbance.
A_0 = Reagent blank absorbance.
B_s = (See 8.2.2.3).

9.2.3 *Conversion of μg./m.³ to p.p.m.* = If desired, the concentration of sulfur dioxide

may be calculated as p.p.m. SO_2 at reference conditions as follows:

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

10. *References.*

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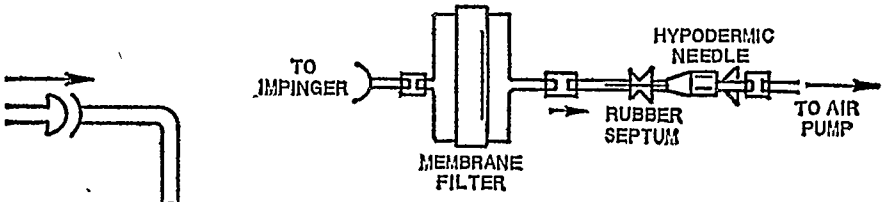

Figure A1a. Critical orifice flow control.

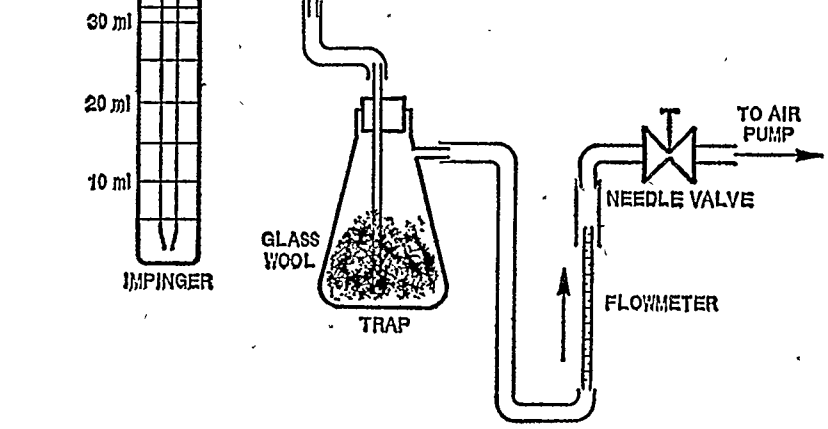

Figure A1. Sampling train.

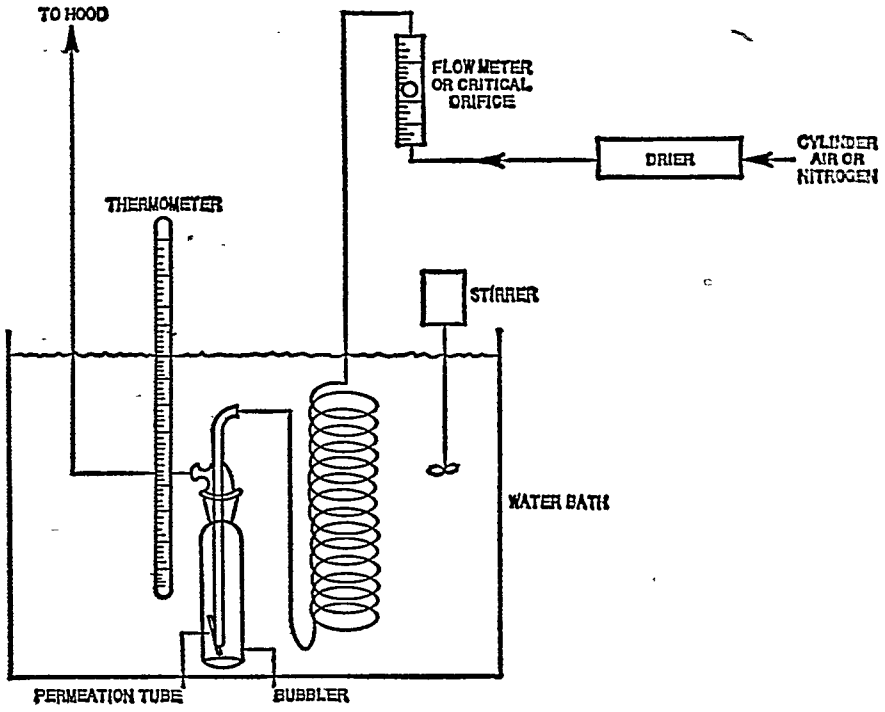

Figure A2. Apparatus for gravimetric calibration and field use.

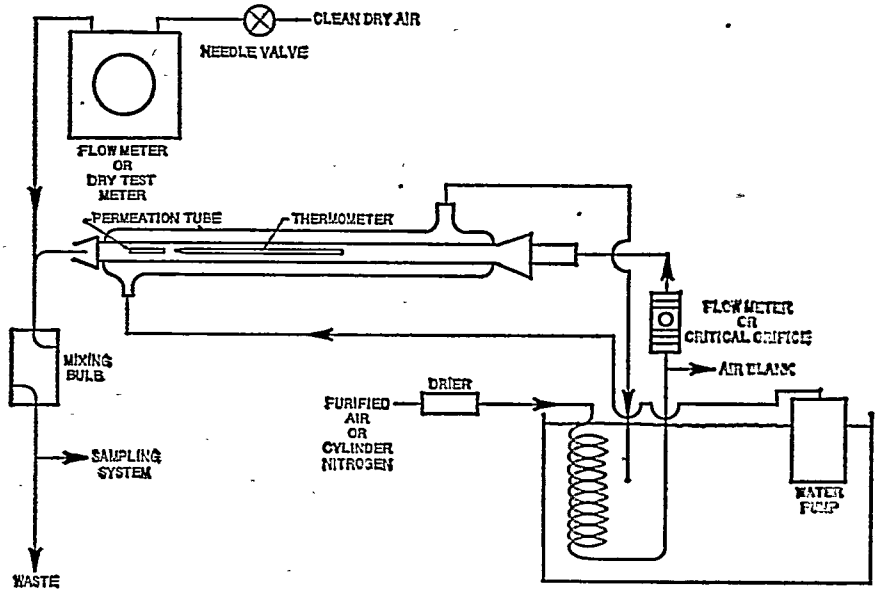

Figure A3. Permeation tube schematic for laboratory use.

APPENDIX B—REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE (HIGH VOLUME METHOD)

1. *Principle and Applicability.*

1.1 Air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.13 to 1.70 m.³/min.; 40 to 60 ft.³/min.) that allows suspended particles having diameters of less than 100 μm. (Stokes equivalent diameter) to pass to the filter surface. (*1*) Particles within the size range of 100 to 0.1μm. diameter are ordinarily collected on glass fiber filters. The mass concentration of suspended particulates in the ambient air (μg./m.³) is computed by measuring the mass of collected particulates and the volume of air sampled.

1.2 This method is applicable to measurement of the mass concentration of suspended particulates in ambient air. The size of the sample collected is usually adequate for other analyses.

2. *Range and Sensitivity.*

2.1 When the sampler is operated at an average flow rate of 1.70 m.³/min. (60 ft.³/min.) for 24 hours, an adequate sample will be obtained even in an atmosphere having concentrations of suspended particulates as low as 1 μg./m.³. If particulate levels are unusually high, a satisfactory sample may be obtained in 6 to 8 hours or less. For determination of average concentrations of suspended particulates in ambient air, a standard sampling period of 24 hours is recommended.

2.2 Weights are determined to the nearest milligram, airflow rates are determined to the nearest 0.03 m.³/min. (1.0 ft.³/min.), times are determined to the nearest 2 minutes, and mass concentrations are reported to the nearest microgram per cubic meter.

3. *Interferences.*

3.1 Particulate matter that is oily, such as photochemical smog or wood smoke, may block the filter and cause a rapid drop in airflow at a nonuniform rate. Dense fog or high humidity can cause the filter to become too wet and severely reduce the airflow through the filter.

3.2 Glass-fiber filters are comparatively insensitive to changes in relative humidity, but collected particulates can be hygroscopic. (*2*)

4. *Precision, Accuracy, and Stability.*

4.1 Based upon collaborative testing, the relative standard deviation (coefficient of variation) for single analyst variation (repeatability of the method) is 3.0 percent. The corresponding value for multilaboratory variation (reproducibility of the method) is 3.7 percent. (*3*)

4.2 The accuracy with which the sampler measures the true average concentration depends upon the constancy of the airflow rate through the sampler. The airflow rate is affected by the concentration and the nature of the dust in the atmosphere. Under these conditions the error in the measured average concentration may be in excess of ± 50 percent of the true average concentration, depending on the amount of reduction of airflow rate and on the variation of the mass concentration of dust with time during the 24-hour sampling period. (*4*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *Sampler.* The sampler consists of three units: (1) the faceplate and gasket, (2) the filter adapter assembly, and (3) the motor unit. Figure B1 shows an exploded view of these parts, their relationship to each other, and how they are assembled. The sampler must be capable of passing environmental air through a 406.5 cm.² (63 in.²) portion of a clean 20.3 by 25.4 cm. (8- by 10-in.) glass-fiber filter at a rate of at least 1.70 m.³/min. (60 ft.³/min.). The motor must be capable of continuous operation for 24-hour periods with input voltages ranging from 110 to 120 volts, 50–60 cycles alternating current and must have third-wire safety ground. The housing for the motor unit may be of any convenient construction so long as the unit remains airtight and leak-free. The life of the sampler motor can be extended by lowering the voltage by about 10 percent with a small "buck or boost" transformer between the sampler and power outlet.

