SUBCHAPTER C—AIR PROGRAMS

PART 50—NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS

AMBIENT AIR QUALITY STANDARDS FOR OZONE

AUTHORITY: 42 U.S.C. 7401, *et seq.*

SOURCE: 36 FR 22384, Nov. 25, 1971, unless otherwise noted.

§ 50.1 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 (42 U.S.C. 1857–18571, as amended by Pub. L. 91–604).

(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 the ambient air for an air pollutant that is specified as a reference method in an appendix to this part, or a method that has been designated as a reference method in accordance with part 53 of this chapter; it does not include a method for which a reference method designation has been cancelled in accordance with § 53.11 or § 53.16 of this chapter.

(g) *Equivalent method* means a method of sampling and analyzing the ambient air for an air pollutant that has been designated as an equivalent method in accordance with part 53 of this chapter; it does not include a method for which an equivalent method designation has been cancelled in accordance with § 53.11 or § 53.16 of this chapter.

(h) *Traceable* means that a local standard has been compared and certified either directly or via not more than one intermediate standard, to a primary standard such as a National Bureau of Standards Standard Reference Material (NBS SRM), or a USEPA/NBS-approved Certified Reference Material (CRM).

(i) *Indian country* is as defined in 18 U.S.C. 1151.

(j) *Exceptional event* means an event(s) and its resulting emissions that affect air quality in such a way that there exists a clear causal relationship between the specific event(s) and the monitored exceedance(s) or violation(s), is not reasonably controllable or preventable, is an event(s) caused by human activity that is unlikely to recur at a particular location or a natural event(s), and is determined by the Administrator in accordance with 40 CFR 50.14 to be an exceptional event. It does not include air pollution relating to source noncompliance. Stagnation of air masses and meteorological inversions do not directly cause pollutant emissions and are not exceptional events. Meteorological events involving high temperatures or lack of precipitation (*i.e.*, severe, extreme or exceptional drought) also do not directly cause pollutant emissions and are not considered exceptional events. However, conditions involving high temperatures or lack of precipitation may promote occurrences of particular types of exceptional events, such as wildfires or high wind events, which do directly cause emissions.

(k) *Natural event* means an event and its resulting emissions, which may recur at the same location, in which human activity plays little or no direct causal role. For purposes of the definition of a natural event, anthropogenic sources that are reasonably controlled shall be considered to not play a direct role in causing emissions.

(l) *Exceedance with respect to a national ambient air quality standard* means one occurrence of a measured or modeled concentration that exceeds the specified concentration level of such standard for the averaging period specified by the standard.

(m) *Prescribed fire* is any fire intentionally ignited by management actions in accordance with applicable laws, policies, and regulations to meet specific land or resource management objectives.

(n) *Wildfire* is any fire started by an unplanned ignition caused by lightning; volcanoes; other acts of nature; unauthorized activity; or accidental, human-caused actions, or a prescribed fire that has developed into a wildfire. A wildfire that predominantly occurs on wildland is a natural event.

(o) *Wildland* means an area in which human activity and development are essentially non-existent, except for roads, railroads, power lines, and similar transportation facilities. Structures, if any, are widely scattered.

(p) *High wind dust event* is an event that includes the high-speed wind and the dust that the wind entrains and transports to a monitoring site.

(q) *High wind threshold* is the minimum wind speed capable of causing particulate matter emissions from natural undisturbed lands in the area affected by a high wind dust event.

(r) *Federal land manager* means, consistent with the definition in 40 CFR 51.301, the Secretary of the department with authority over the Federal Class I area (or the Secretary's designee) or, with respect to Roosevelt-Campobello International Park, the Chairman of the Roosevelt-Campobello International Park Commission.

[36 FR 22384, Nov. 25, 1971, as amended at 41 FR 11253, Mar. 17, 1976; 48 FR 2529, Jan. 20, 1983; 63 FR 7274, Feb. 12, 1998; 72 FR 13580, Mar. 22, 2007; 81 FR 68276, Oct. 3, 2016]

§ 50.2 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 or Indian country.

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

[36 FR 22384, Nov. 25, 1971, as amended at 63 FR 7274, Feb. 12, 1998]

§ 50.3 Reference conditions.

All measurements of air quality that are expressed as mass per unit volume (e.g., micrograms per cubic meter) other than for particulate matter ($PM_{2.5}$) standards contained in §§ 50.7, 50.13, and 50.18, and lead standards contained in § 50.16 shall be corrected to a reference temperature of 25 (deg) C and a reference pressure of 760 millimeters of mercury (1,013.2 millibars). Measurements of $PM_{2.5}$ for purposes of comparison to the standards contained in §§ 50.7, 50.13, and 50.18, and of lead for purposes of comparison to the standards contained in § 50.16 shall be reported based on actual ambient air volume measured at the actual ambient temperature and pressure at the monitoring site during the measurement period.

[78 FR 3277, Jan. 15, 2013]

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

(a) The level of the annual standard is 0.030 parts per million (ppm), not to be exceeded in a calendar year. The annual arithmetic mean shall be rounded to three decimal places (fractional parts equal to or greater than 0.0005 ppm shall be rounded up).

(b) The level of the 24-hour standard is 0.14 parts per million (ppm), not to be exceeded more than once per calendar year. The 24-hour averages shall be determined from successive nonoverlapping 24-hour blocks starting at midnight each calendar day and shall be rounded to two decimal places (fractional parts equal to or greater than 0.005 ppm shall be rounded up).

(c) Sulfur oxides shall be measured in the ambient air as sulfur dioxide by the reference method described in appendix A to this part or by an equivalent method designated in accordance with part 53 of this chapter.

(d) To demonstrate attainment, the annual arithmetic mean and the second-highest 24-hour averages must be based upon hourly data that are at least 75 percent complete in each calendar quarter. A 24-hour block average shall be considered valid if at least 75 percent of the hourly averages for the 24-hour period are available. In the event that only 18, 19, 20, 21, 22, or 23 hourly averages are available, the 24-hour block average shall be computed as the sum of the available hourly averages using 18, 19, etc. as the divisor. If fewer than 18 hourly averages are available, but the 24-hour average would exceed the level of the standard when zeros are substituted for the missing values, subject to the rounding rule of paragraph (b) of this section, then this shall be considered a valid 24-hour average. In this case, the 24-hour block average shall be computed as the sum of the available hourly averages divided by 24.

