

# ENVIRONMENTAL PROTECTION AGENCY

[ 42 CFR Part 410 ]

## NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS

### Notice of Proposed Standards for Sulfur Oxides, Particulate Matter, Carbon Monoxide, Photochemical Oxidants, Hydrocarbons, and Nitrogen Oxides

Section 109 of the Clean Air Act, as amended December 31, 1970 (Public Law 91-640), directs the Administrator of the Environmental Protection Agency to publish, no later than January 30, 1971, proposed national primary and secondary ambient air quality standards for each pollutant for which air quality criteria were issued prior to enactment of the amendments. The section also provides that after December 31, 1970, the Administrator shall, simultaneously with his issuance of air quality criteria and information on control techniques for a pollutant, publish proposed national primary and secondary ambient air quality standards for that pollutant. Primary ambient air quality standards define levels of air quality which the Administrator judges necessary, based on the air quality criteria and allowing an adequate margin of safety, to protect the public health. Secondary ambient air quality standards define levels of air quality which the Administrator judges necessary, based on the air quality criteria to protect the public welfare from any known or anticipated adverse effects of an air pollutant.

Prior to December 31, 1970, air quality criteria had been issued for these five pollutants: Sulfur oxides and particulate matter (34 F.R. 1988); carbon monoxide, photochemical oxidants, and hydrocarbons (35 F.R. 4768). The Administrator has determined that nitrogen oxides, which are present in the ambient air as a result of emissions from numerous and diverse mobile and stationary sources and for which air quality criteria were not issued prior to December 31, 1970, are air pollutants which adversely affect public health and welfare. In accordance with section 108 of the Act, the following are published in a notice in this issue of the FEDERAL REGISTER:

1. A list of air pollutants, required to be published no later than January 30, 1971, which identifies nitrogen oxides as air pollutants for which air quality criteria will be issued and for which national primary and secondary ambient air quality standards will be promulgated, and

2. An announcement of the issuance of air quality criteria for nitrogen oxides.

Pursuant to section 109 of the Clean Air Act, notice is hereby given of proposed national primary and secondary ambient air quality standards as set forth in Part 410 below, which would be added to Chapter IV of Title 42, Code of Fed-

eral Regulations. With respect to carbon monoxide, hydrocarbons, photochemical oxidants, and nitrogen oxides, adverse welfare effects have not been observed to occur at levels below the levels of the proposed primary standards. For each of those pollutants, therefore, the proposed secondary standard has been specified at the level of the proposed primary standard.

The characteristics of the six air pollutants named above are, briefly, as follows:

**Sulfur oxides.** Sulfur oxides, which arise primarily from the combustion of sulfur-containing fossil fuels, are prevalent in polluted air. Their presence in the ambient air has been associated with a variety of respiratory diseases and increased mortality rates. They represent a significant economic burden and have a nuisance impact. Sulfur dioxide is an indicator of the presence of sulfur oxides in polluted air and is an important index of the effects which have been associated with these contaminants.

Detailed information on sulfur oxides is presented in the document "Air Quality Criteria for Sulfur Oxides" (NAPCA Publication No. AP-50), which provided a basis for the development of the standards set forth below.

**Particulate matter.** Particulate matter refers to any matter dispersed in the air, whether solid or liquid, in which the individual particles are larger than small molecules but smaller than 500 microns. Particles smaller than 1 micron in diameter originate in the atmosphere principally through condensation and combustion, while larger particles arise principally from erosion and abrasion. Particulate matter of technological origin is pervasive in its distribution and is associated with a variety of adverse effects on public health and welfare. Particulate matter in the respiratory tract may produce injury by itself, or it may act in conjunction with gases, altering their sites or their mode of action. Particles cleared from the respiratory tract by transfer to the lymph, blood, or gastrointestinal tract may produce effects elsewhere in the body.

Detailed information on particulate matter is presented in the document "Air Quality Criteria for Particulate Matter" (NAPCA Publication No. AP-49), which provided a basis for the development of the standards set forth below.

**Carbon monoxide.** Carbon monoxide is the product of incomplete combustion of carbonaceous fuels and is widely prevalent in ambient air. It is absorbed through the lungs and reacts primarily with the hemoglobin in red blood cells. It decreases the oxygen carrying capacity of the blood and reduces the availability of oxygen transported to vital tissues by the blood.

Detailed information on carbon monoxide is presented in the document "Air Quality Criteria for Carbon Monoxide" (NAPCA Publication No. AP-62), which provided a basis for the development of the standards set forth below.

**Photochemical oxidants.** Photochemical oxidants are produced in the atmosphere when reactive organic substances,

principally reactive hydrocarbons, and nitrogen oxides are exposed to sunlight. Photochemical oxidants cause irritation of the mucous membranes, damage to vegetation, and deterioration of materials. They affect the clearance mechanism of the lungs and alter resistance to respiratory bacterial infection. Photochemical oxidants have been implicated as accelerators in the aging process.

Detailed information on photochemical oxidants is presented in the document "Air Quality Criteria for Photochemical Oxidants" (NAPCA Publication No. AP-63) which provided a basis for the development of the standards set forth below.

**Hydrocarbons.** Hydrocarbons are primarily associated with the processing, marketing, and use of petroleum products and are widely prevalent in the ambient air. They constitute the principal portion of these volatile reactive organic substances in the atmosphere which are the precursors of other compounds formed in the atmospheric photochemical system and which result in the manifestations of photochemical smog. Methane, which occurs naturally in the atmosphere at relatively high levels, is not considered to be involved in the photochemical reactions. The only direct effect attributable to ambient levels of hydrocarbons is the vegetation damage from ethylene.

Detailed information on hydrocarbons is presented in the document "Air Quality Criteria for Hydrocarbons" (NAPCA Publication No. AP-64) which provided a basis for the development of the standards set forth below.

**Nitrogen oxides.** Nitrogen oxides result from the fixation of nitrogen and oxygen at high temperatures and are typically associated with combustion processes. They are also related to certain chemical processes. The principal nitrogen oxide formed in the combustion process is nitric oxide. This compound has not been shown to have health or welfare effects at present or anticipated ambient concentrations. However, there are several atmospheric reactions which lead to the oxidation of nitric oxide to nitrogen dioxide, and the presence of nitrogen dioxide in ambient air has been associated with a variety of respiratory diseases. Nitrogen dioxide is essential to the production of photochemical smog. At higher concentrations, its presence has been implicated in the corrosion of electrical components as well as vegetation damage.

Detailed information on nitrogen oxides is presented in the document "Air Quality Criteria for Nitrogen Oxides" (EPA Publication No. AP-84) which provided a basis for the development of the standards set forth below.

The air quality criteria documents referred to above are available from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. Prices are as follows:

Sulfur oxides (AP-50)-----	\$1.25
Particulate matter (AP-49)-----	1.75
Carbon monoxide (AP-62)-----	1.50
Hydrocarbons (AP-64)-----	1.25
Photochemical oxidants (AP-63)-----	1.75
Nitrogen oxides (AP-84)-----	1.50

Orders for any of the above documents should be accompanied by a check or money order payable to the Superintendent of Documents.

Copies of the summary-and-conclusions chapter of each air quality criteria document are available free of charge from the Air Pollution Control Office, Environmental Protection Agency, 5600 Fishers Lane, Rockville, MD 20852, Attention: Publications Section.

Interested persons may submit written comments in triplicate to the Office of the Acting Commissioner, Air Pollution Control Office, Environmental Protection Agency, Parklawn Building, Room 17-59, 5600 Fishers Lane, Rockville, MD 20852. All relevant comments received not later than 45 days after the publication of this proposal will be considered. The standards, modified as the Administrator deems appropriate after consideration of comments, will be promulgated no later than 90 days from the date of publication of this notice, as required by the Act.

This notice of proposed rulemaking is issued under the authority of section 4, Public Law 91-604, 84 Stat. 1679.

Dated: January 25, 1971.

WILLIAM D. RUCKELSHAUS,  
Administrator.

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

**PART 410—NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS**

Sec.  
410.1 Definitions.  
410.2 Scope.  
410.3 Measurement corrections.  
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 standards for photochemical oxidants.  
410.10 National primary and secondary ambient air quality standards for hydrocarbons.  
410.11 National primary and secondary ambient air quality standards for nitrogen dioxide.  
Appendix A—Method for Determination of Sulfur Dioxide (Pararosaniline Method).  
Appendix B—Procedure for Determination of Suspended Particulates (High Volume Method).  
Appendix C—Method for Continuous Measurement of Carbon Monoxide (Nondispersive Infrared Spectrometry).  
Appendix D—Method for Determination of Oxidants (Neutral Buffered Potassium Iodide Method).  
Appendix E—Part 1: Method for Continuous Measurement of Hydrocarbons (Flame Ionization Method).  
Part 2: Method for Measurement of Methane.