5.1.2 *Sampler Shelter.* It is important that the sampler be properly installed in a suitable shelter. The shelter is subjected to extremes of temperature, humidity, and all types of air pollutants. For these reasons the materials of the shelter must be chosen carefully. Properly painted exterior plywood or heavy gauge aluminum serve well. The sampler must be mounted vertically in the shelter so that the glass-fiber filter is parallel with the ground. The shelter must be provided with a roof so that the filter is protected from precipitation and debris. The internal arrangement and configuration of a suitable shelter with a gable roof are shown in Figure B2. The clearance area between the main housing and the roof at its closest point should be 520.5±193.5 cm.² (80±30 in.²). The main housing should be rectangular, with dimensions of about 29 by 36 cm. (11½ by 14 in.).

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

5.1.4 *Orifice Calibration Unit.* Consisting of a metal tube 7.6 cm. (3 in.) ID and 15.9 cm. (6¼ in.) long with a static pressure tap 5.1 cm. (2 in.) from one end. See Figure B3. The tube end nearest the pressure tap is flanged to about 10.8 cm. (4¼ in.) OD with a male thread of the same size as the inlet end of the high-volume air sampler. A single metal plate 9.2 cm. (3⅝ in.) in diameter and 0.24 cm. (3/32 in.) thick with a central orifice 2.9 cm. (1⅛ in.) in diameter is held in place at the air inlet end with a female threaded ring. The other end of the tube is flanged to hold a loose female threaded coupling, which screws onto the inlet of the sampler. An 18-hole metal plate, an integral part of the unit, is positioned between the orifice and sampler to simulate the resistance of a clean glass-fiber filter. An orifice calibration unit is shown in Figure B3.

5.1.5 *Differential Manometer.* Capable of measuring to at least 40 cm. (16 in.) of water.

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

5.1.7 *Barometer.* Capable of measuring atmospheric pressure to the nearest mm.

5.2 *Analysis.*

5.2.1 *Filter Conditioning Environment.* Balance room or desiccator maintained at 15° to 35°C. and less than 50 percent relative humidity.

5.2.2 *Analytical Balance.* Equipped with a weighing chamber designed to handle unfolded 20.3 by 25.4 cm. (8- by 10-in.) filters and having a sensitivity of 0.1 mg.

5.2.3 *Light Source.* Frequently a table of the type used to view X-ray films.

5.2.4 *Numbering Device.* Capable of printing identification numbers on the filters.

6. *Reagents.*

6.1 *Filter Media.* Glass-fiber filters having a collection efficiency of at least 99 percent for particles of 0.3 μm. diameter, as measured by the DOP test, are suitable for the quantitative measurement of concentrations of suspended particulates, (5) although some other medium, such as paper, may be desirable for some analyses. If a more detailed analysis is contemplated, care must be exercised to use filters that contain low background concentrations of the pollutant being investigated. Careful quality control is required to determine background values of these pollutants.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Filter Preparation.* Expose each filter to the light source and inspect for pinholes, particles, or other imperfections. Filters with visible imperfections should not be used. A small brush is useful for removing particles. Equilibrate the filters in the filter conditioning environment for 24 hours. Weigh the filters to the nearest milligram; record tare weight and filter identification number. Do not bend or fold the filter before collection of the sample.

7.1.2 *Sample Collection.* Open the shelter, loosen the wing nuts, and remove the faceplate from the filter holder. Install a numbered, preweighed, glass-fiber filter in position (rough side up), replace the faceplate without disturbing the filter, and fasten securely. Undertightening will allow air leakage, overtightening will damage the sponge-rubber faceplate gasket. A very light application of talcum powder may be used on the sponge-rubber faceplate gasket to prevent the filter from sticking. During inclement weather the sampler may be removed to a protected area for filter change. Close the roof of the shelter, run the sampler for about 5 minutes, connect the rotameter to the nipple on the back of the sampler, and read the rotameter ball with rotameter in a vertical position. Estimate to the nearest whole number. If the ball is fluctuating rapidly, tip the rotameter and slowly straighten it until the ball gives a constant reading. Disconnect the rotameter from the nipple; record the initial rotameter reading and the starting time and date on the filter folder. (The rotameter should never be connected to the sampler except when the flow is being measured.) Sample for 24 hours from midnight to midnight and take a final rotameter reading. Record the final rotameter reading and ending time and date on the filter folder. Remove the faceplate as described above and carefully remove the filter from the holder, touching only the outer edges. Fold the filter lengthwise so that only surfaces with collected particulates are in contact, and place in a manila folder. Record on the folder the filter number, location, and any other factors, such as meteorological conditions or razing of nearby buildings, that might affect the results. If the sample is defective, void it at this time. In order to obtain a valid sample, the high-volume sampler must be operated with the same rotameter and tubing that were used during its calibration.

7.2 *Analysis.* Equilibrate the exposed filters for 24 hours in the filter conditioning environment, then reweigh. After they are weighed, the filters may be saved for detailed chemical analysis.

7.3 *Maintenance.*

7.3.1 *Sampler Motor.* Replace brushes before they are worn to the point where motor damage can occur.

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

7.3.3 *Rotameter.* Clean as required, using alcohol.

8. *Calibration.*

8.1 *Purpose.* Since only a small portion of the total air sampled passes through the rotameter during measurement, the rotameter must be calibrated against actual airflow with the orifice calibration unit. Before the orifice calibration unit can be used to calibrate the rotameter, the orifice calibration unit itself must be calibrated against the positive displacement primary standard.

8.1.1 *Orifice Calibration Unit.* Attach the orifice calibration unit to the intake end of the positive displacement primary standard and attach a high-volume motor blower unit to the exhaust end of the primary standard. Connect one end of a differential manometer to the differential pressure tap of the orifice calibration unit and leave the other end open to the atmosphere. Operate the high-volume motor blower unit so that a series of different, but constant, airflows (usually six) are obtained for definite time periods. Record the reading on the differential manometer at each airflow. The different constant airflows are obtained by placing a series of loadplates, one at a time, between the calibration unit and the primary standard. Placing the orifice before the inlet reduces the pressure at the inlet of the primary standard below atmospheric; therefore, a correction must be made for the increase in volume caused by this decreased inlet pressure. Attach one end of a second differential manometer to an inlet pressure tap of the primary standard and leave the other open to the atmosphere. During each of the constant airflow measurements made above, measure the true inlet pressure of the primary standard with this second differential manometer. Measure atmospheric pressure and temperature. Correct the measured air volume to true air volume as directed in 9.1.1, then obtain true airflow rate, Q, as directed in 9.1.3. Plot the differential manometer readings of the orifice unit versus Q.

8.1.2 *High-Volume Sampler.* Assemble a high-volume sampler with a clean filter in place and run for at least 5 minutes. Attach a rotameter, read the ball, adjust so that the ball reads 65, and seal the adjusting mechanism so that it cannot be changed easily. Shut off motor, remove the filter, and attach the orifice calibration unit in its place. Operate the high-volume sampler at a series of different, but constant, airflows (usually six). Record the reading of the differential manometer on the orifice calibration unit, and record the readings of the rotameter at each flow. Measure atmospheric pressure and temperature. Convert the differential manometer reading to m.³/min., Q, then plot rotameter reading versus Q.

8.1.3 *Correction for Differences in Pressure or Temperature.* See Addendum B.

9. *Calculations.*

9.1 *Calibration of Orifice.*

9.1.1 *True Air Volume.* Calculate the air volume measured by the positive displacement primary standard.

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

V_a = True air volume at atmospheric pressure, m.³
P_a = Barometric pressure, mm. Hg.
P_m = Pressure drop at inlet of primary standard, mm. Hg.
V_M = Volume measured by primary standard, m.³

9.1.2 *Conversion Factors.*
Inches Hg. × 25.4 = mm. Hg.
Inches water × 73.48 × 10^{-3} = inches Hg.
Cubic feet air × 0.0284 = cubic meters air.

9.1.3 *True Airflow Rate.*

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

Q = Flow rate, m.³/min.
T = Time of flow, min.

9.2 *Sample Volume.*

9.2.1 *Volume Conversion.* Convert the initial and final rotameter readings to true airflow rate, Q, using calibration curve of 8.1.2.

9.2.2 *Calculate volume of air sampled*

$$V = \frac{Q_1 Q_f}{2} \times T$$

V = Air volume sampled, m.³
Q_1 = Initial airflow rate, m.³/min.
Q_f = Final airflow rate, m.³/min.
T = Sampling time, min.

9.3 *Calculate mass concentration of suspended particulates*

$$S.P. = \frac{(W_f - W_i) \times 10^9}{V}$$

S.P. = Mass concentration of suspended particulates, μg/m.³
W_i = Initial weight of filter, g.
W_f = Final weight of filter, g.
V = Air volume sampled, m.³
10^9 = Conversion of g. to μg.