(e) The standards set forth in this section will remain applicable to all areas notwithstanding the promulgation of SO_2 national ambient air quality standards (NAAQS) in §50.17. The SO_2 NAAQS set forth in this section will no longer apply to an area one year after the effective date of the designation of that area, pursuant to section 107 of the Clean Air Act, for the SO_2 NAAQS set forth in §50.17; except that for areas designated nonattainment for the SO_2 NAAQS set forth in this section as of the effective date of §50.17, and areas not meeting the requirements of a SIP call with respect to requirements for the SO_2 NAAQS set forth in this section, the SO_2 NAAQS set forth in this section will apply until that area submits, pursuant to section 191 of the Clean Air Act, and EPA approves, an implementation plan providing for attainment of the SO_2 NAAQS set forth in §50.17.

[61 FR 25579, May 22, 1996, as amended at 75 FR 35592, June 22, 2010]

§50.5 National secondary ambient air quality standard for sulfur oxides (sulfur dioxide).

(a) The level of the 3-hour standard is 0.5 parts per million (ppm), not to be exceeded more than once per calendar year. The 3-hour averages shall be determined from successive nonoverlapping 3-hour blocks starting at midnight each calendar day and shall be rounded to 1 decimal place (fractional parts equal to or greater than 0.05 ppm shall be rounded up).

(b) Sulfur oxides shall be measured in the ambient air as sulfur dioxide by the reference method described in appendix A of this part or by an equivalent method designated in accordance with part 53 of this chapter.

(c) To demonstrate attainment, the second-highest 3-hour average must be based upon hourly data that are at least 75 percent complete in each calendar quarter. A 3-hour block average shall be considered valid only if all three hourly averages for the 3-hour period are available. If only one or two hourly averages are available, but the 3-hour average would exceed the level of the standard when zeros are substituted for the missing values, subject to the rounding rule of paragraph (a) of this section, then this shall be considered a valid 3-hour average. In all cases, the 3-hour block average shall be computed as the sum of the hourly averages divided by 3.

[61 FR 25580, May 22, 1996]

§50.6 National primary and secondary ambient air quality standards for PM_{10}.

(a) The level of the national primary and secondary 24-hour ambient air quality standards for particulate matter is 150 micrograms per cubic meter (µg/m^3), 24-hour average concentration. The standards are attained when the expected number of days per calendar year with a 24-hour average concentration above 150 µg/m^3, as determined in accordance with appendix K to this part, is equal to or less than one.

(b) [Reserved]

(c) For the purpose of determining attainment of the primary and secondary standards, particulate matter shall be measured in the ambient air as PM_{10} (particles with an aerodynamic diameter less than or equal to a nominal 10 micrometers) by:

(1) A reference method based on appendix J and designated in accordance with part 53 of this chapter, or

(2) An equivalent method designated in accordance with part 53 of this chapter.

[52 FR 24663, July 1, 1987, as amended at 62 FR 38711, July 18, 1997; 65 FR 80779, Dec. 22, 2000; 71 FR 61224, Oct. 17, 2006]

§50.7 National primary and secondary ambient air quality standards for $PM_{2.5}$.

(a) The national primary and secondary ambient air quality standards for particulate matter are 15.0 micrograms per cubic meter (µg/m^3) annual arithmetic mean concentration, and 65 µg/m^3 24-hour average concentration measured in the ambient air as $PM_{2.5}$ (particles with an aerodynamic diameter less than or equal to a nominal 2.5 micrometers) by either:

(1) A reference method based on appendix L of this part and designated in accordance with part 53 of this chapter; or

(2) An equivalent method designated in accordance with part 53 of this chapter.

(b) The annual primary and secondary $PM_{2.5}$ standards are met when the annual arithmetic mean concentration, as determined in accordance with appendix N of this part, is less than or equal to 15.0 micrograms per cubic meter.

(c) The 24-hour primary and secondary $PM_{2.5}$ standards are met when the 98th percentile 24-hour concentration, as determined in accordance with appendix N of this part, is less than or equal to 65 micrograms per cubic meter.

[62 FR 38711, July 18, 1997, as amended at 69 FR 45595, July 30, 2004]

§50.8 National primary ambient air quality standards for carbon monoxide.

(a) The national primary ambient air quality standards for carbon monoxide are:

(1) 9 parts per million (10 milligrams per cubic meter) for an 8-hour average concentration not to be exceeded more than once per year and

(2) 35 parts per million (40 milligrams per cubic meter) for a 1-hour average concentration not to be exceeded more than once per year.

(b) The levels of carbon monoxide in the ambient air shall be measured by:

(1) A reference method based on appendix C and designated in accordance with part 53 of this chapter, or

(2) An equivalent method designated in accordance with part 53 of this chapter.

(c) An 8-hour average shall be considered valid if at least 75 percent of the hourly average for the 8-hour period are available. In the event that only six (or seven) hourly averages are available, the 8-hour average shall be computed on the basis of the hours available using six (or seven) as the divisor.

(d) When summarizing data for comparision with the standards, averages shall be stated to one decimal place. Comparison of the data with the levels of the standards in parts per million shall be made in terms of integers with fractional parts of 0.5 or greater rounding up.

[50 FR 37501, Sept. 13, 1985]

§50.9 National 1-hour primary and secondary ambient air quality standards for ozone.

(a) The level of the national 1-hour primary and secondary ambient air quality standards for ozone measured by a reference method based on appendix D to this part and designated in accordance with part 53 of this chapter, is 0.12 parts per million (235 µg/m^3). The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 parts per million (235 µg/m^3) is equal to or less than 1, as determined by appendix H to this part.

(b) The 1-hour standards set forth in this section will remain applicable to all areas notwithstanding the promulgation of 8-hour ozone standards under §50.10. The 1-hour NAAQS set forth in paragraph (a) of this section will no longer apply to an area one year after the effective date of the designation of that area for the 8-hour ozone NAAQS pursuant to section 107 of the Clean Air Act. Area designations and classifications with respect to the 1-hour standards are codified in 40 CFR part 81.

[62 FR 38894, July 18, 1997, as amended at 65 FR 45200, July 20, 2000; 68 FR 38163, June 26, 2003, 69 FR 23996, Apr. 30, 2004; 77 FR 28441, May 14, 2012]

§50.10 National 8-hour primary and secondary ambient air quality standards for ozone.