Appendix F—Method for Determination of Nitrogen Dioxide in the Atmosphere (24-Hour Sampling Method).

**§ 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).

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

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

**§ 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 Measurement corrections.**

All measurements of air quality are corrected to a reference temperature of 20° C. and to a reference pressure of 760 millimeters of mercury.

**§ 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 a method referenced to the pararosaniline method, as described in Appendix A to this part, are:

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

(b) 365 micrograms per cubic meter—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 a method referenced to the pararosaniline method, as described in Appendix A to this part, are:

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

(b) 260 micrograms per cubic meter—maximum 24-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 high-volume sampling method, as described in Appendix B to this part, 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 high-volume sampling method, as described in Appendix B to this part, are:

(a) 60 micrograms per cubic meter—annual geometric mean.

(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 nondispersive infrared method, as described in Appendix C to this part, or equivalent method, are:

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

(b) 15 milligrams per cubic meter—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 standards for photochemical oxidants, measured by a method referenced to the neutral-buffered 1 percent potassium iodide colorimetric technique and corrected for interferences due to nitrogen oxides and sulfur dioxide, as described in Appendix D to this part, are: 125 micrograms per cubic meter—maximum 1-hour concentration not to be exceeded more than once per year.

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

The national primary and secondary ambient air quality standards for hydrocarbons, measured by the flame ionization detection method, as described in Appendix E to this part (Part 1), and corrected for methane in the sampled air by the procedures described in Appendix E to this part, or by an equivalent procedure, are: 125 micrograms per cubic meter—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 standards for nitrogen dioxide.

The national primary and secondary ambient air quality standards for nitrogen dioxide, measured by a method referenced to the 24-hour sampling method, as described in Appendix F to this part, are:

(a) 100 micrograms per cubic meter—annual arithmetic mean.

(b) 250 micrograms per cubic meter—24-hour concentration not to be exceeded more than once per year.

#### APPENDIX A

#### PART 1—METHOD FOR DETERMINATION OF SULFUR DIOXIDE (PARAROSANILINE METHOD)

1. *Principle and applicability of method.*  
1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachloromercurate (TCM). A dichlorosulfite-mercurate complex, which resists oxidation by the oxygen in the air, is formed.<sup>1,2</sup> Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen).

1.2 The complex is reacted with pararos-aniline and formaldehyde to form intensely colored pararos-aniline methyl sulfonic acid. The absorbance of the solution is measured spectrophotometrically.

2. *Range and sensitivity.* 2.1 Concentrations of sulfur dioxide in the range of 25 to 1,000  $\mu\text{g}/\text{m}^3$  (0.01 to 0.40 p.p.m.) can be measured under the conditions given. One can extrapolate to concentrations below 25  $\mu\text{g}/\text{m}^3$  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.

2.2 The lower limit of detection of sulfur dioxide in 10 ml. TCM is 0.75  $\mu\text{g}$ . (based on twice the standard deviation) representing a concentration of 25  $\mu\text{g}/\text{m}^3$   $\text{SO}_2$  (0.01 p.p.m.) in an air sample of 30 liters.

2.3 Beer's Law is followed through the working range from 0.0 to 1.0 absorbance units (0 to 27  $\mu\text{g}$  of sulfite ion in 25 ml. final solution computed as  $\text{SO}_2$ ).

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

4.2 After sample collection the solutions are relatively stable. At 25° C. losses of sulfur dioxide occur at the rate of 1.5 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  $\text{SO}_2$  in solution, and the rate of decay is independent of the concentration of  $\text{SO}_2$ .<sup>7</sup>

#### 5. Apparatus. 5.1 Sampling.

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

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 Volume Meter—Capable of measuring air flow within  $\pm 2$  percent. A wet or dry gas meter, with manometer, or a specially calibrated rotameter, is satisfactory. A 22-gauge hypodermic needle 1-in. long may be used as a critical orifice to give a flow of about 1 liter/min. if it has first been calibrated in the system. Use a membrane filter to protect the needle.

#### 5.2 Analysis.

5.2.1 Spectrophotometer—Suitable for measurement of absorbance at 548 nm. with an effective spectral band of less than 15 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:

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

#### 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 (Ethylenediaminetetraacetic acid disodium 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.<sup>7</sup> The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

#### 6.2 Analysis.

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

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

6.2.2 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  $\times 0.100$ .

6.2.3 Standardized Sulfite Solution for Preparation of Working Sulfite-TCM Solution—Dissolve 0.30 g. sodium metabisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$  or 0.40 g. sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) 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  $\mu\text{g}/\text{ml}$ . of  $\text{SO}_2$ . 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 min. 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:

$$\mu\text{g. SO}_2/\text{ml.} = \frac{(A-B) (N) (32,000) \times 0.02}{25}$$

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 0.003 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 ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ) 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 complete the titration. 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.

32,000 = Milliequivalent wt.,  $\mu\text{g}$ .

A = Volume thiosulfate for blank, ml.

B = Volume thiosulfate for sample, ml.

N = Normality of thiosulfate titrant.

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.

6.2.10.1 Dye Specifications—The pararos-aniline 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 8.2.1) should have a slope of  $0.030 \pm 0.003$  absorbance units/ $\mu\text{g}$ .  $\text{SO}_2$  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 pararos-aniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Herleco\*). If this cannot be obtained, the stock solution may be prepared by dissolving 0.200 g. of the purified dye in 100 ml. of 1 N hydrochloric acid in a 100 ml. glass stoppered graduated cylinder. (See Scaringelli, et al.<sup>4</sup> for the purification and assay procedures.)

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

6.2.11 Pararosaniline Reagent—To a 250-ml. volumetric flask, add 20 ml. stock pararosaniline solution. Add an additional 0.2 ml. stock solution for each percent the stock 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 min.) and for long term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Fixing sample volume at 30 liters maintains linearity between absorbance and concentration over this dynamic range.

7.1.1 30-Minute Sampling—Insert a midget impinger into the sampling system, Figure 1. Add 10 ml. TCM solution to the impinger. Collect sample at 1 liter/min. for 30 min. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Record the actual volume of air by multiplying the flow rate by the time in minutes. 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 15–20 ml. TCM solution in a midget impinger or 50 ml. in a larger impinger and collect the sample at 0.2 liter/min. for 24 hours. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Record the total volume of sample by multiplying the flow rate by the time in minutes. 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 Sample—Transfer the sample quantitatively to a 25-ml. volumetric flask; use about 5 ml. distilled water for rinsing. Delay analyses for 20 min. to allow any ozone to decompose.

7.2.1.2 24-Hour Sample—Dilute the entire sample to 25 ml. for the midget impinger or 50 ml. for the larger impinger, with absorbing solution. Pipet one-tenth of the sample into a 25 ml. volumetric flask for chemical analyses. Delay analyses for 20 min. 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 8ml. 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 min. 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 min. and before 60 min., determine the absorbances of the sample, reagent blank 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 on-scale readings within 10 percent of the true absorbance value.

8. Calibration and efficiencies. 8.1 Flowmeters and Hypodermic Needle—Calibrate flowmeters and hypodermic needle 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 (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<sub>2</sub> for the corresponding solution. The total µg. SO<sub>2</sub> in solution equals the concentration of the standard (Section 6.2.9) in µg. SO<sub>2</sub>/ml. times the ml. sulfite solution added (µg. SO<sub>2</sub> = µg./ml. SO<sub>2</sub> × ml. added). A linear relationship should be obtained, and the y-intercept should be within 0.02 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. Under these conditions the plot need be determined only once to determine the calibration factor (reciprocal of the slope of the line). (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<sub>2</sub> for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 Procedure with SO<sub>2</sub> Gas—See Part 3.

8.3 Sampling Efficiency—Collection efficiency is above 98 percent; efficiency may fall off, however, at concentrations below 25 µg./m.<sup>3</sup>.

9. Calculations. 9.1 Conversion of Volume—Convert the volume of air sampled to the volume at standard conditions of 25° C., 760 mm. Hg.:

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

V<sub>s</sub> = Volume of air at 25° C. and 760 mm. Hg.

V = Volume of air sampled, liters.  
P = Barometric pressure, mm. Hg.  
t = Temperature of air sample, °C.

Ordinarily, the correction for pressure is slight and may be neglected.