10. *References.*

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

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

(3) Unpublished data based on a collaborative test involving 12 participants, conducted under the direction of the Methods Standardization Services Section of the National Air Pollution Control Administration, October, 1970.

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

(5) Pate, J. B., and Tabor, E. C., "Analytical Aspects of the Use of Glass-Fiber Filters for the Collection and Analysis of Atmospheric Particulate Matter", *Am. Ind. Hyg. Assoc. J. 23*, 144–150 (1962).

ADDENDA

A. *Alternative Equipment.*

A modification of the high-volume sampler incorporating a method for recording the actual airflow over the entire sampling period has been described, and is acceptable for measuring the concentration of suspended particulates (Henderson, J. S., Eighth Conference on Methods in Air Pollution and Industrial Hygiene Studies, 1967, Oakland, Calif.). This modification consists of an exhaust orifice meter assembly connected through a transducer to a system for continuously recording airflow on a circular chart. The volume of air sampled is calculated by the following equation:

$$V = Q \times T.$$

Q=Average sampling rate, m^3/min.
T=Sampling time, minutes.

The average sampling rate, Q, is determined from the recorder chart by estimation if the flow rate does not vary more than 0.11 m^3/min. (4 ft^3/min.) during the sampling period. If the flow rate does vary more than 0.11 m^3 (4 ft^3/min.) during the sampling period, read the flow rate from the chart at 2-hour intervals and take the average.

B. *Pressure and Temperature Corrections.*

If the pressure or temperature during high-volume sampler calibration is substantially different from the pressure or temperature during orifice calibration, a correction of the flow rate, Q, may be required. If the pressures differ by no more than 15 percent and the temperatures differ by no more than 100 percent (°C), the error in the uncorrected flow rate will be no more than 15 percent. If necessary, obtain the corrected flow rate as directed below. This correction applies only to orifice meters having a constant orifice coefficient. The coefficient for the calibrating orifice described in 5.1.4 has been shown experimentally to be constant over the normal operating range of the high-volume sampler (0.6 to 2.2 m^3/min.; 20 to 78 ft^3/min.). Calculate corrected flow rate:

$$Q_2 = Q_1\left[\frac{T_2 P_1}{T_1 P_2}\right]^{1/2}$$

Q_2=Corrected flow rate, m^3/min.
Q_1=Flow rate during high-volume sampler calibration (Section 8.1.2), m^3/min.
T_1=Absolute temperature during orifice unit calibration (Section 8.1.1), °K or °R.
P_1=Barometric pressure during orifice unit calibration (Section 8.1.1), mm. Hg.
T_2=Absolute temperature during high-volume sampler calibration (Section 8.1.2), °K or °R.
P_2=Barometric pressure during high-volume sampler calibration (Section 8.1.2), mm. Hg.

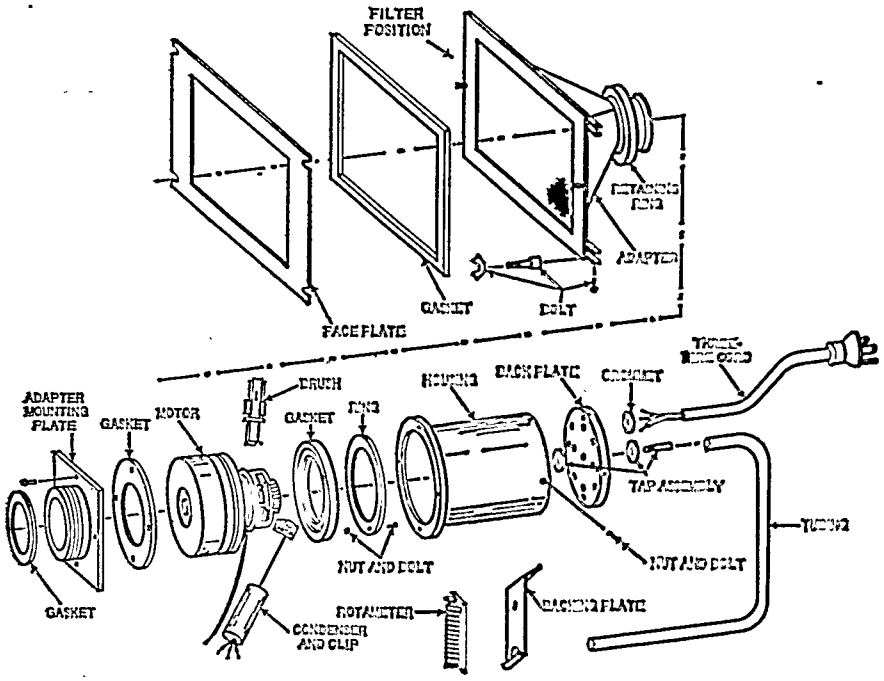

Figure B1. Exploded view of typical high-volume air sampler parts.

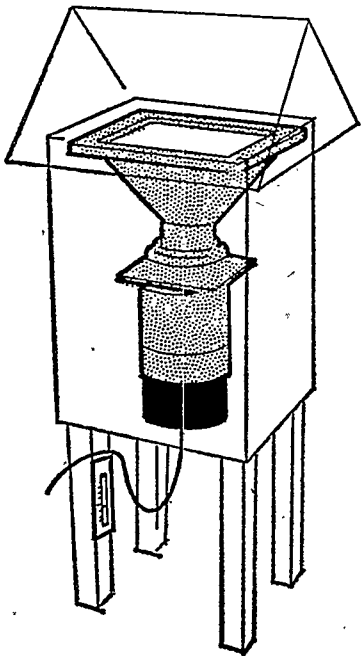

Figure B2. Assembled sampler and shelter.

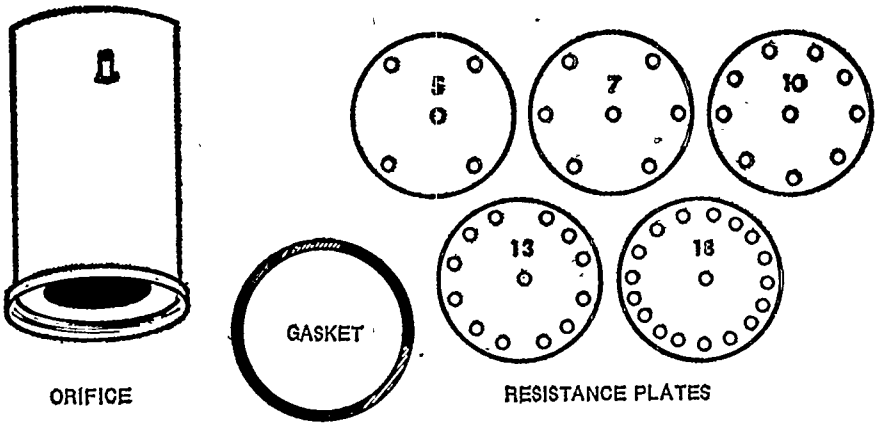

Figure B3. Orifice calibration unit.

APPENDIX C—REFERENCE METHOD FOR THE CONTINUOUS MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED SPECTROMETRY)

1. *Principle and Applicability.*

1.1 This method is based on the absorption of infrared radiation by carbon monoxide. Energy from a source emitting radiation in the infrared region is split into parallel beams and directed through reference and sample cells. Both beams pass into matched cells, each containing a selective detector and CO. The CO in the cells absorb infrared radiation only at its characteristic frequencies and the detector is sensitive to those frequencies. With a nonabsorbing gas in the reference cell, and with no CO in the sample cell, the signals from both detectors are balanced electronically. Any CO introduced into the sample cell will absorb radiation, which reduces the temperature and pressure in the detector cell and displaces a diaphram. This displacement is detected electronically and amplified to provide an output signal.

1.2 This method is applicable to the determination of carbon monoxide in ambient air, and to the analysis of gases under pressure.

2. *Range and Sensitivity.*

2.1 Instruments are available that measure in the range of 0 to 58 mg./m.³ (0–50 p.p.m.), which is the range most commonly used for urban atmospheric sampling. Most instruments measure in additional ranges.

2.2 Sensitivity is 1 percent of full-scale response per 0.6 mg. CO/m.³ (0.5 p.p.m.).

3. *Interferences.*

3.1 Interferences vary between individual instruments. The effect of carbon dioxide interference at normal concentrations is minimal. The primary interference is water vapor, and with no correction may give an interference equivalent to as high as 12 mg. CO/m.³ Water vapor interference can be minimized by (a) passing the air sample through silica gel or similar drying agents, (b) maintaining constant humidity in the sample and calibration gases by refrigeration, (c) saturating the air sample and calibration gases to maintain constant humidity or (d) using narrowband optical filters in combination with some of these measures.

3.2 Hydrocarbons at ambient levels do not ordinarily interfere.

4. *Precision, Accuracy, and Stability.*

4.1 Precision determined with calibration gases is ±0.5 percent full scale in the 0–58 mg./m.³ range.

4.2 Accuracy depends on instrument linearity and the absolute concentrations of the calibration gases. An accuracy of ±1 percent of full scale in the 0–58 mg./m.³ range can be obtained.