(a) The level of the national 8-hour primary and secondary ambient air quality standards for ozone, measured by a reference method based on appendix D to this part and designated in accordance with part 53 of this chapter, is 0.08 parts per million (ppm), daily maximum 8-hour average.

(b) The 8-hour primary and secondary ozone ambient air quality standards are met at an ambient air quality monitoring site when the average of the annual fourth-highest daily maximum 8-hour average ozone concentration is less than or equal to 0.08 ppm, as determined in accordance with appendix I to this part.

(c) Until the effective date of the final Implementation of the 2008 National Ambient Air Quality Standards for Ozone: State Implementation Plan Requirements Rule (final SIP Requirements Rule) to be codified at 40 CFR 51.1100 *et seq.*, the 1997 ozone NAAQS set forth in this section will continue in effect, notwithstanding the promulgation of the 2008 ozone NAAQS under §50.15. The 1997 ozone NAAQS set forth in this section will no longer apply upon the effective date of the final SIP Requirements Rule. For purposes of the anti-backsliding requirements of §51.1105, §51.165 and Appendix S to part 51, the area designations and classifications with respect to the revoked 1997 ozone NAAQS are codified in 40 CFR part 81.

[62 FR 38894, July 18, 1997, as amended at 77 FR 30170, May 21, 2012; 80 FR 12312, Mar. 6, 2015]

§50.11 National primary and secondary ambient air quality standards for oxides of nitrogen (with nitrogen dioxide as the indicator).

(a) The level of the national primary annual ambient air quality standard for oxides of nitrogen is 53 parts per billion (ppb, which is 1 part in 1,000,000,000), annual average concentration, measured in the ambient air as nitrogen dioxide.

(b) The level of the national primary 1-hour ambient air quality standard for oxides of nitrogen is 100 ppb, 1-hour average concentration, measured in the ambient air as nitrogen dioxide.

(c) The level of the national secondary ambient air quality standard for nitrogen dioxide is 0.053 parts per million (100 micrograms per cubic meter), annual arithmetic mean concentration.

(d) The levels of the standards shall be measured by:

(1) A reference method based on appendix F to this part; or

(2) By a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter.

(e) The annual primary standard is met when the annual average concentration in a calendar year is less than or equal to 53 ppb, as determined in accordance with appendix S of this part for the annual standard.

(f) The 1-hour primary standard is met when the three-year average of the annual 98th percentile of the daily maximum 1-hour average concentration is less than or equal to 100 ppb, as determined in accordance with appendix S of this part for the 1-hour standard.

(g) The secondary standard is attained when the annual arithmetic mean concentration in a calendar year is less than or equal to 0.053 ppm, rounded to three decimal places (fractional parts equal to or greater than 0.0005 ppm must be rounded up). To demonstrate attainment, an annual mean must be based upon hourly data that are at least 75 percent complete or upon data derived from manual methods that are at least 75 percent complete for the scheduled sampling days in each calendar quarter.

[75 FR 6531, Feb. 9, 2010]

§50.12 National primary and secondary ambient air quality standards for lead.

(a) National primary and secondary ambient air quality standards for lead and its compounds, measured as elemental lead by a reference method based on appendix G to this part, or by an equivalent method, are: 1.5 micrograms per cubic meter, maximum arithmetic mean averaged over a calendar quarter.

(b) The standards set forth in this section will remain applicable to all areas notwithstanding the promulgation of lead national ambient air quality standards (NAAQS) in §50.16. The lead NAAQS set forth in this section will no longer apply to an area one year after the effective date of the designation of that area, pursuant to section 107 of the Clean Air Act, for the lead NAAQS set forth in §50.16; except that for areas designated nonattainment for the lead NAAQS set forth in this section as of the effective date of §50.16, the lead NAAQS set forth in this section will apply until that area submits, pursuant to section 191 of the Clean Air Act, and EPA approves, an implementation plan providing for attainment and/or maintenance of the lead NAAQS set forth in §50.16.

(Secs. 109, 301(a) Clean Air Act as amended (42 U.S.C. 7409, 7601(a)))

[43 FR 46258, Oct. 5, 1978, as amended at 73 FR 67051, Nov. 12, 2008]

§50.13 National primary and secondary ambient air quality standards for $PM_{2.5}$.

(a) The national primary and secondary ambient air quality standards for particulate matter are 15.0 micrograms per cubic meter ($\mu g/m^3$) annual arithmetic mean concentration, and 35 $\mu g/m^3$ 24-hour average concentration measured in the ambient air as $PM_{2.5}$ (particles with an aerodynamic diameter less than or equal to a nominal 2.5 micrometers) by either:

(1) A reference method based on appendix L of this part and designated in accordance with part 53 of this chapter; or

(2) An equivalent method designated in accordance with part 53 of this chapter.

(b) The annual primary and secondary $PM_{2.5}$ standards are met when the annual arithmetic mean concentration, as determined in accordance with appendix N of this part, is less than or equal to 15.0 $\mu g/m^3$.

(c) The 24-hour primary and secondary $PM_{2.5}$ standards are met when the 98th percentile 24-hour concentration, as determined in accordance with appendix N of this part, is less than or equal to 35 $\mu g/m^3$.

(d) Until the effective date of the final Fine Particulate Matter National Ambient Air Quality Standards: State Implementation Plan Requirements rule to be codified at 40 CFR 51.1000 through 51.1016, the 1997 annual $PM_{2.5}$ NAAQS set forth in this section will continue in effect, notwithstanding the promulgation of the 2012 primary annual $PM_{2.5}$ NAAQS under §50.18. The 1997 primary annual $PM_{2.5}$ NAAQS set forth in this section will no longer apply upon the effective date of the final Fine Particulate Matter National Ambient Air Quality Standards: State Implementation Plan Requirements rule; except that for areas designated nonattainment for the 1997 annual $PM_{2.5}$ NAAQS set forth in this section as of the effective date of the final Fine Particulate Matter National Ambient Air Quality Standards: State Implementation Plan Requirements rule, the requirements applicable to the 1997 primary annual $PM_{2.5}$ NAAQS set forth in this section will apply until the effective date of an area's redesignation to attainment for the 1997 annual $PM_{2.5}$ NAAQS pursuant to the requirements of section 107 of the Clean Air Act. The 1997 secondary annual $PM_{2.5}$ NAAQS and the 1997 24-hour $PM_{2.5}$ NAAQS shall remain in effect. The area designations and classifications with respect to the 1997 annual and 24-hour $PM_{2.5}$ NAAQS remain codified in 40 CFR part 81 in order to provide information on where the 1997 primary annual $PM_{2.5}$ NAAQS has been revoked and to facilitate the implementation of the 1997 secondary annual $PM_{2.5}$ NAAQS and the 1997 24-hour $PM_{2.5}$ NAAQS.