9.2 Sulfur Dioxide Concentration—Compute the concentration of sulfur dioxide in the sample by the following formula:

$$SO_2, \mu g./m.^3 = \frac{(A-A_0)(10^6)(D)}{V_s}$$

A = Sample absorbance.  
A<sub>0</sub> = Reagent blank absorbance.  
10<sup>6</sup> = Conversion of liters to cubic meters.  
V<sub>s</sub> = The sample volume corrected to 25° C. and 760 mm. Hg., liters.

$B = \frac{1}{\text{Slope of calibration}} = \text{calibration factor, } \mu g./\text{absorbance unit with curve, absorbance units}/\mu g.$

9.2.1 Conversion of µg./m.<sup>3</sup> to p.p.m.—If desired, the concentration of sulfur dioxide may be calculated as p.p.m. SO<sub>2</sub> at standard conditions as follows:

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

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PART 2

A. Gaseous calibration. Certified permeation tubes containing liquified sulfur dioxide are available from the National Bureau of Standards and may be used for gaseous calibration.

(1) Commercially available permeation tubes\* may be calibrated as follows: Obtain an FEP Teflon permeation tube that emits sulfur dioxide at a rate of 0.2 to 0.4  $\mu\text{g./min.}$  (0.08 to 0.15  $\mu\text{l./min.}$  at standard conditions of 25° C. and 1 atmosphere.) A permeation tube with an effective length of 2 to 4 cm., and outer diameter of 0.63 cm. will yield the desired permeation rate if held at a constant temperature of 20° C. Using the system shown in Figure 2, calibrate the tube gravimetrically at the intended operating temperature to a precision within  $\pm 2$  percent. The temperature of the tube must be controlled within 0.1° C. Permeation tubes are calibrated under a stream of dry nitrogen to prevent the formation of blisters in the walls and sulfuric acid inside the tube. Periodically, about every 4 days, remove the bubbler from the constant temperature bath and thoroughly dry the bubbler. Remove the permeation tube from the bubbler with a Teflon-tipped forcep and weigh the tube to the nearest 0.1 mg. Record weight and time to the nearest minute. Immediately return tube to bubbler and bubbler to bath. Plot gross weight (10 mg. to the inch) against time (1,000 minutes to the inch). Compute the slope of the linear portion from the line that best fits the points. Linear regression is recommended. Alternately, tubes can be rapidly calibrated using a coulometric  $\text{SO}_2$  analyzer operating under ideal conditions.<sup>14</sup>

(2) A system designed for the preparation of standard concentrations of sulfur dioxide in the laboratory is shown in Figure 3. (Alternately, the apparatus shown in Figure 2 for gravimetric calibration and field use may be used.) Assemble the apparatus, consisting of a water-cooled condenser, a constant-temperature water bath maintained at 20° C., a cylinder containing pure, dry air or nitrogen, and appropriate pressure regulators, needle valves, and flow meters for the nitrogen and dry air diluent gas streams. The diluent gases are brought to temperature by passage through a 2-meter copper coil immersed in the water bath. Insert a calibrated permeation tube into the central tube of the condenser maintained at 20° C. by circulating water from the constant-temperature bath and pass a stream of air or nitrogen over the tube at a fixed rate of approximately 50 ml./min. Dilute this gas stream to the desired concentration by varying the air flow rate. Normally this flow rate can be varied from 1.1 to 15 liters/min. The flow rate of the sampling system determines the lower limit for the flow rate of the diluent gases. With a tube permeating sulfur dioxide at a rate of 0.4  $\mu\text{g./min.}$ , the range of concentration of sulfur dioxide will be between 27 and 260  $\mu\text{g./m.}^3$  (0.01 to 0.14 p.p.m.), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate and use longer permeation tubes.

B. Procedure for preparing calibration curves. One can prepare a multitude of curves by selecting different combinations of sampling rate and sampling time. (Calibration should be made under the same conditions used in sampling and analyses). Twenty-four hour samples must be calibrated for 24 hours. The above description represents a typical procedure for simulating ambient air sampling of short duration. The system is designed to provide an accurate measurement of sulfur dioxide in the range of 0.01 to 0.5 p.p.m. It can be modified easily to meet special needs. The concentration of standard  $\text{SO}_2$  in air is computed as follows:

$$C = \frac{Pr \times 10^3}{R + r}$$

C = Concentration of  $\text{SO}_2$ ,  $\mu\text{g./m.}^3$

Pr = Permeation rate,  $\mu\text{g./min.}$

R = Flow rate of diluent air, liters/min.

r = Flow rate of diluent nitrogen, liters/min.

Data for a typical calibration curve are listed in Table I. A plot of the concentration of sulfur dioxide in  $\mu\text{g./m.}^3$  (X-axis) against absorbance of the final solution (Y-axis) will yield a straight line, the reciprocal of the slope of which is the factor for conversion of absorbance to  $\mu\text{g./m.}^3$ . This factor includes the correction for collection efficiency. Any deviation from linearity at the lower concentration range indicates a change in collec-

tion efficiency of the sampling system. Actually, the standard concentrations of 25  $\mu\text{g./m.}^3$  and below of sulfur dioxide are slightly below the dynamic range of the method. If this is the range of interest, the diluent air stream must be adjusted to deliver these lower concentrations, and the total volume of air collected must be increased to obtain sufficient color within the dynamic range of the procedure. The calibration factor must be reestablished, if collection efficiency differs significantly from that obtained above 25  $\mu\text{g./m.}^3$ . The remainder of the analytical procedure is the same as described in section 7.

TABLE I—TYPICAL CALIBRATION DATA

Concentrations of $\text{SO}_2$ , $\mu\text{g./m.}^3$	Amount of $\text{SO}_2$ in $\mu\text{g.}$ for 30 liters	Absorbance of sample
15	0.45	0.013
25	0.75	0.022
100	3.0	0.089
200	6.0	0.179
500	15.0	0.448
1000	30.0	0.710
1600	30.0	0.893
1100	33.0	0.985

$$\text{SO}_2, \mu\text{g./m.}^3 = A \times F,$$

Where:

F =  $1.1 \times 10^3$  = factor, as derived from equation in 9.2.

A = Absorbance of solution for 30 liters of sample and a volume of 25 ml. for the colored solution.

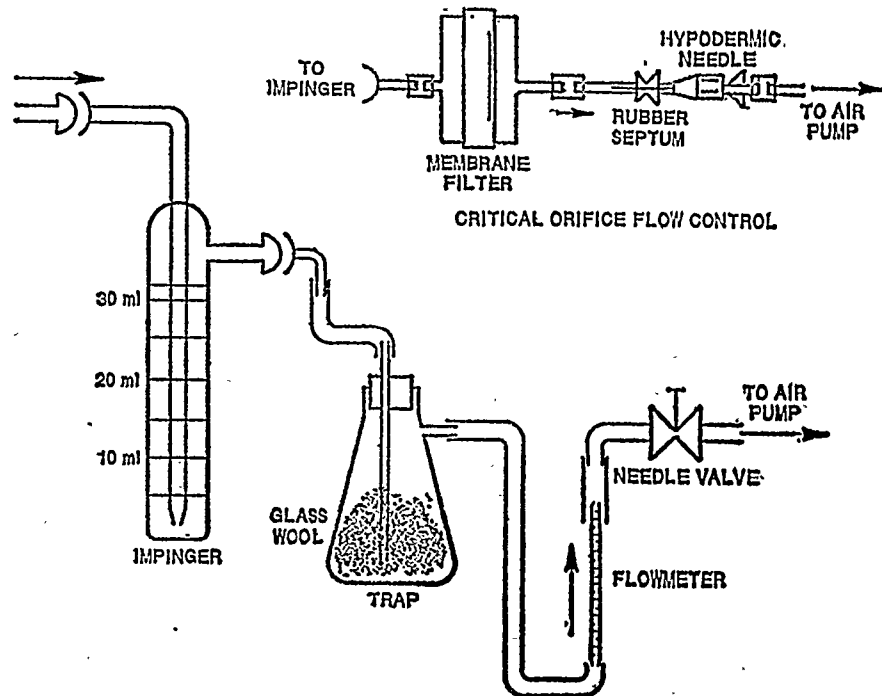


Figure 1. Sampling train.

\*Available from Metronics, Inc., 3201 Porter Drive, Palo Alto, CA 94304 and Analytical Instrument Developments, Inc., 250 South Franklin Street, West Chester, PA 19380.