4.3 Variations in ambient room temperature can cause changes equivalent to as much as 0.5 mg. CO/m.³ per °C. This effect can be minimized by operating the analyzer in a temperature-controlled room. Pressure changes between span checks will cause changes in instrument response. Zero drift is usually less than ±1 percent of full scale per 24 hours, if cell temperature and pressure are maintained constant.

5. *Apparatus.*

5.1 *Carbon Monoxide Analyzer.* Commercially available instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed manufacturers specifications and those described in this method.

5.2 *Sample Introduction System.* Pump, flow control valve, and flowmeter.

5.3 *Filter (In-line).* A filter with a porosity of 2 to 10 microns should be used to keep large particles from the sample cell.

5.4 *Moisture Control.* Refrigeration units are available with some commercial instruments for maintaining constant humidity. Drying tubes (with sufficient capacity to operate for 72 hours) containing indicating silica gel can be used. Other techniques that prevent the interference of moisture are satisfactory.

6. *Reagents.*

6.1 *Zero Gas.* Nitrogen or helium containing less than 0.1 mg. CO/m.³

6.2 *Calibration Gases.* Calibration gases corresponding to 10, 20, 40, and 80 percent of full scale are used. Gases must be provided with certification or guaranteed analysis of carbon monoxide content.

6.3 *Span Gas.* The calibration gas corresponding to 80 percent of full scale is used to span the instrument.

7. *Procedure.*

7.1 Calibrate the instrument as described in 8.1. All gases (sample, zero, calibration, and span) must be introduced into the entire analyzer system. Figure C1 shows a typical flow diagram. For specific operating instructions, refer to the manufacturer's manual.

8. *Calibration.*

8.1 *Calibration Curve.* Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value on the recorder scale (e.g. on 0–58 mg./m.³ scale, set the 46 mg./m.³ standard at 80 percent of the recorder chart). Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a smooth curve is not obtained, calibration gases may need replacement.

9. *Calculations.*

9.1 Determine the concentrations directly from the calibration curve. No calculations are necessary.

9.2 Carbon monoxide concentrations in mg./m.³ are converted to p.p.m. as follows:

$$\text{p.p.m. CO} = \text{mg. CO/m.}^3 \times 0.873$$

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ADDENDA

A. *Suggested Performance Specifications for NDIR Carbon Monoxide Analyzers:*

Range (minimum)	0–58 mg./m.³ (0–50 p.p.m.).
Output (minimum)	0–10, 100, 1,000, 5,000 mv. full scale.
Minimum detectable sensitivity.	0.6 mg./m.³ (0.5 p.p.m.).
Lag time (maximum)	15 seconds.
Time to 90 percent response (maximum).	30 seconds.
Rise time, 90 percent (maximum).	15 seconds.
Fall time, 90 percent (maximum).	15 seconds.
Zero drift (maximum)	3 percent/week, not to exceed 1 percent/24 hours.
Span drift (maximum)	3 percent/week, not to exceed 1 percent/24 hours.
Precision (minimum)	±0.5 percent.
Operational period (minimum).	3 days.
Noise (maximum)	±0.5 percent.
Interference equivalent (maximum).	1 percent of full scale.
Operating temperature range (minimum).	5–40° C.
Operating humidity range (minimum).	10–100 percent.
Linearity (maximum deviation).	1 percent of full scale.

B. *Suggested Definitions of Performance Specifications:*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full Scale—The maximum measuring limit for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale

Lag Time—The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Fall Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating Humidity Range—The range of ambient relative humidity over which the instrument will meet all performance specifications.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

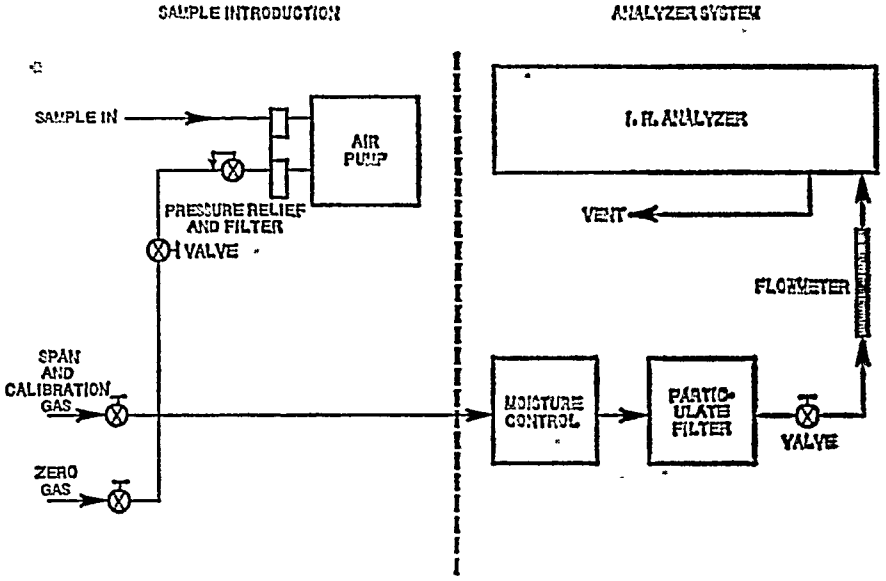

Figure C1. Carbon monoxide analyzer flow diagram.

APPENDIX D—REFERENCE METHOD FOR THE MEASUREMENT OF PHOTOCHEMICAL OXIDANTS CORRECTED FOR INTERFERENCES DUE TO NITROGEN OXIDES AND SULFUR DIOXIDE

1. *Principle and Applicability.*

1.1 Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

1.2 The method is applicable to the continuous measurement of ozone in ambient air.

2. *Range and Sensitivity.*

2.1 The range is 9.8 μg. O_3/m.³ to greater than 1960 Ng. O_3/m.³ (0.005 p.p.m. O_3 to greater than 1 p.p.m. O_3).

2.2 The sensitivity is 9.8 μg. O_3/m.³ (0.005 p.p.m. O_3).

3. *Interferences.*

3.1 Other oxidizing and reducing species normally found in ambient air do not interfere.

4. *Precision and Accuracy.*

4.1 The average deviation from the mean of repeated single measurements does not exceed 5 percent of the mean of the measurements.

4.2 The method is accurate within ±7 percent.

5. *Apparatus.*

5.1 *Detector Cell.* Figure D1 is a drawing of a typical detector cell showing flow paths of gases, the mixing zone, and placement of the photomultiplier tube. Other flow paths in which the air and ethylene streams meet

at a point near the photomultiplier tube are also allowable.

5.2 *Air Flowmeter.* A device capable of controlling air flows between 0–1.5 l/min.

5.3 *Ethylene Flowmeter.* A device capable of controlling ethylene flows between 0–50 ml./min. At any flow in this range, the device should be capable of maintaining constant flow rate within ±3 ml./min.

5.4 *Air Inlet Filter.* A Teflon filter capable of removing all particles greater than 5 microns in diameter.

5.5 *Photomultiplier Tube.* A high gain low dark current (not more than 1×10^{-9} ampere) photomultiplier tube having its maximum gain at about 430 nm. The following tubes are satisfactory: RCA 4507, RCA 8575, EMI 9750, EMI 9524, and EMI 9536.

5.6 *High Voltage Power Supply.* Capable of delivering up to 2,000 volts.

5.7 *Direct Current Amplifier.* Capable of full scale amplification of currents from 10^{-10} to 10^{-7} ampere; an electrometer is commonly used.

5.8 *Recorder.* Capable of full scale display of voltages from the DC amplifier. These voltages commonly are in the 1 millivolt to 1-volt range.

5.9 *Ozone Source and Dilution System.* The ozone source consists of a quartz tube into which ozone-free air is introduced and then irradiated with a very stable low pressure mercury lamp. The level of irradiation is controlled by an adjustable aluminum sleeve which fits around the lamp. Ozone concentrations are varied by adjustment of this sleeve. At a fixed level of irradiation, ozone is produced at a constant rate. By carefully controlling the flow of air through the quartz tube, atmospheres are generated which contain constant concentrations of ozone. The levels of ozone in the test atmospheres are determined by the neutral buffered potassium iodide method (see section 8). This ozone source and dilution system is shown schematically in Figures D2 and D3, and has been described by Hodgeson, Stevens, and Martin.

5.10 *Apparatus for Calibration*

5.10.1 *Absorber.* All-glass impingers as shown in Figure D4 are recommended. The impingers may be purchased from most major glassware suppliers. Two absorbers in series are needed to insure complete collection of the sample.

5.10.2 *Air Pump.* Capable of drawing 1 liter/minute through the absorbers. The pump should be equipped with a needle valve on the inlet side to regulate flow.

5.10.3 *Thermometer.* With an accuracy of ±2° C.

5.10.4 *Barometer.* Accurate to the nearest mm. Hg.

5.10.5 *Flowmeter.* Calibrated metering device for measuring flow up to 1 liter/minute within ±2 percent. (For measuring flow through impingers.)

5.10.6 *Flowmeter.* For measuring airflow past the lamp; must be capable of measuring flows from 2 to 15 liters/minute within ±5 percent.

5.10.7 *Trap.* Containing glass wool to protect needle valve.