[71 FR 61224, Oct. 17, 2006, as amended at 81 FR 58149, Aug. 24, 2016]

§50.14 Treatment of air quality monitoring data influenced by exceptional events.

(a) *Requirements*—(1) *Scope.* (i) This section applies to the treatment of data showing exceedances or violations of any national ambient air quality standard for purposes of the following types of regulatory determinations by the Administrator:

(A) An action to designate an area, pursuant to Clean Air Act section 107(d)(1), or redesignate an area, pursuant to Clean Air Act section 107(d)(3), for a particular national ambient air quality standard;

(B) The assignment or re-assignment of a classification category to a nonattainment area where such classification is based on a comparison of pollutant design values, calculated according to the specific data handling procedures in 40 CFR part 50 for each national ambient air quality standard, to the level of the relevant national ambient air quality standard;

(C) A determination regarding whether a nonattainment area has attained the level of the appropriate national ambient air quality standard by its specified deadline;

(D) A determination that an area has data for the specific NAAQS, which qualify the area for an attainment date extension under the CAA provisions for the applicable pollutant;

(E) A determination under Clean Air Act section 110(k)(5), if based on an area violating a national ambient air quality standard, that the state implementation plan is inadequate under the requirements of Clean Air Act section 110; and

(F) Other actions on a case-by-case basis as determined by the Administrator.

(ii) A State, federal land manager or other federal agency may request the Administrator to exclude data showing exceedances or violations of any national ambient air quality standard that are directly due to an exceptional event from use in determinations identified in paragraph (a)(1)(i) of this section by demonstrating to the Administrator's satisfaction that such event caused a specific air pollution concentration at a particular air quality monitoring location.

(A) For a federal land manager or other federal agency to be eligible to initiate such a request for data exclusion, the federal land manager or other federal agency must:

(*1*) Either operate a regulatory monitor that has been affected by an exceptional event or manage land on which an exceptional event occurred that influenced a monitored concentration at a regulatory monitor; and

(*2*) Initiate such a request only after the State in which the affected monitor is located concurs with the federal land manager's or other federal agency's submittal.

(B) With regard to such a request, all provisions in this section that are expressed as requirements applying to a State shall, except as noted, be requirements applying to the federal land manager or other federal agency.

(C) Provided all provisions in this section are met, the Administrator shall allow a State to submit demonstrations for any regulatory monitor within its jurisdictional bounds, including those operated by federal land managers, other federal agencies and delegated local agencies.

(D) Where multiple agencies within a state submit demonstrations for events that meet the requirements of the Exceptional Events Rule, a State submittal shall have primacy for any regulatory monitor within its jurisdictional bounds.

(2) A demonstration to justify data exclusion may include any reliable and accurate data, but must specifically address the elements in paragraphs (c)(3)(iv) and (v) of this section.

(b) *Determinations by the Administrator*—(1) *Generally*. The Administrator shall exclude data from use in determinations of exceedances and violations identified in paragraph (a)(1)(i) of this section where a State demonstrates to the Administrator's satisfaction that an exceptional event caused a specific air pollution concentration at a particular air quality monitoring location and otherwise satisfies the requirements of this section.

(2) *Fireworks displays*. The Administrator shall exclude data from use in determinations of exceedances and violations where a State demonstrates to the Administrator's satisfaction that emissions from fireworks displays caused a specific air pollution concentration in excess of one or more national ambient air quality standards at a particular air quality monitoring location and otherwise satisfies the requirements of this section. Such data will be treated in the same manner as exceptional events under this rule, provided a State demonstrates that such use of fireworks is significantly integral to traditional national, ethnic, or other cultural events including, but not limited to, July Fourth celebrations that satisfy the requirements of this section.

(3) *Prescribed fires*. (i) The Administrator shall exclude data from use in determinations of exceedances and violations, where a State demonstrates to

the Administrator's satisfaction that emissions from prescribed fires caused a specific air pollution concentration in excess of one or more national ambient air quality standards at a particular air quality monitoring location and otherwise satisfies the requirements of this section.

(ii) In addressing the requirements set forth in paragraph (c)(3)(iv)(D) of this section regarding the not reasonably controllable or preventable criterion:

(A) With respect to the requirement that a prescribed fire be not reasonably controllable, the State must either certify to the Administrator that it has adopted and is implementing a smoke management program or the State must demonstrate that the burn manager employed appropriate basic smoke management practices identified in Table 1 to §50.14. Where a burn manager employs appropriate basic smoke management practices, the State may rely on a statement or other documentation provided by the burn manager that he or she employed those practices. If an exceedance or violation of a NAAQS occurs when a prescribed fire is employing an appropriate basic smoke management practices approach, the State and the burn manager must undertake a review of the subject fire, including a review of the basic smoke management practices applied during the subject fire to ensure the protection of air quality and public health and progress towards restoring and/or maintaining a sustainable and resilient wildland ecosystem. If the prescribed fire becomes the subject of an exceptional events demonstration, documentation of the post-burn review must accompany the demonstration.

(B) If the State anticipates satisfying the requirements of paragraph (c)(3)(iv)(D) of this section by employing the appropriate basic smoke management practices identified in Table 1 to §50.14, then:

(*1*) The State, federal land managers, and other entities as appropriate, must periodically collaborate with burn managers operating within the jurisdiction of the State to discuss and document the process by which air agencies and land managers will work together to protect public health and manage air quality impacts during the conduct of prescribed fires on wildland. Such discussions must include outreach and education regarding general expectations for the selection and application of appropriate basic smoke management practices and goals for advancing strategies and increasing adoption and communication of the benefits of appropriate basic smoke management practices;

(*2*) The State, federal land managers and burn managers shall have an initial implementation period, defined as being 2 years from September 30, 2016, to implement the collaboration and outreach effort identified in paragraph (b)(3)(ii)(B)(*1*) of this section; and

(*3*) Except as provided in paragraph (b)(3)(ii)(B)(*2*) of this section, the Administrator shall not place a concurrence flag in the appropriate field for the data record in the AQS database, as specified in paragraph (c)(2)(ii) of this section, if the data are associated with a prescribed fire on wildland unless the requirements of paragraph (b)(3)(ii)(B)(*1*) of this section have been met and associated documentation accompanies any applicable exceptional events demonstration. The Administrator may nonconcur or defer action on such a demonstration.