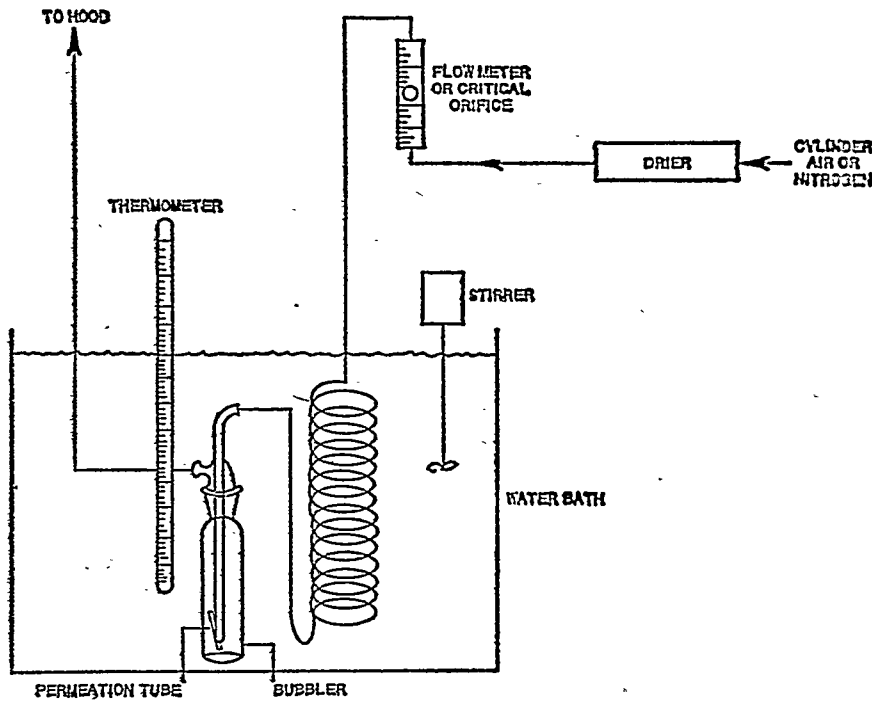


Figure 2. Apparatus for gravimetric calibration and field use.

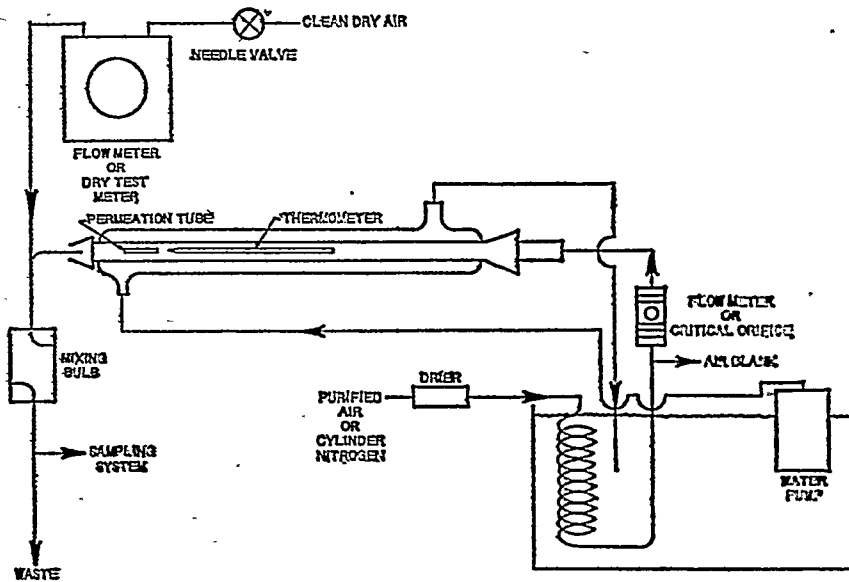


Figure 3. Permeation tube schematic for laboratory use.

APPENDIX B

PROCEDURE FOR DETERMINATION OF SUSPENDED PARTICULATES (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<sup>3</sup>/min.; 40 to 60 ft.<sup>3</sup>/min.) that allows suspended particles having diameters of less than 100 μm, (Stokes equivalent diameter) to pass to the filter surface.<sup>1</sup> The particles are ordinarily collected on a glass-fiber filter within the size range of 100 to 0.1 μm diameter.

1.2 The mass concentration of suspended particulate in the ambient air (μg./m.<sup>3</sup>) is

computed by measuring the mass of collected particulate and the volume of air sampled.

1.3 This method is applicable to measurement of the mass concentration of suspended particulate in ambient air. This method does not control the flow of air during sampling and for this reason is most applicable to trend measurement. 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<sup>3</sup>/min. (60 ft.<sup>3</sup>/min.) for 24 hours, an adequate sample will be obtained even in an atmosphere having concentrations of suspended particulate as low as 1 μg./m.<sup>3</sup> 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 particulate in ambient air, a standard sampling period of 24 hours is recommended.

2.2 Weights are determined to the nearest milligram; air flow rates are determined to the nearest 0.03 m<sup>3</sup>/min. (1.0 ft.<sup>3</sup>/min.) times are determined to the nearest 2 min. and mass concentrations are reported to the nearest microgram per cubic meter.

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

3.2 Glass-fiber filters are comparatively insensitive to change in relative humidity, but collected particulate can be hygroscopic.<sup>2</sup>

4. Precision, accuracy, and stability. 4.1 At an average mass concentration of 112 μg./m.<sup>3</sup> of particulate matter in ambient air the standard deviation is 10 μg./m.<sup>3</sup> (corresponding to a relative standard deviation of 9 percent); at an average of 39 μg./m.<sup>3</sup> the standard deviation is 6 μg./m.<sup>3</sup> (corresponding to a relative standard deviation of 15 percent).<sup>3</sup>

4.2 The accuracy with which the sampler measures the true average concentration depends upon the degree of constant air flow rate maintained in the sampler. The air flow rate is affected by the concentration and the nature of the dust in the atmosphere, which may clog the filter and significantly reduce the air flow rate. Under these conditions the error in the measured average concentration may be as much as ±50 percent or more of the true average concentration, depending on the amount of reduction of air flow rate and on the variation of the mass concentration of dust with time during the 24-hour sampling period.<sup>4</sup>

5. Apparatus. 5.1 Sampling.

5.1.1 Sampler—The sampler consists of three units: (1) the face plate and gasket, (2) the filter adapter assembly, and (3) the motor unit. Figure 1 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.<sup>2</sup> (63 in.<sup>2</sup>) portion of a clean 20- by 25-cm. (8- by 10-in.) glass-fiber filter at a rate of at least 1.70 m<sup>3</sup>/min. (60 ft.<sup>3</sup>/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 air-tight 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 environmental conditions such as high and low temperatures, extremes of 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 sample 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 clearance area between the edge of the roof and the main housing should be 645±65 cm.<sup>2</sup> (100±10 in.<sup>2</sup>). The main housing should be rectangular, with dimensions of 29 by 38 cm. (11½ by 14 in.).

5.1.3 Rotameter—Marked in arbitrary units, frequently 0 to 70, and capable of being calibrated.

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. 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. (3½ in.) in diameter and 0.24 cm. (¾ in.) thick with a central orifice 2.9 cm. (1½ 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 on to 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.

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

5.1.6 Flow Measuring Device—Positive displacement type; 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.

5.1.8 Folders—Manila cardboard folders, 22 by 28 cm. (8½ by 11 in.) creased.

## 5.2 Analysis.

5.2.1 Balance Room Environment—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- by 25-cm. (8- by 10-in.) filters and having a sensitivity of 0.1 mg.

5.2.3 Light Table—Of the type used to view X-ray films.

5.2.4 Numbering Machine—Capable of printing identification numbers of 4 to 8 digits on the filter.

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 particulate, although some other medium, such as paper, may be desirable for some analyses. Care must be exercised to prevent use of filters that contain high 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—Place each filter on a light table and inspect for pinholes, dark particles, or other imperfections. Filters with visible imperfections should not be used. A small brush is useful for removing particles. Equilibrate the filters to the conditions of the balance room 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 face plate from the filter holder. Install a numbered, preweighted, glass-fiber filter in position (rough side up), replace the face plate without disturbing the filter, and fasten securely. Undertightening will allow air leakage, overtightening will damage the sponge-rubber face-plate gasket. A very light application of talcum powder may be used on the sponge-rubber face-plate 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 min., 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. Let the sampler run for the desired time (usually 24 hours) and take a final rotameter reading. Record the final rotameter reading and ending time and date on the filter folder. Remove the face plate 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 particulate are in contact, and place in a filter 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.

## 7.1.3 Maintenance.

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

7.1.3.2 Face Plate Gasket—Replace when the margins of samplers are no longer sharp. Seal the gasket to the face plate with rubber cement or double-sided adhesive tape.

7.1.3.3 Rotameter—clean as required, using alcohol.

## 7.2 Analysis

7.2.1 Equilibrate the exposed filters for 24 hours in the environment of the balance room, then reweigh. After they are weighed, the filters may be saved for detailed chemical analysis.