5.10.8 *Volumetric Flasks.* 25, 100, 500, 1,000 ml.

5.10.9 *Buret.* 50 ml.

5.10.10 *Pipets.* 0.5, 1, 2, 3, 4, 10, 25, and 50 ml. volumetric.

5.10.11 Erlenmeyer Flasks. 300 ml.

5.10.12 *Spectrophotometer.* Capable of measuring absorbance at 352 nm. Matched 1-cm. cells should be used.

6. *Reagents.*

6.1 *Ethylene.* C. P. grade (minimum).

6.2 *Cylinder Air.* Dry grade.

6.3 *Activated Charcoal Trap.* For filtering cylinder air.

6.4 *Purified Water.* Used for all reagents. To distilled or deionized water in an all-glass distillation apparatus, add a crystal of potassium permanganate and a crystal of barium hydroxide, and redistill.

6.5 *Absorbing Reagent.* Dissolve 13.6 g. potassium dihydrogen phosphate (KH_2PO_4), 14.2 g. anhydrous disodium hydrogen phosphate (Na_2HPO_4) or 35.8 g. dodecahydrate salt ($Na_2HPO_4{\cdot}12H_2O$), and 10.0 g. potassium iodide (KI) in purified water and dilute to 1,000 ml. The pH should be 6.8±0.2. The solution is stable for several weeks, if stored in a glass-stoppered amber bottle in a cool, dark place.

6.6 *Standard Arsenious Oxide Solution (0.05 N).* Use primary standard grade arsenious oxide (As_2O_3). Dry 1 hour at 105° C. immediately before using. Accurately weigh 2.4 g. arsenious oxide from a small glass-stoppered weighing bottle. Dissolve in 25 ml. 1 N sodium hydroxide in a flask or beaker on a steam bath. Add 25 ml. 1 N sulfuric acid. Cool, transfer quantitatively to a 1,000-ml. volumetric flask, and dilute to volume. NOTE: Solution must be neutral to litmus, not alkaline.

$$\text{Normality } As_2O_3 = \frac{\text{wt } As_2O_3 \text{ (g.)}}{49.46}$$

6.7 *Starch Indicator Solution (0.2 percent).* Triturate 0.4 g. soluble starch and approximately 2 mg. mercuric iodide (preservative) with a little water. Add the paste slowly to 200 ml. of boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle.

6.8 *Standard Iodine Solution (0.05 N).*

6.8.1 *Preparation.* Dissolve 5.0 g. potassium iodide (KI) and 3.2 g. resublimed iodine (I_2) in 10 ml. purified water. When the iodine dissolves, transfer the solution to a 500-ml. glass-stoppered volumetric flask. Dilute to mark with purified water and mix thoroughly. Keep solution in a dark brown glass-stoppered bottle away from light, and restandardize as necessary.

6.8.2 *Standardization.* Pipet accurately 20 ml. standard arsenious oxide solution into a 300-ml. Erlenmeyer flask. Acidify slightly with 1:10 sulfuric acid, neutralize with solid sodium bicarbonate, and add about 2 g. excess. Titrate with the standard iodine solution using 5 ml. starch solution as indicator. Saturate the solution with carbon dioxide near the end point by adding 1 ml. of 1:10 sulfuric acid. Continue the titration to the first appearance of a blue color which persists for 30 seconds.

$$\text{Normality } I_2 = \frac{\text{ml. } As_2O_3 \times \text{Normality } As_2O_3}{\text{ml. } I_2}$$

6.9 *Diluted Standard Iodine.* Immediately before use, pipet 1 ml. standard iodine solution into a 100-ml. volumetric flask and dilute to volume with absorbing reagent.

7. *Procedure.*

7.1 Instruments can be constructed from the components given here or may be purchased. If commercial instruments are used, follow the specific instructions given in the manufacturer's manual. Calibrate the instrument as directed in section 8. Introduce samples into the system under the same conditions of pressure and flow rate as are used in calibration. By proper adjustments of zero and span controls, direct reading of ozone concentration is possible.

8. *Calibration.*

8.1 *KI Calibration Curve.* Prepare a curve of absorbance of various iodine solutions against calculated ozone equivalents as follows:

8.1.1 Into a series of 25 ml. volumetric flasks, pipet 0.5, 1, 2, 3, and 4 ml. of diluted standard iodine solution (6.9). Dilute each to the mark with absorbing reagent. Mix thoroughly, and immediately read the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference.

8.1.2 Calculate the concentration of the solutions as total $\mu g.\ O_3$ as follows:

$$\text{Total } \mu g.\ O_3 = (N)\ (96)\ (V_1)$$

N = Normality I_2 (see 6.8.2), meq./ml.

V_1 = Volume of diluted standard I_2 added, ml. (0.5, 1, 2, 3, 4).

Plot absorbance versus total $\mu g.\ O_3$.

8.2 *Instrument Calibration.*

8.2.1 *Generation of Test Atmospheres.* Assemble the apparatus as shown in Figure D3. The ozone concentration produced by the generator can be varied by changing the position of the adjustable sleeve. For calibration of ambient air analyzers, the ozone source should be capable of producing ozone concentrations in the range 100 to 1,000 $\mu g./m.^3$ (0.05 to 0.5 p.p.m.) at a flow rate of at least 5 liters per minute. At all times the airflow through the generator must be greater than the total flow required by the sampling systems.

8.2.2 *Sampling and Analyses of Test Atmospheres.* Assemble the KI sampling train as shown in Figure D4. Use ground-glass connections upstream from the impinger. Butt-to-butt connections with Tygon tubing may be used. The manifold distributing the test atmospheres must be sampled simultaneously by the KI sampling train and the instrument to be calibrated. Check assembled systems for leaks. Record the instrument response in nanoamperes at each concentration (usually six). Establish these concentrations by analysis, using the neutral buffered potassium iodide method as follows:

8.2.2.1 *Blank.* With ozone lamp off, flush the system for several minutes to remove residual ozone. Pipet 10 ml. absorbing reagent into each absorber. Draw air from the ozone-generating system through the sampling train at 0.2 to 1 liter/minute for 10 minutes. Immediately transfer the exposed solution to a clean 1-cm. cell. Determine the absorbance at 352 nm. against unexposed absorbing reagent as the reference. If the system blank gives an absorbance, continue flushing the ozone generation system until no absorbance is obtained.

8.2.2.2 *Test Atmospheres.* With the ozone lamp operating, equilibrate the system for about 10 minutes. Pipet 10 ml. of absorbing reagent into each absorber and collect samples for 10 minutes in the concentration range desired for calibration. Immediately transfer the solutions from the two absorbers to clean 1-cm. cells. Determine the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference. Add the absorbances of the two solutions to obtain total absorbance. Read total $\mu g.O_3$ from the calibration curve (see 8.1). Calculate total volume of air sampled corrected to reference conditions of 25° C. and 760 mm. Hg. as follows:

$$V_R = V \times \frac{P}{760} \times \frac{298}{t+273} \times 10^{-3}$$

V_R = Volume of air at reference conditions, $m.^3$

V = Volume of air at sampling conditions, liters.

P = Barometric pressure at sampling conditions, mm. Hg.

t = Temperature at sampling conditions, °C.

10^{-3} = Conversion of liters to $m.^3$

Calculate ozone concentration in p.p.m. as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{V_n} \times 5.10 \times 10^{-4}$$

8.2.3 *Instrument Calibration Curve.* Instrument response from the photomultiplier tube is ordinarily in current or voltage. Plot the current, or voltage if appropriate, (y-axis) for the test atmospheres against ozone concentration as determined by the neutral buffered potassium iodide method, in p.p.m. (x-axis).

9. *Calculations.*

9.1 If a recorder is used which has been properly zeroed and spanned, ozone concentrations can be read directly.

9.2 If the DC amplifier is read directly, the reading must be converted to ozone concentrations using the instrument calibration curve (8.2.3).