(C) With respect to the requirement that a prescribed fire be not reasonably preventable, the State may rely upon and reference a multi-year land or resource management plan for a wildland area with a stated objective to establish, restore and/or maintain a sustainable and resilient wildland ecosystem and/or to preserve endangered or threatened species through a program of prescribed fire provided that the Administrator determines that there is no compelling evidence to the contrary in the record and the use of prescribed fire in the area has not exceeded the frequency indicated in that plan.

(iii) Provided the Administrator determines that there is no compelling evidence to the contrary in the record, in addressing the requirements set forth in paragraph (c)(3)(iv)(E) of this section regarding the human activity unlikely to recur at a particular location criterion for demonstrations involving prescribed fires on wildland, the State must describe the actual frequency with which a burn was conducted, but may rely upon and reference an assessment of the natural fire return interval or the prescribed fire frequency needed to establish, restore and/or maintain a sustainable and resilient wildland ecosystem contained in a multi-year land or resource management plan with a stated objective to establish, restore and/or maintain a sustainable and resilient wildland ecosystem and/or to preserve endangered or threatened species through a program of prescribed fire.

Table 1 to §50.14—Summary of Basic Smoke Management Practices, Benefit Achieved With the BSMP, and When it is Applied[a]

Basic Smoke Management Practice[b]	Benefit achieved with the BSMP	When the BSMP is applied—before/during/after the burn
Evaluate Smoke Dispersion Conditions.	Minimize smoke impacts	Before, During, After.
Monitor Effects on Air Quality	Be aware of where the smoke is going and degree it impacts air quality.	Before, During, After.
Record-Keeping/Maintain a Burn/Smoke Journal.	Retain information about the weather, burn and smoke. If air quality problems occur, documentation helps analyze and address air regulatory issues..	Before, During, After.
Communication—Public Notification	Notify neighbors and those potentially impacted by smoke, especially sensitive receptors.	Before, During.
Consider Emission Reduction Techniques.	Reducing emissions through mechanisms such as reducing fuel loading can reduce downwind impacts.	Before, During, After.
Share the Airshed—Coordination of Area Burning.	Coordinate multiple burns in the area to manage exposure of the public to smoke.	Before, During, After.

[a] The EPA believes that elements of these BSMP could also be practical and beneficial to apply to wildfires for areas likely to experience recurring wildfires.

[b] The listing of BSMP in this table is not intended to be all-inclusive. Not all BSMP are appropriate for all burns. Goals for applicability should retain flexibility to allow for onsite variation and site-specific conditions that can be variable on the day of the burn. Burn managers can consider other appropriate BSMP as they become available due to technological advancement or programmatic refinement.

(4) *Wildfires*. The Administrator shall exclude data from use in determinations of exceedances and violations where a State demonstrates to the Administrator's satisfaction that emissions from wildfires caused a specific air pollution concentration in excess of one or more national ambient air quality standard at a particular air quality monitoring location and otherwise satisfies the requirements of this section. Provided the Administrator determines that there is no compelling evidence to the contrary in the record, the Administrator will determine every wildfire occurring predominantly on wildland to have met the requirements identified in paragraph (c)(3)(iv)(D) of this section regarding the not reasonably controllable or preventable criterion.

(5) *High wind dust events*. (i) The Administrator shall exclude data from use in determinations of exceedances and violations, where a State demonstrates to the Administrator's satisfaction that emissions from a high wind dust event caused a specific air pollution concentration in excess of one or more national ambient air quality standards at a particular air quality monitoring location and otherwise satisfies the requirements of this section provided that such emissions are from high wind dust events.

(ii) The Administrator will consider high wind dust events to be natural events in cases where windblown dust is entirely from natural undisturbed lands in the area or where all anthropogenic sources are reasonably controlled as determined in accordance with paragraph (b)(8) of this section.

(iii) The Administrator will accept a high wind threshold of a sustained wind of 25 mph for areas in the States of Arizona, California, Colorado, Kansas, Nebraska, Nevada, New Mexico, North Dakota, Oklahoma, South Dakota, Texas, Utah, and Wyoming provided this value is not contradicted by evidence in the record at the time the State submits a demonstration. In lieu of this threshold, States can identify and use an Administrator-approved alternate area-specific high wind threshold that is more representative of local or regional conditions, if appropriate.

(iv) In addressing the requirements set forth in paragraph (c)(3)(iv)(D) of this section regarding the not reasonably preventable criterion, the State shall not be required to provide a case-specific justification for a high wind dust event.

(v) With respect to the not reasonably controllable criterion of paragraph (c)(3)(iv)(D) of this section, dust controls on an anthropogenic source shall be considered reasonable in any case in which the controls render the anthropogenic source as resistant to high winds as natural undisturbed lands in the area affected by the high wind dust event. The Administrator may determine lesser controls reasonable on a case-by-case basis.

(vi) For large-scale and high-energy high wind dust events, the Administrator will generally consider a demonstration documenting the nature and extent of the event to be sufficient with respect to the not reasonably controllable criterion of paragraph (c)(3)(iv)(D) of this section provided the State provides evidence showing that the event satisfies the following:

(A) The event is associated with a dust storm and is the focus of a Dust Storm Warning.

(B) The event has sustained winds that are greater than or equal to 40 miles per hour.

(C) The event has reduced visibility equal to or less than 0.5 miles.

(6) *Stratospheric Intrusions.* Where a State demonstrates to the Administrator's satisfaction that emissions from stratospheric intrusions caused a specific air pollution concentration in excess of one or more national ambient air quality standard at a particular air quality monitoring location and otherwise satisfies the requirements of this section, the Administrator will determine stratospheric intrusions to have met the requirements identified in paragraph (c)(3)(iv)(D) of this section regarding the not reasonably controllable or preventable criterion and shall exclude data from use in determinations of exceedances and violations.