8. Calibration. 8.1 Sampling—Since only a small portion of the total air sampled passes through the rotameter during measurement, the rotameter must be calibrated against actual air flow 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, air flows (usually six) are obtained for definite time periods. Record the reading on the differential manometer at each air flow. The different constant air flows can be obtained either by placing a series of load plates, one at a time, between the calibration unit and the primary standard or by varying the speed of the sampler motor with a variable speed transformer with the No. 18 plate in position. The latter method is considerably more convenient and flexible. 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 air 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 end open to the atmosphere. During each of the constant air flow measurements made

above, measure the true inlet pressure of the primary standard with this second differential manometer. Measure atmospheric pressure with a barometer. Correct the measured air volume to true air volume as directed in 9.1.1 then obtain true air flow rate,  $Q$ , as directed in 9.1.2. 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 min. 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, air flows (usually six). Record the reading of the differential manometer on the orifice calibration unit, and record the reading of the rotameter at each flow. Convert the differential manometer reading to  $m^2/min.$ ,  $Q$ , then plot rotameter reading versus  $Q$ .

8.1.2.1 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 in Appendix C. 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  $m^2/min.$ ; 20 to 78  $ft^2/min.$ ).

## 9. Calculations. 9.1 Calibration of Orifice.

9.1.1 Calculate the true air volume measured by the positive displacement primary standard.

$$P_a V_a = P_M V_M \\ P_M = P_a - P_m$$

Combining these relationships:

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

$V_a$  = Volume of air at atmospheric pressure,  $m^3$

$P_a$  = Barometric pressure, mm. Hg.

$P_M$  = Pressure at inlet of the primary standard, mm. Hg.

$P_m$  = Pressure difference between inlet of primary standard and atmospheric, mm. Hg.

$V_M$  = Volume measured by primary standard,  $m^3$

### 9.1.1.1 Conversion Factors:

In. water  $\times 73.48 \times 10^3 =$  in. Hg.

In. Hg.  $\times 25.4 =$  mm. Hg.

Cubic feet  $\times 0.0284 = m^3$

### 9.1.2 Calculate flow rate:

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

$Q$  = Flow rate,  $m^3/min.$

$T$  = Time of flow, min.

## 9.2 Sample Volume.

9.2.1 Convert the initial and final rotameter readings to  $m^2/min.$  using calibration curve of 8.1.2.

9.2.2 Calculate volume of air sampled.

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

$V$  = Air volume sampled,  $m^3$

$Q_i$  = Initial air flow rate,  $m^2/min.$

$Q_f$  = Final air flow rate,  $m^2/min.$

$T$  = Sampling time, min.





## PROPOSED RULE MAKING

p.p.m. CO=mg. CO/m.<sup>3</sup>×0.873

10. *Bibliography.* 1. MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Pittsburgh, Pa.

2. Beckman Instruction 1635B, Models 215A, 315A, and 415A Infrared Analyzers, Beckman Instrument Co., Fullerton, Calif.

3. Continuous CO Monitoring System, Model A 5611 Intertech Corp., Princeton, N.J.

4. Bendix-UNOR Infrared Gas Analyzers, Ronceverte, W.Va.

11. *Definitions of performance specifications used in this method—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  $\pm$  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 inlet concentration.

*Fall time (90 percent).* The interval between initial response time and time to 90 percent response time 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 up-scale value; usually expressed as percent full scale.

*Precision.* The degree of agreement between repeated measurements of the same concentration and 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.

12. *Suggested minimum performance specifications for NDIR carbon monoxide analyzers.*

Range (minimum)---	0-58 mg./m. <sup>3</sup> (0-50 p.p.m.).
Output (minimum)---	0-10, 100, 1,000, 5,000 mv. full scale.
Minimum detectable sensitivity.	0.6 mg./m. <sup>3</sup> (0.5 p.p.m.).
Lag time (maximum)---	15 seconds.
Time to 90% response (maximum).	30 seconds.
Rise time (90% maximum).	15 seconds.
Fall time (90% maximum).	15 seconds.
Zero drift (maximum).	3%/week not to exceed 1%/24 hours.

Span drift (maximum).	3%/week not to exceed 1%/24 hours.
Precision (maximum).	$\pm$ 0.5%.
Operational period (minimum).	3 days.
Noise (maximum)---	$\pm$ 0.5%.
Interference equivalent (maximum).	1% of full scale.
Operating temperature range (minimum).	5-40° C.
Operating humidity range (minimum).	10-100%.
Linearity (maximum).	1%.

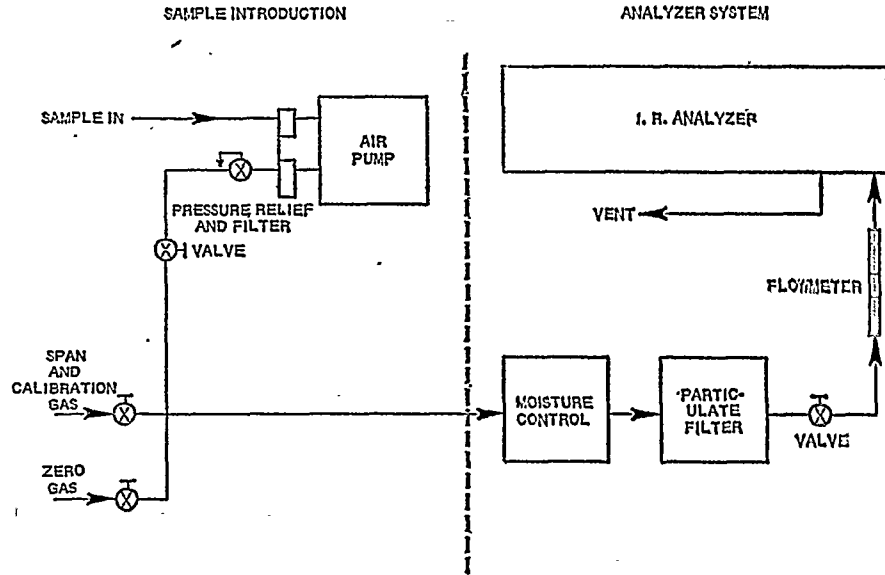


Figure 1. Carbon monoxide analyzer flow diagram.

## APPENDIX D

## METHOD FOR DETERMINATION OF OXIDANTS (NEUTRAL BUFFERED POTASSIUM IODIDE METHOD)

1. *Principle and applicability.* 1.1 A sample of ambient air is drawn through a chromium trioxide scrubber to remove sulfur dioxide and then through two absorbers in series containing potassium iodide reagent to collect the oxidants.

1.2 Oxidants are defined by this method as those compounds capable of liberating iodine from a 1 percent potassium iodide solution buffered with disodium phosphate and potassium dihydrogen phosphate. The iodine produced in the absorbing reagent is measured spectrophotometrically as the tri-iodide ion.

1.3 This method is intended for the measurement of total oxidants as ozone in the atmosphere. However, the various oxidizing species, such as ozone, nitrogen dioxide, peroxyacetyl nitrate, and peroxides are present in widely varying concentrations and react with the reagent at different rates. Also, reducing compounds in the atmosphere have a negative effect on the oxidant reading. Thus the number obtained is a "net" oxidant value, which describes a condition of the atmosphere and is not the total concentration of the oxidizing species present.

2. *Range and sensitivity.* 2.1 Concentrations of oxidants in the range of about 20 to 20,000  $\mu\text{g./m.}^3$  (0.01 to 10 p.p.m.) can be determined.

2.2 At a sampling rate of 2 liters/min. for 15 min. using 10 ml. absorbing reagent, 20  $\mu\text{g./m.}^3$  (0.01 p.p.m.) should produce an absorbance of approximately 0.025 measured in

1-cm. cells. At concentrations below 100  $\mu\text{g./m.}^3$  (0.05 p.p.m.) readings may be quite imprecise because of the instability of oxidants or iodine at very low concentrations.

2.3 The above limits are based on a molar absorptivity of 24,200 liters/mole/cm.

3. *Interferences.* 3.1 Reducing gases such as sulfur dioxide and hydrogen sulfide give very serious negative interferences. Sulfur dioxide gives a 100 percent negative interference of an equivalent molar concentration of ozone. The interference from sulfur dioxide, even when it is present at ambient concentrations, can be eliminated by a properly conditioned chromium trioxide-scrubber (see 6.3, 7.1).

3.2 The oxidant reading contains a contribution of 10 percent of the molar concentration of  $\text{NO}_2$ . When a chromium trioxide scrubber is used,  $\text{NO}$  is converted to  $\text{NO}_2$ , thus contributing to the oxidant reading to the same extent as  $\text{NO}_2$ . If an oxidant value less  $\text{NO}_2$  is desired,  $\text{NO} + \text{NO}_2$  must be measured simultaneously and a correction factor of 10 percent of the  $\text{NO}_{10}$  concentration must be subtracted.