9.3 Conversion between p.p.m. and $\mu g./m.^3$ values for ozone can be made as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{m.^3} \times 5.10 \times 10^{-4}$$

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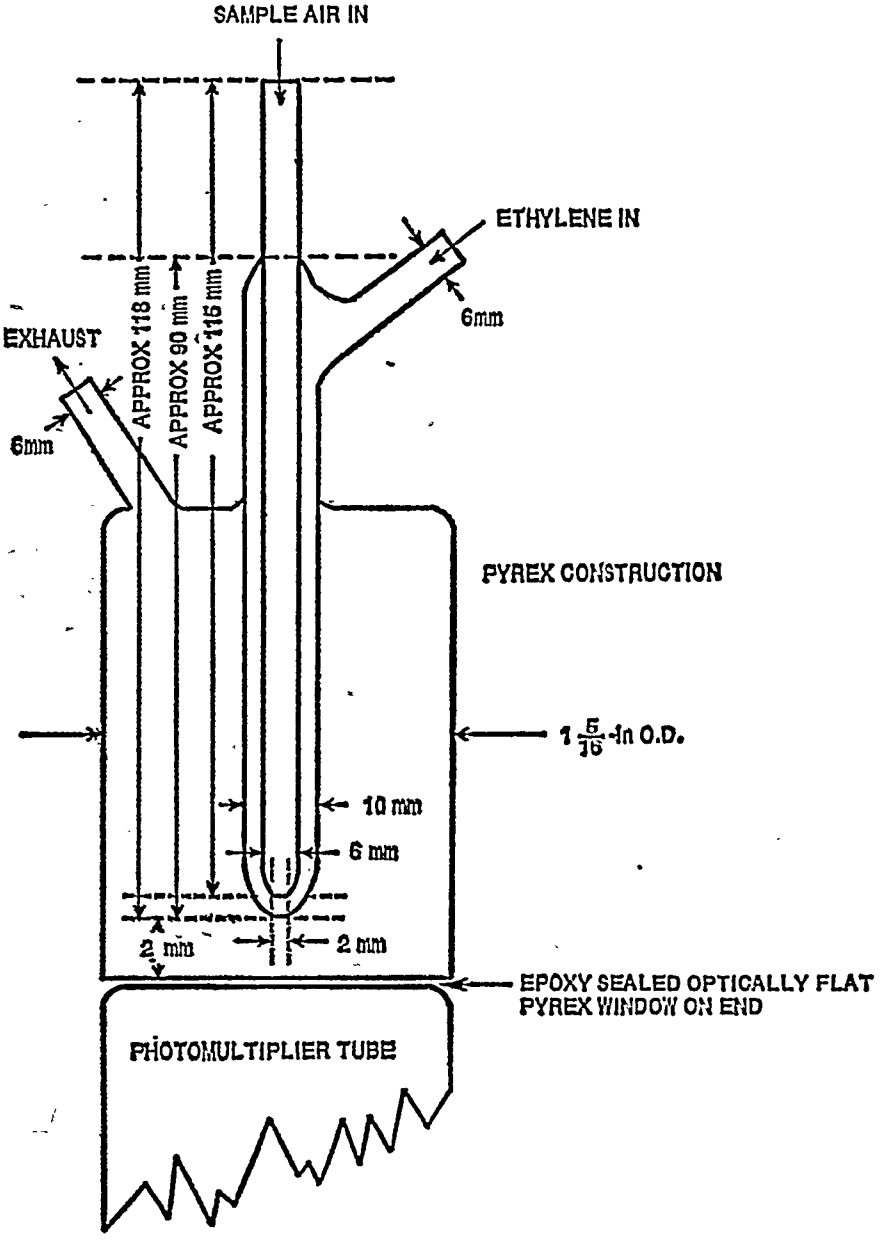

Figure D1. Detector cell.

APPENDIX E—REFERENCE METHOD FOR DETERMINATION OF HYDROCARBONS CORRECTED FOR METHANE

1. *Principle and Applicability.*

1.1 Measured volumes of air are delivered semicontinuously (4 to 12 times per hour) to a hydrogen flame ionization detector to measure its total hydrocarbon (THC) content. An aliquot of the same air sample is introduced into a stripper column which removes water, carbon dioxide, hydrocarbons other than methane, and carbon monoxide. Methane and carbon monoxide are passed quantitatively to a gas chromatographic column where they are separated. The methane is eluted first, and is passed unchanged through a catalytic reduction tube into the flame ionization detector. The carbon monoxide is eluted into the catalytic reduction tube where it is reduced to methane before passing through the flame ionization detector. Between analyses the stripper column is backflushed to prepare it for subsequent analysis. Hydrocarbon concentrations corrected for methane are determined by subtracting the methane value from the total hydrocarbon value.

Two modes of operation are possible: (1) A complete chromatographic analysis showing the continuous output from the detector for each sample injection; (2) The system is programed for automatic zero and span to display selected band widths of the chromatogram. The peak height is then used as the measure of the concentration. The former operation is referred to as the chromatographic or spectro mode and the latter as the barographic or "normal" mode depending on the make of analyzer.

1.2 The method is applicable to the semicontinuous measurement of hydrocarbons corrected for methane in ambient air. The carbon monoxide measurement, which is simultaneously obtained in this method, is not required in making measurements of hydrocarbons corrected for methane and will not be dealt with here.

2. *Range and Sensitivity.*

2.1 Instruments are available with various range combinations. For atmospheric analysis the THC range is 0–13.1 mg./m.^{3} (0–20 p.p.m.) carbon (as CH_4) and the methane range is 0–6.55 mg/m.^{3} (0–10 p.p.m.). For special applications, lower ranges are available and in these applications the range for THC is 0–1.31 mg./m.^{3} (0–2 p.p.m.) carbon (as CH_4) and for methane the range is 0–1.31 mg./m.^{3} (0–2 p.p.m.).

2.2 For the higher, atmospheric analysis ranges the sensitivity for THC is 0.065 mg./m.^{3} (0.1 p.p.m.) carbon (as CH_4) and for methane the sensitivity is 0.033 mg./m.^{3} (0.05 p.p.m.). For the lower, special analysis ranges the sensitivity is 0.016 mg./m.^{3} (0.025 p.p.m.) for each gas.

3. *Interferences.*

3.1 No interference in the methane measurement has been observed. The THC measurement typically includes all or a portion of what is generally classified as the air peak interference. This effect is minimized by proper plumbing arrangements or is negated electronically.

4. *Precision, Accuracy, and Stability.*

4.1 Precision determined with calibration gases is +0.5 percent of full scale in the higher, atmospheric analysis ranges.

4.2 Accuracy is dependent on instrument linearity and absolute concentration of the calibration gases. An accuracy of 1 percent of full scale in the higher, atmospheric analysis ranges and 2 percent of full scale in the lower, special analysis ranges can be obtained.

4.3 Variations in ambient room temperature can cause changes in performance characteristics. This is due to shifts in oven temperature, flow rates, and pressure with ambient temperature change. The instrument should meet performance specifications with room temperature changes of ±3° C. Baseline drift is automatically corrected in the barographic mode.

5. *Apparatus.*

5.1 *Commercially Available THC, CH_4, and CO Analyzer.* Instruments should be installed on location and demonstrated, preferably by the manufacturer, or his representative, to meet or exceed manufacturer's specifications and those described in this method.

5.2 *Sample Introduction System.* Pump, flow control valves, automatic switching valves, and flowmeter.

5.3 *Filter (In-line).* A binder-free, glass-fiber filter with a porosity of 3 to 5 microns should be immediately downstream from the sample pump.

5.4 *Stripper or Precolumn.* Located outside of the oven at ambient temperature. The column should be repacked or replaced after the equivalent of 2 months of continuous operation.

5.5 *Oven.* For containing the analytical column and catalytic converter. The oven should be capable of maintaining an elevated temperature constant within ±0.5° C. The specific temperature varies with instrument manufacturer.

6. *Reagents.*

6.1 *Combustion Gas.* Air containing less than 1.3 mg./m.^{3} (2 p.p.m.) hydrocarbon as methane.

6.2 *Fuel.* Hydrogen or a mixture of hydrogen and inert gas containing less than 0.065 mg./m.^{3} (0.1 p.p.m.) hydrocarbons as methane.

6.3 *Carrier Gas.* Helium, nitrogen, air or hydrogen containing less than 0.065 mg./m.^{3} (0.1 p.p.m.) hydrocarbons as methane.

6.4 *Zero Gas.* Air containing less than 0.065 mg./m.^{3} (0.1 p.p.m.) total hydrocarbons as methane.

6.5 *Calibration Gases.* Gases needed for linearity checks (peak heights) are determined by the ranges used. Calibration gases corresponding to 10, 20, 40, and 80 percent of full scale are needed. Gases must be provided with certification or guaranteed analysis. Methane is used for both the total hydrocarbon measurement and methane measurement.

6.6 *Span Gas.* The calibration gas corresponding to 80 percent of full scale is used to span the instrument.

7. *Procedure.*

7.1 Calibrate the instrument as described in 8.1. Introduce sample into the system under the same conditions of pressure and flow rates as are used in calibration. (The pump is bypassed only when pressurized cylinder gases are used.) Figure E1 shows a typical flow diagram; for specific operating instructions refer to manufacturer's manual.

8. *Calibration.*

8.1 *Calibration Curve.* Determine the linearity of the system for THC and methane in the barographic mode by introducing zero gas and adjusting the respective zeroing controls to indicate a recorder reading of zero. Introduce the span gas and adjust the span control to indicate the proper value on the recorder scale. Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a smooth curve is not obtained, calibration gases may need replacement.

9. *Calculation.*

9.1 Determine concentrations of total hydrocarbons (as CH_4) and CH_4, directly from the calibration curves. No calculations are necessary.

9.2 Determine concentration of hydrocarbons corrected for methane by subtracting the methane concentration from the total hydrocarbon concentration.