(7) *Determinations with respect to event aggregation, multiple national ambient air quality standards for the same pollutant, and exclusion of 24-hour values for particulate matter.*

(i) Where a State demonstrates to the Administrator's satisfaction that for national ambient air quality standards with averaging or cumulative periods less than or equal to 24 hours the aggregate effect of events occurring on the same day has caused an exceedance or violation, the Administrator shall determine such collective data to satisfy the requirements in paragraph (c)(3)(iv)(B) of this section regarding the clear causal relationship criterion. Where a State demonstrates to the Administrator's satisfaction that for national ambient air quality standards with averaging or cumulative periods longer than 24 hours the aggregate effect of events occurring on different days has caused an exceedance or violation, the Administrator shall determine such collective data to satisfy the requirements in paragraph (c)(3)(iv)(B) of this section regarding the clear causal relationship criterion.

(ii) The Administrator shall accept as part of a demonstration for the clear causal relationship in paragraph (c)(3)(iv)(B) of this section with respect to a 24-hour NAAQS, a State's comparison of a 24-hour concentration of any national ambient air quality standard pollutant to the level of a national ambient air quality standard for the same pollutant with a longer averaging period. The Administrator shall also accept as part of a demonstration for the clear causal relationship in paragraph (c)(3)(iv)(B) of this section with respect to a NAAQS with a longer averaging period, a State's comparison of a 24-hour concentration of any national ambient air quality standard pollutant to the level of the national ambient air quality standard for the same pollutant with a longer averaging period, without the State having to demonstrate that the event caused the annual average concentration of the pollutant to exceed the level of the NAAQS with the longer averaging period.

(iii) Where a State operates a continuous analyzer that has been designated as a Federal Equivalent Method monitor as defined in 40 CFR 50.1(g) that complies with the monitoring requirements of 40 CFR part 58, Appendix C, and the State believes that collected data have been influenced by an event, in following the process outlined in paragraph (c)(2) of this section, the State shall create an initial event description and flag the associated event-influenced data that have been submitted to the AQS database for the affected monitor. Where a State demonstrates to the Administrator's satisfaction that such data satisfy the requirements in paragraph (c)(3)(iv)(B) of this section regarding the clear causal relationship criterion and otherwise satisfy the requirements of this section, the Administrator shall agree to exclude all data within the affected calendar day(s).

(8) *Determinations with respect to the not reasonably controllable or preventable criterion.* (i) The not reasonably controllable or preventable criterion has two prongs that the State must demonstrate: prevention and control.

(ii) The Administrator shall determine that an event is not reasonably preventable if the State shows that reasonable measures to prevent the event were applied at the time of the event.

(iii) The Administrator shall determine that an event is not reasonably controllable if the State shows that reasonable measures to control the impact of the event on air quality were applied at the time of the event.

(iv) The Administrator shall assess the reasonableness of available controls for anthropogenic sources based on information available as of the date of the event.

(v) Except where a State, tribal or federal air agency is obligated to revise its state implementation plan, tribal implementation plan, or federal implementation plan, the Administrator shall consider enforceable control measures implemented in accordance with a state implementation plan, tribal implementation plan, or federal implementation plan, approved by the EPA within 5 years of the date of the event, that address the event-related pollutant and all sources necessary to fulfill the requirements of the Clean Air Act for the state implementation plan, tribal implementation plan, or federal implementation plan to be reasonable controls with respect to all anthropogenic sources that have or may have contributed to the monitored exceedance or violation.

(vi) Where a State, tribal or federal air agency is obligated to revise its state implementation plan, tribal implementation plan, or federal implementation plan, the deference to enforceable control measures identified in paragraph (b)(8)(v) of this section shall remain only until the due date of the required state implementation plan, tribal implementation plan, or federal implementation plan revisions. However, where an air agency is obligated to revise the enforceable control measures identified in paragraph (b)(8)(v) of this section in its implementation plan as a result of an action pursuant to Clean Air Act section 110(k)(5), the deference, if any, to those enforceable control measures shall be determined on a case-by-case basis.

(vii) The Administrator shall not require a State to provide case-specific justification to support the not reasonably controllable or preventable criterion for emissions-generating activity that occurs outside of the State's jurisdictional boundaries within which the concentration at issue was monitored. In the case of a tribe treated as a state under 40 CFR 49.2 with respect to exceptional events requirements, the tribe's jurisdictional boundaries for purposes of requiring or directly implementing emission controls apply. In the case of a federal land manager or other federal agency submitting a demonstration under the requirements of this section, the jurisdictional boundaries that apply are those of the State or the tribe depending on which has jurisdiction over the area where the event has occurred.

(viii) In addition to the provisions that apply to specific event types identified in paragraphs (b)(3)(ii) and (b)(5)(i) through (iii) of this section in addressing the requirements set forth in paragraph (c)(3)(iv)(D) of this section regarding the not reasonably controllable or preventable criterion, the State must include the following components:

(A) Identification of the natural and anthropogenic sources of emissions causing and contributing to the monitored exceedance or violation, including the contribution from local sources.

(B) Identification of the relevant state implementation plan, tribal implementation plan, or federal implementation plan or other enforceable control measures in place for the sources identified in paragraph (b)(8)(vii)(A) of this section and the implementation status of these controls.

(C) Evidence of effective implementation and enforcement of the measures identified in paragraph (b)(8)(vii)(B) of this section.

(D) The provisions in this paragraph shall not apply if the provisions in paragraph (b)(4), (b)(5)(vi), or (b)(6) of this section apply.

(9) *Mitigation plans.* (i) Except as provided for in paragraph (b)(9)(ii) of this section, where a State is subject to the requirements of 40 CFR 51.930(b), the Administrator shall not place a concurrence flag in the appropriate field for the data record in the AQS database, as specified in paragraph (c)(2)(ii) of this section, if the data are of the type and pollutant that are the focus of the mitigation plan until the State fulfills its obligations under the requirements of 40 CFR 51.930(b). The Administrator may nonconcur or defer action on such a demonstration.

(ii) The prohibition on placing a concurrence flag in the appropriate field for the data record in the AQS database by the Administrator stated in paragraph (b)(9(i) of this section does not apply to data that are included in an exceptional events demonstration that is:

(A) submitted in accordance with paragraph (c)(3) of this section that is also of the type and pollutant that is the focus of the mitigation plan, and

(B) submitted within the 2-year period allowed for mitigation plan development as specified in 40 CFR 51.930(b)(3).