3.3 Glassware should be cleaned with chromic acid, since dust or foreign materials may interfere.

3.4 Direct sunlight will affect the iodine concentration.

4. *Precision, accuracy, and stability.* 4.1 4-5 percent relative standard deviation can be obtained at a concentration of 1,000  $\mu\text{g./m.}^3$  (0.5 p.p.m.) of ozone.

4.2 Accuracy cannot be defined, since the sensitivity of the potassium iodine reagent varies widely with the different oxidizing species.

4.3 Analysis should be completed immediately after sampling to obtain consistent results. This is necessary because some oxidants release iodine slowly to enhance color, while fading due to slow decomposition of iodine may occur.

5. Apparatus—5.1 Absorber. All-glass impingers as shown in Figure 1 are recommended. These impingers may be purchased from major glassware suppliers. Two absorbers in series are needed to insure complete collection of the sample.

5.2 Air pump. Capable of drawing 2 liters/min. through the absorbers. The pump should be equipped with a needle valve at the inlet side to regulate flow. If a critical orifice (5.7) is used, the pump must be capable of maintaining 0.7 atmosphere vacuum.

5.3 U tube. 140 ml, for the chromium trioxide scrubber.

5.4 Thermometer. Or other temperature-measuring device with an accuracy of  $\pm 2^\circ$  C.

5.5 Barometer. Atmospheric, accurate to the nearest mm. Hg.

5.6 Wet test meter. 1 or 3 liters/revolution.

5.7 Flowmeter. Calibrated metering device for measuring flow of 2 liters/min. within  $\pm 5$  percent. A 20-gauge hypodermic needle 1 in. long acting as a critical orifice can be used to give a flow of approximately 2 liters/min.

5.8 Drying tube. Containing an indicating drying agent to protect flowmeter.

5.9 Prescrubber. Tube filled with granular  $MnO_2$  and charcoal to remove oxidants.

5.10 Volumetric flasks. 25, 100, 500, 1,000 ml.

5.11 Buret. 50 ml.

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

5.13 Erlenmeyer flasks. 300 ml.

5.14 Oven. Capable of maintaining  $105^\circ$  C.

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

6. Reagents—6.1 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.

6.2 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), and 10.0 g. potassium iodide (KI) in purified water and dilute to 1,000 ml. The pH should be  $6.8 \pm 0.2$ . Store the solution in a glass-stoppered amber bottle in a cool, dark place. It is stable for several weeks.

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

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

6.4 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. boiling water. Continue boiling until the solution is clear, then allow to cool, and transfer to glass-stoppered bottle.

6.5 Standard iodine solution (0.05 N)—6.5.1 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.

6.5.2 Standardization. Pipet accurately 50 ml. standard arsenious oxide solution into a 300-ml. Erlenmeyer flask. Acidify slightly with a 1:10 dilution of 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 at end of titration by adding 1 ml. of 1:10 sulfuric acid just before the end point is reached.

6.6 Chromium trioxide scrubber. Dissolve 125 g. chromium trioxide ( $CrO_3$ ) crystals in 35 ml. concentrated sulfuric acid and add to 750 ml. distilled water. Place a 15-by-25-cm. sheet of a flash-fired glass-fiber filter in an oven rack equipped with glass rod attachments to prevent the filter from touching metal. Saturate the filter with 10 ml. chromium trioxide solution. Place the filter in an oven set at  $65-70^\circ$  C. for 1 hour. A freshly prepared filter is brownish pink. At the end of this time remove the filter and fold every 1.3 cm. along the 15-cm. dimension in an accordion fashion. While the sheet is folded, cut the 15-cm. length into 10 equal widths. As each strip is cut, place it in the 140-ml. U-tube. Place five cut strips in each tube, rotating alternate strips  $90^\circ$  so that folds will not match. Before the scrubber is used for sampling, condition for several hours to ozone at a high concentration from an ozone source such as a UV photolysis lamp. As the filters absorb moisture, scrubbing efficiency is decreased. This condition is evident as a green color. Caution: When working with chromium trioxide and sulfuric acid, wear gloves to prevent irritation of the skin.

7. Procedure—7.1 Sampling. Assemble the apparatus as shown in Figure 1. Use ground-glass connections upstream from the impinger. Butt-to-butt connections with Tygon tubing may be used. Check assembled system for leaks. Pipet 10 ml. absorbing reagent into first absorber and place  $MnO_2$  prescrubber on the sample probe. Draw air through the prescrubber and the sampling train for 15 min. at 2 liter/min. If an absorbance reading at 352 nm. is obtained, repeat until zero or constant absorbance is obtained. This system blank absorbance should be subtracted from the absorbance of the first absorber when analyzing for oxidants. Remove the prescrubber. Pipet 10 ml. absorbing reagent into each absorber. Draw ambient air through the sampling train at 2 liters/min. for 15 min.

7.2 Analysis. Immediately transfer the solutions from each absorber to separate clean 1-cm. cells. Determine the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference. Add the absorbance of the two solutions to obtain total absorbance. Read total  $\mu g. O_3$  from the calibration curve (see 8.2).

8. Calibration, standards, and efficiencies—8.1 Sampling. The flowmeter must be calibrated with the sampling train assembled and solution in the absorbers. Connect the wet test meter to the sample probe and calibrate the flowmeter.

8.2 Analysis. Pipet 1 ml. standard iodine solution into a 100-ml. volumetric flask. Dilute to mark with absorbing reagent. Prepare fresh before use. Into a series of 25-ml. volumetric flasks, pipet 0.5, 1, 2, 3, and 4 ml. of diluted standard iodine solution, and 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. Calculate the concentration of the solutions as total  $\mu g. O_3$ , as follows:

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

N = Normality  $I_2$  (see 6.5.2), meq./ml.

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

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

8.3 Sampling efficiency. Sampling efficiency in the first absorber may be 90-95 percent depending upon the impinger orifice and the ozone concentration. When two absorbers are placed in series essentially all ozone is collected.

9. Calculations—9.1 Sampling. Correct the volume of air sampled to the volume at standard conditions of  $25^\circ$  C. and 760 mm. Hg.

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

$V_s$  = Volume of air at standard conditions, liters.

V = Volume of air at sampling conditions, liters.

P = Barometric pressure of mercury, mm. Hg.

t = Temperature of sample,  $^\circ$ C.

9.2 Calculate ozone concentration in  $\mu g./m.^3$  at standard conditions.

$$\mu g. O_3/m.^3 = \frac{A (10^3)}{V_s}$$

A = Total  $\mu g. O_3$  read from calibration curve.

$10^3$  = conversion of liters to cubic meters.

$V_s$  = volume sampled at standard conditions, liters.

9.2.1 If desired, concentration of oxidant may be calculated as p.p.m.  $O_3$  at standard conditions of  $25^\circ$  C. and 760 mm. Hg.

$$\text{p.p.m. } O_3 = (\mu g. O_3/m.^3) (5.034 \times 10^{-4})$$

Derivation of above equation:

(1) Total  $\mu g. O_3 = [N_0 \text{ (meq./ml.)} \times (10 \text{ ml.)} + (24,000 \mu g./\text{meq.})]$

(2)  $N_0$  = Normality of diluted calibration standard.

$$N_0 = \left[ \frac{1}{100} (\text{1st dilution}) \times \frac{V}{25} (\text{2nd dilution}) \right]$$

(3) Therefore: Total  $\mu g. O_3 = (N) (96) (V)$ .

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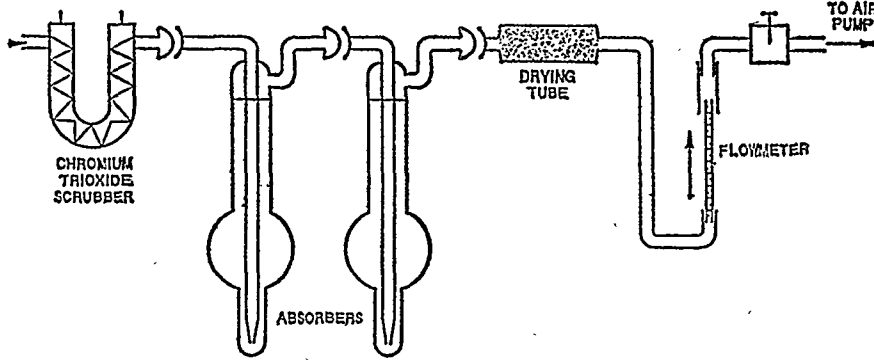


Figure 1 Sampling train.