9.3 Conversion between p.p.m. and mg./m.^{3} values for total hydrocarbons (as CH_4) methane and hydrocarbons corrected for methane are made as follows:

p.p.m. carbon (as CH_4) = [mg. carbon (as CH_4)/m.^{3}] × 1.53

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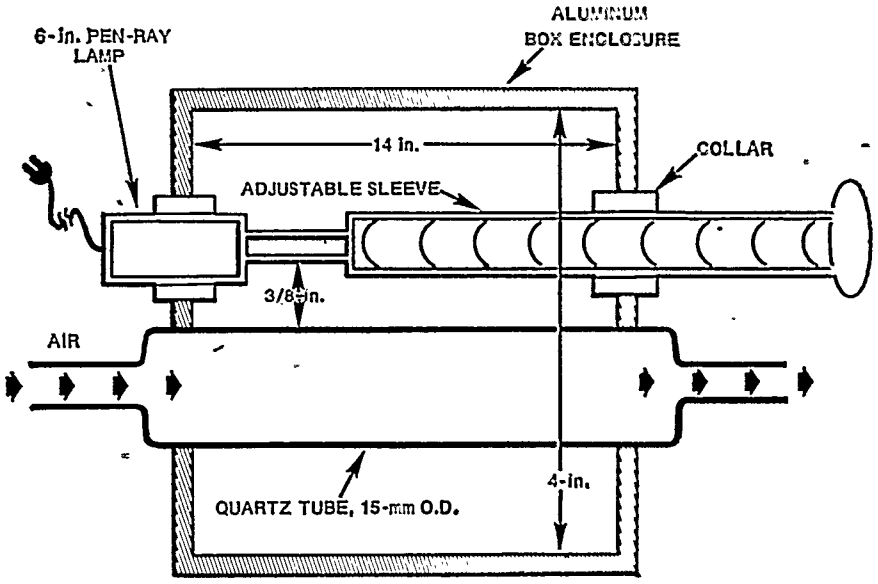

Figure D2. Ozone source.

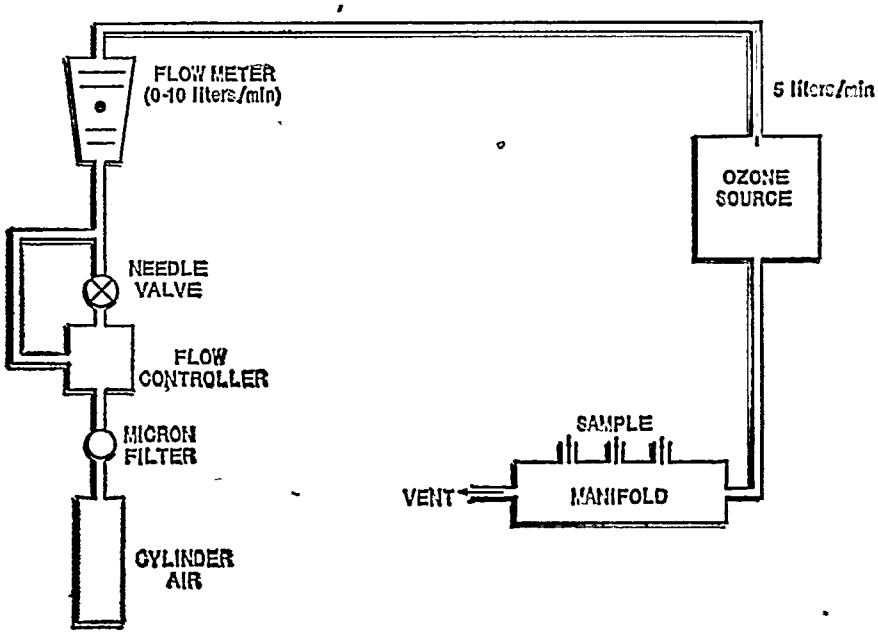

Figure D3. Ozone calibration air supply, source, and manifold system.

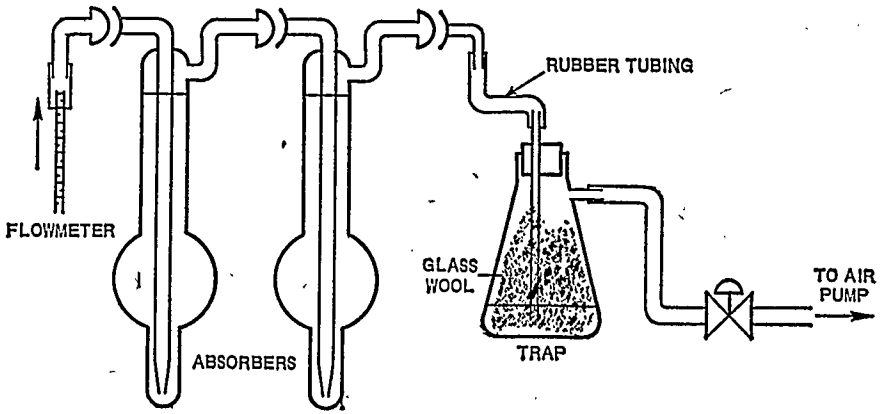

Figure D4. KI sampling train.

ADDENDA

A. *Suggested Performance Specifications for Atmospheric Analyzers for Hydrocarbons Corrected for Methane:*

Range (minimum)	0–5 p.p.m. THC.
Output (minimum)	0–5 p.p.m. CH_4.
Minimum detectable sensitivity	0–10 mv. full scale.
Zero drift (maximum)	0.1 p.p.m. THC.
Span drift (maximum)	0.1 p.p.m. CH_4.
Precision (minimum)	Not to exceed 1 percent/24 hours.
Operational period (minimum)	Not to exceed 1 percent/24 hours.
Operating temperature range (minimum)	±0.5 percent.
Operating humidity range (minimum)	3 days.
Linearity (maximum)	5–40° C.
	10–100 percent.
	1 percent of full scale.

B. *Suggested Definitions of Performance Specifications:*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedence.

Full Scale—The maximum measuring limit for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed at ± percent of full scale.

Lag Time—The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 Percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration. It is expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating Humidity Range—The range of ambient relative humidity over which the instrument will meet all performance specifications.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

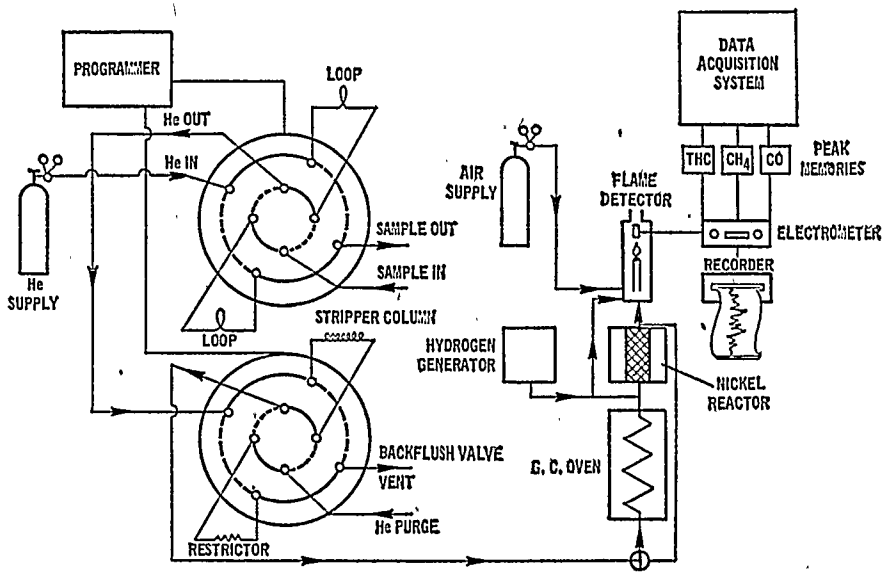

Figure E1. Typical flow diagram.

APPENDIX F—REFERENCE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (24-HOUR SAMPLING METHOD)

1. *Principle and Applicability.*

1.1 Nitrogen dioxide is collected by bubbling air through a sodium hydroxide solution to form a stable solution of sodium nitrite. The nitrite ion produced during sampling is determined colorimetrically by reacting the exposed absorbing reagent with phosphoric acid, sulfanilamide, and N-1-naphthylethylenediamine dihydrochloride.

1.2 The method is applicable to collection of 24-hour samples in the field and subsequent analysis in the laboratory.

2. *Range and Sensitivity.*

2.1 The range of the analysis is 0.04 to 1.5 $\mu g.$ NO_2/ml. With 50 ml. absorbing reagent and a sampling rate of 200 ml./min. for 24 hours, the range of the method is 20–740 $\mu g./m.^3$ (0.01–0.4 p.p.m.) nitrogen dioxide.

2.2 A concentration of 0.04 $\mu g.$ NO_2/ml. will produce an absorbance of 0.02 using 1-cm. cells.

3. *Interferences.*

3.1 The interference of sulfur dioxide is eliminated by converting it to sulfuric acid with hydrogen peroxide before analysis. (*1*)

4. *Precision, Accuracy, and Stability.*

4.1 The relative standard deviations are 14.4 percent and 21.5 percent at nitrogen dioxide concentrations of 140 $\mu g./m.^3$ (0.072 p.p.m.) and 200 $\mu g./m.^3$ (0.103 p.p.m.), respectively, based on an automated analysis of

samples collected from a standard test atmosphere. Precision would probably be different when the analysis is performed manually.

4.2 No accuracy data are available.

4.3 Samples are stable for at least 6 weeks.

5. *Apparatus.*

5.1 *Sampling.* See Figure F1.