(c) *Schedules and procedures*—(1) *Public notification.* (i) In accordance with the mitigation requirement at 40 CFR 51.930(a)(1), all States and, where applicable, their political subdivisions must notify the public promptly whenever an event occurs or is reasonably anticipated to occur which may result in the exceedance of an applicable air quality standard.

(ii) [Reserved]

(2) *Initial notification of potential exceptional event.* (i) A State shall notify the Administrator of its intent to request exclusion of one or more measured exceedances of an applicable national ambient air quality standard as being due to an exceptional event by creating an initial event description and flagging the associated data that have been submitted to the AQS database and by engaging in the Initial Notification of Potential Exceptional Event process as follows:

(A) The State and the appropriate EPA Regional office shall engage in regular communications to identify those data that have been potentially influenced by an exceptional event, to determine whether the identified data may affect a regulatory determination and to discuss whether the State should develop and submit an exceptional events demonstration according to the requirements in this section;

(B) For data that may affect an anticipated regulatory determination or where circumstances otherwise compel the Administrator to prioritize the resulting demonstration, the Administrator shall respond to a State's Initial Notification of Potential Exceptional Event with a due date for demonstration submittal that considers the nature of the event and the anticipated timing of the associated regulatory decision;

(C) The Administrator may waive the Initial Notification of Potential Exceptional Event process on a case-by-case basis.

(ii) The data shall not be excluded from determinations with respect to exceedances or violations of the national ambient air quality standards unless and until, following the State's submittal of its demonstration pursuant to paragraph (c)(3) of this section and the Administrator's review, the Administrator notifies the State of its concurrence by placing a concurrence flag in the appropriate field for the data record in the AQS database.

(iii) [Reserved]

(iv) [Reserved]

(v) [Reserved]

(vi) Table 2 to § 50.14 identifies the submission process for data that will or may influence the initial designation of areas for any new or revised national ambient air quality standard.

TABLE 2 TO § 50.14—SCHEDULE FOR INITIAL NOTIFICATION AND DEMONSTRATION SUBMISSION FOR DATA INFLUENCED BY EXCEPTIONAL EVENTS FOR USE IN INITIAL AREA DESIGNATIONS

Exceptional events/Regulatory action	Condition	Exceptional events deadline schedule[d]
(A) Initial Notification deadline for data years 1, 2 and 3.[a].	If state and tribal initial designation recommendations for a new/revised national ambient air quality standard are due August through January,	then the Initial Notification deadline will be the July 1 prior to the recommendation deadline.
(B) Initial Notification deadline for data years 1, 2 and 3.[a].	If state and tribal recommendations for a new/revised national ambient air quality standard are due February through July,	then the Initial Notification deadline will be the January 1 prior to the recommendation deadline.
(C) Exceptional events demonstration submittal deadline for data years 1, 2 and 3[a].	None	no later than the later of November 29, 2016 or the date that state and tribal recommendations are due to the Administrator.
(D) Initial Notification and exceptional events demonstration submittal deadline for data year 4[b] and, where applicable, data year 5.[c].	None	by the last day of the month that is 1 year and 7 months after promulgation of a new/revised national ambient air quality standard, unless either paragraph (E) or paragraph (F) applies.
(E) Initial Notification and exceptional events demonstration submittal deadline for data year 4[b] and, where applicable, data year 5.[c].	If the Administrator follows a 3-year designation schedule.	the deadline is 2 years and 7 months after promulgation of a new/revised national ambient air quality standard.
(F) Initial Notification and exceptional events demonstration submittal deadline for data year 4[b] and, where applicable, data year 5.[c].	If the Administrator notifies the state/tribe that it intends to complete the initial area designations process according to a schedule between 2 and 3 years,.	the deadline is 5 months prior to the date specified for final designations decisions in such Administrator notification.

[a] Where data years 1, 2, and 3 are those years expected to be considered in state and tribal recommendations.

[b] Where data year 4 is the additional year of data that the Administrator may consider when making final area designations for a new/revised national ambient air quality standard under the standard designations schedule.

[c] Where data year 5 is the additional year of data that the Administrator may consider when making final area designations for a new/revised national ambient air quality standard under an extended designations schedule.

[d] The date by which air agencies must certify their ambient air quality monitoring data in AQS is annually on May 1 of the year following the year of data collection as specified in 40 CFR 58.15(a)(2). In some cases, however, air agencies may choose to certify a prior year's data in advance of May 1 of the following year, particularly if the Administrator has indicated intent to promulgate final designations in the first 8 months of the calendar year. Exceptional events demonstration deadlines for "early certified" data will follow the deadlines for "year 4" and "year 5" data.

(3) *Submission of demonstrations.* (i) Except as provided under paragraph (c)(2)(vi) of this section, a State that has flagged data as being due to an exceptional event and is requesting exclusion of the affected measurement data shall, after notice and opportunity for public comment, submit a demonstration to justify data exclusion to the Administrator according to the schedule established under paragraph (c)(2)(i)(B).

(ii) [Reserved]

(iii) [Reserved]

(iv) The demonstration to justify data exclusion must include:

(A) A narrative conceptual model that describes the event(s) causing the exceedance or violation and a discussion of how emissions from the event(s) led to the exceedance or violation at the affected monitor(s);

(B) A demonstration that the event affected air quality in such a way that there exists a clear causal relationship between the specific event and the monitored exceedance or violation;

(C) Analyses comparing the claimed event-influenced concentration(s) to concentrations at the same monitoring site at other times to support the requirement at paragraph (c)(3)(iv)(B) of this section. The Administrator shall not require a State to prove a specific percentile point in the distribution of data;

(D) A demonstration that the event was both not reasonably controllable and not reasonably preventable; and

(E) A demonstration that the event was a human activity that is unlikely to recur at a particular location or was a natural event.

(v) With the submission of the demonstration containing the elements in paragraph (c)(3)(iv) of this section, the State must:

(A) Document that the State followed the public comment process and that the comment period was open for a minimum of 30 days, which could be concurrent with the beginning of the Administrator's initial review period of the associated demonstration provided the State can meet all requirements in this paragraph;

(B) Submit the public comments it received along with its demonstration to the Administrator; and

(C) Address in the submission to the Administrator those comments disputing or contradicting factual evidence provided in the demonstration.