## APPENDIX E

## PART 1: METHOD FOR CONTINUOUS MEASUREMENT OF HYDROCARBONS (FLAME IONIZATION METHOD)

**1. Principle and applicability.** 1.1 The sampling system is an integral part of the most commercial total hydrocarbon analyzers designed to measure continuously the concentration of hydrocarbons (and other organic compounds) in the atmosphere. The sample line is attached to the inlet and the sample is pumped into a flame ionization detector. A sensitive electrometer coupled with a potentiometric recorder detects the increase in ion intensity resulting from the introduction into a hydrogen flame of a sample of air containing any organic compound (e.g. hydrocarbons, aldehydes, alcohols). The response is approximately proportional to the number of carbon-hydrogen bonds in the sample. The analyzer is calibrated using methane and the results reported as methane equivalents. See addendum for description of method for measurement of methane.

1.2 The sample introduction pump may be bypassed for analysis of gases under pressure as is done with calibration gases.

**2. Range and sensitivity.** 2.1 The range of the analyzer may be varied so that full scale may be 2.6 mg./m.<sup>3</sup> (4 p.p.m.) to 1960 mg./m.<sup>3</sup> (3,000 p.p.m.) hydrocarbon as methane by varying the attenuation and the sample flow rate to the detector. The 13 mg./m.<sup>3</sup> (20 p.p.m.) range is normally for atmospheric sampling.

2.2 Sensitivity is 1 percent of full scale recorder response.

**3. Interferences.** 3.1 Carbon atoms bound to oxygen, nitrogen, or halogens give reduced or no response. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor.

**4. Precision accuracy and stability.** 4.1 Precision is approximately 0.5 percent full recorder scale on the 13 mg./m.<sup>3</sup> (20 p.p.m.) scale.

4.2 Accuracy is dependent on instrument linearity and absolute concentration of the calibration gases used. Generally, accuracy is  $\pm 1$  percent of full scale on the 0-13 mg./m.<sup>3</sup> range.

4.3 Zero drift necessitates frequent calibration. The magnitude of the drift depends on the air flow rate, sample flow rate, fuel flow rate, ambient temperature changes, detector contamination, and electronic drift. Zero drift observations on various instruments indicate 2 percent/24 hours on the 13 mg./m.<sup>3</sup> scale.

**5. Apparatus—5.1 Commercially available total hydrocarbon analyzer.** Instruments obtained should be installed on location and demonstrated preferably by the manufacturer to meet or exceed manufacturers

specifications and those described in this method. Generally, hydrocarbon analyzers consist of a regulated fuel and air delivery system for the hydrocarbon burner, a regulated sample injection system, electrometer for measuring the flame ion current, meter readout with connections for a recorder, and a sample pump.

**5.2 Recorder.** Potentiometric type, compatible with analyzer with an accuracy of 0/5 percent or better.

**5.3 Sample line.** Any tubing that is not a source interferences or an absorbant of hydrocarbons. Inert materials such as glass, stainless steel, and Teflon are recommended.

**6. Reagents—6.1 Combustion air.** High purity air containing less than 1.3 mg./m.<sup>3</sup> (2 p.p.m.) hydrocarbon as methane.

**6.2 Fuel.** Hydrogen or a hydrogen-inert gas mixture; when ordering specify hydrocarbon-free gas. A hydrogen generator is strongly advised for safety reasons.

**6.3 Zero gas.** Less than 0.05 mg./m.<sup>3</sup> (0.1 p.p.m.) hydrocarbon as methane in air.

**6.4 Span gas.** Methane in air corresponding to 80 percent of full scale, 10.4 mg./m.<sup>3</sup> (16.0 p.p.m.) for 13 mg./m.<sup>3</sup>. A certified or guaranteed analysis is required.

**7. Procedure.** 7.1 For specific operating instructions, see the manufacturer's manual.

**8. Calibration and efficiencies.** 8.1 Calibrate the instrument at the desired flow rate and attenuator setting. Introduce zero gas and set zero control to indicate proper value on the recorder. If a live zero recorder is not used, it is recommended that the zero setting be offset at least 5 percent of scale to allow for negative zero drift. In this case, the span setting must also be offset by an equal amount. Introduce span gas and adjust span control to indicate proper value on recorder scale (e.g. 0-13 mg./m.<sup>3</sup> (0-20 p.p.m.) scale set a 10.4 mg./m.<sup>3</sup> (16.0 p.p.m.) standard to read 80 percent recorder chart). Recheck zero and span until adjustments are no longer necessary. Since the scale is linear, the two-point calibration is valid.

8.1.1 If attenuation is varied, some discrepancy between the true attenuation and the nominal attenuation may exist. The instrument should be calibrated using appropriate standards at each attenuator setting used.

**9. Calculations.** 9.1.1 The recorder is read directly for hydrocarbon concentration.

## PART 2: METHOD FOR MEASUREMENT OF METHANE

**1. Principle and applicability.** 1.1 The atmospheric sample is continuously passed through a treated charcoal column before introduction into the instrument. This column will selectively strip all hydrocarbons other than methane and give a specific analyses for methane.<sup>1</sup> The methane level is continuously monitored by flame ionization techniques.

1.2 The technique may be applied to a gaseous sample containing low concentrations of methane, since the instrument can sample gases at 5 p.s.i. or more pressure or at ambient pressure.

**2. Range and sensitivity.** 2.1 The ranges available on commercial continuous hydrocarbon analyzers are commonly 0 to 10 p.p.m. and 0 to 100 p.p.m. A sensitivity of 0.1 p.p.m. can be obtained in the 0 to 10 p.p.m. range.

**3. Interferences.** 3.1 Ethane is the hydrocarbon most likely to break through the carbon column when ambient urban air is sampled. Thus, service life of the column is measured by introducing known concentrations of ethane in amounts equal to the daily average peak for the sampling zone (ref. 1). This service life has been found to be as long as 6 days. The column must be purged with helium every 3 days.

**4. Precision, accuracy, and stability.** 4.1 Precision is  $\pm 1$  percent for successive identical samples under identical conditions.

4.2 Accuracy is dependent upon the accuracy of standards used to calibrate the instrument.

4.3 At normal temperature, the system is stable.

**5. Apparatus—5.1 Continuous hydrocarbon analyses.** The procedure described is for the Beckman 108A and 109A analyzers.

**5.2 Charcoal column.** A 5-inch long threaded nipple of  $\frac{1}{4}$ -inch pipe packed with 4.5 grams of  $\frac{1}{16}$  mesh activated charcoal. Cloth discs contain the charcoal. The freshly packed tube is blown out forcibly with helium for 2 minutes to remove fine dust, which otherwise would interfere with the detector operation.

**6. Reagents—6.1 Fuel gas.** Pure hydrogen or a 40 percent hydrogen/60 percent nitrogen mixture, relatively hydrocarbon free. A hydrogen generator may be used.

**6.2 Air.** Water-pumped cylinder air.

**6.3 Zero gas.** A calibration gas that contains a relatively low amount of hydrocarbons is required for setting the zero point. If the hydrocarbon content of the burner air is sufficiently low and accurately known, this gas can be used as the zero gas.

**6.4 Span gas.** The span gas is a certified calibration gas used to set an upscale standardization point.

**6.5 Helium.** Cylinder helium (water-pumped) is required to recondition the carbon filter.

**7. Procedure.** 7.1 Check that all units are properly connected according to the diagram. Turn on fuel gas. Allow fuel pressure to reach proper level according to flow desired. Slowly open the air cylinder valve. Adjust air pressure to about 30 p.s.i. Again adjust to obtain desired flow. Check all fittings for leaks. Insert a carbon column in position. Introduce sample and adjust to proper value. If all pressures inside analyzer are proper, turn on analyzer power switch and ignite burner. A small pop indicates that the flame has ignited. The analyzer meter should show an upscale deflection. Adjust attenuator to  $\times 30$  position, and adjust the zero and span\* controls so that meter reading is between 10 and 60. Proceed to calibration.

**8. Calibration, standards, and efficiencies.** 8.1 Check flow rates with a calibrated bubble flow meter so that sample flow corresponds to optimum values.