5.1.1 *Absorber.* Polypropylene tubes 164 x 32 mm., equipped with polypropylene two-port closures.* Rubber stoppers cause high and varying blank values and should not be used. A gas dispersion tube with a fritted end of porosity B (70–100 μm. maximum pore diameter) is used.

5.1.1.1 *Measurement of Maximum Pore Diameter of Frit.* Carefully clean the frit with dichromate-concentrated sulfuric acid cleaning solution and rinse well with distilled water. Insert through one hole of a two-hole rubber stopper and install in a test tube containing sufficient distilled water to cover the fritted portion. Attach a vacuum source to the other hole of the rubber stopper and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. Apply the following equation:

$$\text{maximum pore diameter, } \mu\text{m.} = \frac{30s}{P}$$

s=Surface tension of water in dynes/cm. at the test temperature (73 at 18° C., 72 at 25° C., and 71 at 31° C.).

P=Measured vacuum, mm. Hg.

5.1.2 *Probe.* Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end and a membrane filter to protect the frit. Replace filter after collecting five samples, or more often as indicated by visual observation of the loading.

5.1.3 *Flow Control Device.* Calibrated 27-gauge hypodermic needle, three-eighths of an inch long to maintain a flow of approximately 0.2 liter/minute. The needle should be protected by a membrane filter. Change filter after collecting 10 samples.

5.1.4 *Air Pump.* Capable of maintaining a flow of 0.2 liter/minute through the absorber, and a vacuum of 0.7 atmosphere.

5.1.5 *Calibration Equipment.* Glass flowmeter for measuring airflows up to approximately 275 ml./min. within ±2 percent, stopwatch, and precision wet test meter (1 liter/revolution).

5.2 *Analysis.*

5.2.1 *Volumetric Flasks.* 50, 100, 200, 250, 500, 1,000 ml.

5.2.2 *Graduated Cylinder.* 1,000 ml.

5.2.3 *Pipets.* 1, 2, 5, 10, 15 ml. volumetric; 2 ml., graduated in 1/10 ml. intervals.

5.2.4 *Test Tube.*

5.2.5 *Spectrophotometer of Colorimeter.* Capable of measuring absorbance at 540 nm. Bandwidth is not critical.

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Absorbing Reagent.* Dissolve 4.0 g. sodium hydroxide in distilled water and dilute to 1,000 ml.

6.2 *Analysis.*

6.2.1 *Sulfanilamide.* Dissolve 20 g. sulfanilamide in 700 ml. distilled water. Add, with mixing, 50 ml. concentrated phosphoric acid (85 percent) and dilute to 1,000 ml. This solution is stable for a month if refrigerated.

6.2.2 *NEDA Solution.* Dissolve 0.5 g. N-1-naphthylethylenediamine dihydrochloride in distilled water. This solution is stable for a month if refrigerated and protected from light.

6.2.3 *Hydrogen Peroxide.* Dilute 0.2 ml. 30 percent hydrogen peroxide to 250 ml. with distilled water. This solution may be used for a month if protected from light.

6.2.4 *Standard Nitrite Solution.* Dissolve sufficient desiccated sodium nitrite ($NaNO_2$, assay of 97 percent or greater) and dilute with distilled water to 1,000 ml. so that a solution containing 1,000 μg. NO_2^-/ml. is obtained. The amount of $NaNO_2$ to use is calculated as follows:

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

G=Amount of $NaNO_2$, g.

1.500=Gravimetric factor in converting NO_2 into $NaNO_2$.

A=Assay, percent.

7. *Procedure.*

7.1 *Sampling.* Assemble the sampling train as shown in Figure F1. Add 50 ml. absorbing reagent to the absorber. Disconnect funnel, insert calibrated flowmeter, and measure flow before sampling. If flow rate before sampling is less than 85 percent of needle calibration, check for leak or change filters as necessary. Remove flowmeter and replace funnel. Sample for 24 hours from midnight to midnight and measure flow at end of sampling period.

7.2 *Analysis.* Replace any water lost by evaporation during sampling. Pipet 10 ml. of the collected sample into a test tube. Add 1.0 ml. hydrogen peroxide solution, 10.0 ml. sulfanilamide solution, and 1.4 ml. NEDA solution with thorough mixing after the addition of each reagent. Prepare a blank in the same manner using 10 ml. absorbing reagent. After a 10-minute color-development interval, measure the absorbance at 540 mm. against the blank. Read μg. NO_2^-/ml. from standard curve (Section 8.2).

8. *Calibration and Efficiencies.*

8.1 *Sampling.*

8.1.1 *Calibration of Flowmeter.* Using a wet test meter and a stopwatch, determine the rates of air flow (ml./min.) through the flowmeter at several ball positions. Plot ball positions versus flow rates.

8.1.2 *Calibration of Hypodermic Needle.* Connect the calibrated flowmeter, the needle to be calibrated, and the source of vacuum in such a way that the direction of airflow through the needle is the same as in the sampling train. Read the position of the ball and determine flow rate in ml./min. from the calibration chart prepared in 8.1.1. Reject all needles not having flow rates of 190 to 210 ml./min. before sampling.

8.2 *Calibration Curve.* Dilute 5.0 ml. of the 1,000 μg. NO_2^-/ml. solution to 200 ml. with absorbing reagent. This solution contains 25 μg. NO_2^-/ml. Pipet 1, 2, 5, and 15 ml. of the 25 μg. NO_2^-/ml. solution into 50-, 50-, 100-, and 250-ml. volumetric flasks and dilute to the mark with absorbing reagent. The solutions contain 0.50, 1.00, 1.25, and 1.50 μg. NO_2^-/ml., respectively. Run standards as instructed in 7.2. Plot absorbance vs. μg. NO_2^-/ml.

8.3 *Efficiencies.* An overall average efficiency of 35 per cent was obtained from test atmospheres having nitrogen dioxide concentrations of 140 μg./m.^{3} and 200 μg./m.^{3} by automated analysis.(2)

9. *Calculation.*

9.1 *Sampling.*

9.1.1 Calculate volume of air sampled.

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

V=Volume of air sampled, m.^{3}

F_1=Measured flow rate before sampling, ml./min.

F_2=Measured flow rate after sampling, ml./min.

T=Time of sampling, min.

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

9.2 Calculate the concentration of nitrogen dioxide as μg. NO_2/m.^{3}

$$\mu\text{g. } NO_2/\text{m.}^3 = \frac{(\mu\text{g. } NO_2^-/\text{ml.}) \times 50}{V \times 0.35} \times \frac{(\mu\text{g. } NO_2^-/\text{ml.}) \times 143}{V}$$

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

V=Volume of air sampled, m.^{3}

0.35=Efficiency.

9.2.1 If desired, concentration of nitrogen dioxide may be calculated as p.p.m. NO_2.

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

10. *References.*

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

(2) Purdue, L. J., Dudley, J. E., Clements, J. B., and Thompson, R. J., "Studies in Air Sampling for Nitrogen Dioxide," I. A reinvestigation of the Jacobs-Hochheiser Reagent. In Preparation.

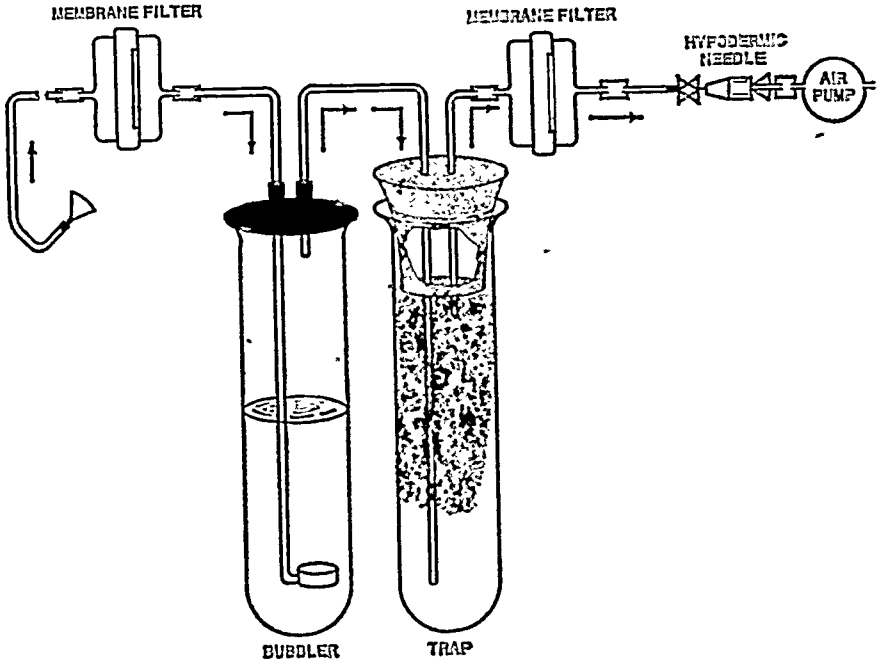

Figure F1. Sampling train.

*Available from Bel-Art Products, Pequannock, N.J.

[FR Doc.71-6142 Filed 4-29-71;8:51 am]