8.2 If the instrument has just been started, wait at least 3 hours before calibrating. Open the cylinder shut-off valves on the span and zero gas cylinders. Observe the sample pressure gauge and adjust to the proper value. Connect the zero gas to the carbon column so that it goes through the column before passing into the analyzer. Allow the instrument to run on zero gas for 5

\*Span control has been added to the Beckman analyzer for convenience.

to 10 minutes. Disconnect the zero gas and connect the span gas to the column so that span gas passes through the column before the analyzer. Allow the instrument to run 5 to 10 minutes. Remove the old column and insert a freshly purged carbon column. Observe the analysis tag attached to zero-gas cylinder and note the indicated p.p.m. Disconnect the span gas and reconnect the zero gas, wait until reading has stopped changing, then adjust the ZERO control to bring the recorder pen to the same reading (in p.p.m.) as indicated on analysis tag. Reconnect the span gas and adjust the recorder with SPAN control to indicated value in p.p.m. Repeat zero and span adjustment until no further adjustments are required. Connect the column back to sample air. Check to see that the sample pressure gauge reading is still the same as originally set. Turn off the zero and span cylinder valves.

9. Calculation. 9.1 Meter is read directly in p.p.m. as CH<sub>4</sub>.

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APPENDIX F

METHOD FOR 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. A dilute solution of sodium nitrite is produced, which need not be analyzed immediately.

1.2 The nitrite ion produced during sampling is determined colorimetrically by reacting the exposed absorbing reagent with phosphoric acid, sulfanilamide, and N-(1-naphthyl)-ethylenediamine dihydrochloride.

1.3 The methods of sampling and analysis are applicable to field collection of 24-hour samples and return to a central laboratory for analysis.

2. Range and sensitivity. 2.1 The range of the analysis is 0.04 to 1.5 µg. NO<sub>2</sub>/ml. For the efficiency stated in section 8.3, 50 ml. absorbing reagent, and a sampling rate of 200 ml./min. for 24 hours; the range of the method is 20-740 µg./m.<sup>3</sup> (0.01-0.4 p.p.m.) nitrogen dioxide.

2.2 A nitrite concentration of 0.04 µg. NO<sub>2</sub>/ml. will produce an absorbance of 0.02 with 1-cm. cells.

3. Interferences. 3.1 The interference of sulfur dioxide is eliminated by conversion to sulfuric acid with hydrogen peroxide before analysis.<sup>1</sup>

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 µg./m.<sup>3</sup> (0.072 p.p.m.) and 200 µg./m.<sup>3</sup> (0.108 p.p.m.). These data are based on 10 samples collected from test atmospheres generated with nitrogen dioxide permeation tubes are analyzed by automating the procedure with a Technicon Autoanalyzer.

4.2 No accuracy data are available.

4.3 Collected samples are stable for at least 6 weeks.

5. Apparatus—5.1 Sampling. See Figure 1.

5.1.1 Absorber—Polypropylene tubes 164 by 32 mm., equipped with polypropylene two-port tube closures. Rubber stoppers cannot be used because high and varying blank values are obtained. A gas dispersion tube with a fritted disc 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 the frit in one hole of a two-hole rubber stopper and install the frit in a tube containing sufficient distilled water to cover. 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=Vacuum, mm. Hg.

5.1.2 Probe. Teflon or glass tube with a polypropylene or glass funnel at the end and a membrane filter to protect the frit. Replace filter after use with no more than five samples.

5.1.3 Flow control device. Calibrated 27-gauge hypodermic needles, 3/8-in. long. The needle should be protected by a membrane filter or fiber glass filter. Change filter after use with 10 samples.

5.1.4 Air pump. Capable of maintaining a flow of 0.2 liter/min. through the absorber, and a vacuum of 0.7 atmosphere.

5.1.5 Calibration equipment. One ball-float flowmeter for measuring air flows up to approximately 275 ml./min., one stopwatch, and one 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 ml.

5.2.4 Test tube.

5.2.5 Spectrophotometer or colorimeter. Capable of measuring absorbance at 540 nm. Band width is not critical.

6. Reagents—6.1 Sampling.

6.1.1 Absorbing reagent. Dissolve 4.0 g. sodium hydroxide and dilute to 1,000 ml. with distilled water.

6.2 Analysis.

6.2.1 Sulfanilamide. Dissolve 20 g. sulfanilamide in 700 ml. distilled water. Add, with mixing, 50 ml. 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-naphthyl)-ethylenediamine 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 is stable for a month if protected from light.

6.2.4 Standard nitrite solution. Dissolve sufficient desiccated sodium nitrite (NaNO<sub>2</sub>, assay of 97 percent or greater) and dilute with distilled water to 1,000 ml. so that a solution containing 100 µg. NO<sub>2</sub>/ml. is obtained. The amount of NaNO<sub>2</sub> to use is calculated as follows:

$$G = \frac{1.500}{A} \times 1000$$

G = Amount of NaNO<sub>2</sub>, g.

1.500 = Gravimetric factor in converting NO<sub>2</sub> into NaNO<sub>2</sub>.

A = Assay, percent.

7. Procedure—7.1 Sampling. Assemble the sampling train as shown in Figure 1. 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. Sample for 24 hours 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-min. color development interval, measure the absorbance at 540 nm. against the blank. Read µg. NO<sub>2</sub>/ml. from standard curve (section 8.2).

8. Calibration and efficiencies—8.1 Sampling.

8.1.1 Calibration of ball float 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 air flow 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<sub>2</sub>/ml. solution to 200 ml. with absorbing reagent. This solution contains 25 µg. NO<sub>2</sub>/ml. Pipette 1, 2, 5, and 15 ml. of the 25 µg. NO<sub>2</sub>/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<sub>2</sub>/ml. respectively. Run standards as instructed in 7.2 Plot absorbance vs. µg. NO<sub>2</sub>/ml.

8.3 Efficiencies. An overall average efficiency of 35 percent was obtained from test atmospheres having nitrogen dioxide concentrations of 140 µg./m.<sup>3</sup> and 200 µg./m.<sup>3</sup> by automated analysis.<sup>2</sup>

9. Calculation—9.1 Sampling.

9.1.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-4}$$

V = Volume of air sampled, m.<sup>3</sup>

F<sub>1</sub> = Measured flow rate before sampling, ml./min.

F<sub>2</sub> = Measured flow rate after sampling, ml./min.

T = Time of sampling, min.

10<sup>-4</sup> = Conversion of ml. to m.<sup>3</sup>

9.2 Calculate the concentration of nitrogen dioxide as µg. NO<sub>2</sub>/m.<sup>3</sup>

$$\mu\text{g. NO}_2/\text{m.}^3 = \frac{(\mu\text{g. NO}_2/\text{ml.}) \times 50}{V \times 0.35} = \frac{(\mu\text{g. NO}_2/\text{ml.}) \times 143}{V}$$

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

V = Volume of air sampled, m.<sup>3</sup>

0.35 = Efficiency.

9.2.1 If desired, concentration of nitrogen dioxide may be calculated as p.p.m. NO<sub>2</sub> at 25° C. and 760 mm.

$$\text{p.p.m.} = (\mu\text{g. NO}_2/\text{m.}^3) \times 5.319 \times 10^{-4}$$

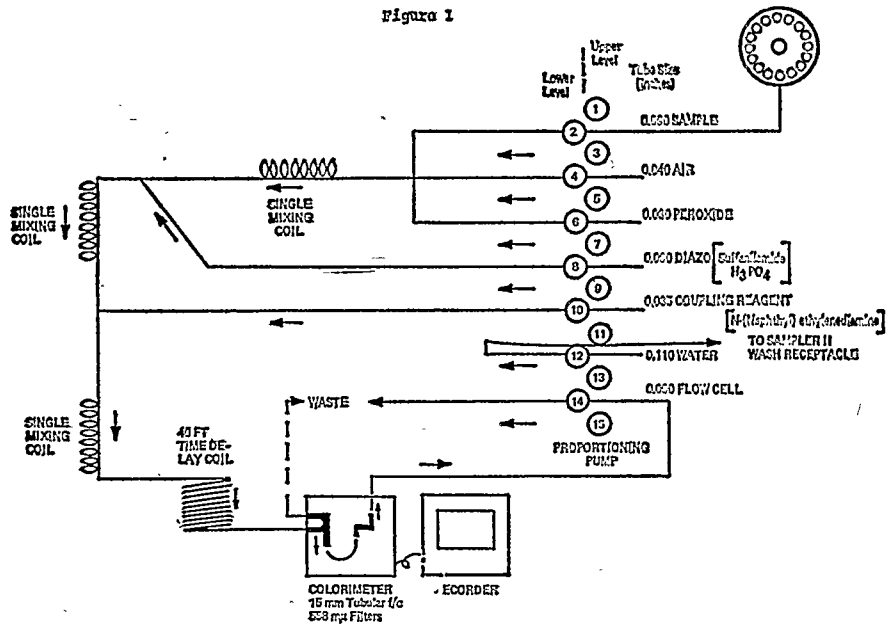
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PROPOSED RULE MAKING

Figure 1



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