(vi) Where the State has submitted a demonstration according to the requirements of this section after September 30, 2016 and the Administrator has reviewed such demonstration and requested additional evidence to support one of the elements in paragraph (c)(3)(iv) of this section, the State shall have 12 months from the date of the Administrator's request to submit such evidence. At the conclusion of this time, if the State has not submitted the requested additional evidence, the Administrator will notify the State in writing that it considers the demonstration to be inactive and will not pursue additional review of the demonstration. After a 12-month period of inactivity by the State, if a State desires to pursue the inactive demonstration, it must reinitiate its request to exclude associated data by following the process beginning with paragraph (c)(2)(i) of this section.

[81 FR 68277, Oct. 3, 2016]

§ 50.15 National primary and secondary ambient air quality standards for ozone.

(a) The level of the national 8-hour primary and secondary ambient air quality standards for ozone (O_3) is 0.075 parts per million (ppm), daily maximum 8-hour average, measured by a reference method based on appendix D to this part and designated in accordance with part 53 of this chapter or an equivalent method designated in accordance with part 53 of this chapter.

(b) The 8-hour primary and secondary O_3 ambient air quality standards are met at an ambient air quality monitoring site when the 3-year average of the annual fourth-highest daily maximum 8-hour average O_3 concentration is less than or equal to 0.075 ppm, as determined in accordance with appendix P to this part.

[73 FR 16511, Mar. 27, 2008]

§ 50.16 National primary and secondary ambient air quality standards for lead.

(a) The national primary and secondary ambient air quality standards for lead (Pb) and its compounds are 0.15 micrograms per cubic meter, arithmetic mean concentration over a 3-month period, measured in the ambient air as Pb either by:

(1) A reference method based on appendix G of this part and designated in accordance with part 53 of this chapter or;

(2) An equivalent method designated in accordance with part 53 of this chapter.

(b) The national primary and secondary ambient air quality standards for Pb are met when the maximum arithmetic 3-month mean concentration for a 3-year period, as determined in accordance with appendix R of this part, is less than or equal to 0.15 micrograms per cubic meter.

[73 FR 67052, Nov. 12, 2008]

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

(a) The level of the national primary 1-hour annual ambient air quality standard for oxides of sulfur is 75 parts per billion (ppb, which is 1 part in 1,000,000,000), measured in the ambient air as sulfur dioxide (SO_2).

(b) The 1-hour primary standard is met at an ambient air quality monitoring site when the three-year average of the annual (99th percentile) of the daily maximum 1-hour average concentrations is less than or equal to 75 ppb, as determined in accordance with appendix T of this part.

(c) The level of the standard shall be measured by a reference method based on appendix A or A–1 of this part, or by a Federal Equivalent Method (FEM) designated in accordance with part 53 of this chapter.

[75 FR 35592, June 22, 2010]

§ 50.18 National primary ambient air quality standards for $PM_{2.5}$.

(a) The national primary ambient air quality standards for $PM_{2.5}$ are 12.0 micrograms per cubic meter (µg/m^3) annual arithmetic mean concentration and 35 µg/m^3 24-hour average concentration measured in the ambient air as $PM_{2.5}$ (particles with an aerodynamic diameter less than or equal to a nominal 2.5 micrometers) by either:

(1) A reference method based on appendix L to this part and designated in accordance with part 53 of this chapter; or

(2) An equivalent method designated in accordance with part 53 of this chapter.

(b) The primary annual $PM_{2.5}$ standard is met when the annual arithmetic mean concentration, as determined in accordance with appendix N of this part, is less than or equal to 12.0 µg/m^3.

(c) The primary 24-hour $PM_{2.5}$ standard is met when the 98th percentile 24-hour concentration, as determined in accordance with appendix N of this part, is less than or equal to 35 µg/m^3.

[78 FR 3277, Jan. 15, 2013]

§ 50.19 National primary and secondary ambient air quality standards for ozone.

(a) The level of the national 8-hour primary ambient air quality standard for ozone (O_3) is 0.070 parts per million (ppm), daily maximum 8-hour average, measured by a reference method based on appendix D to this part and designated in accordance with part 53 of this chapter or an equivalent method designated in accordance with part 53 of this chapter.

(b) The 8-hour primary O_3 ambient air quality standard is met at an ambient air quality monitoring site when the 3-year average of the annual fourth-highest daily maximum 8-hour average O_3 concentration is less than or equal to 0.070 ppm, as determined in accordance with appendix U to this part.

(c) The level of the national secondary ambient air quality standard for O_3 is 0.070 ppm, daily maximum 8-hour average, measured by a reference method based on appendix D to this part and designated in accordance with part 53 of this chapter or an equivalent method designated in accordance with part 53 of this chapter.

(d) The 8-hour secondary O_3 ambient air quality standard is met at an ambient air quality monitoring site when the 3-year average of the annual fourth-highest daily maximum 8-hour average O_3 concentration is less than or equal to 0.070 ppm, as determined in accordance with appendix U to this part.

[80 FR 65452, Oct. 26, 2015]

APPENDIX A–1 TO PART 50—REFERENCE MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF SULFUR DIOXIDE IN THE ATMOSPHERE (ULTRAVIOLET FLUORESCENCE METHOD)

1.0 APPLICABILITY

1.1 This ultraviolet fluorescence (UVF) method provides a measurement of the concentration of sulfur dioxide (SO_2) in ambient air for determining compliance with the national primary and secondary ambient air quality standards for sulfur oxides (sulfur dioxide) as specified in § 50.4, § 50.5, and § 50.17 of this chapter. The method is applicable to the measurement of ambient SO_2 concentrations using continuous (real-time) sampling. Additional quality assurance procedures and guidance are provided in part 58, appendix A, of this chapter and in Reference 3.

2.0 PRINCIPLE

2.1 This reference method is based on automated measurement of the intensity of the characteristic fluorescence released by SO_2 in an ambient air sample contained in a measurement cell of an analyzer when the air sample is irradiated by ultraviolet (UV) light passed through the cell. The fluorescent light released by the SO_2 is also in the ultraviolet region, but at longer wavelengths than the excitation light. Typically, optimum instrumental measurement of SO_2 concentrations is obtained with an excitation wavelength in a band between approximately 190 to 230 nm, and measurement of the SO_2 fluorescence in a broad band around 320 nm, but these wavelengths are not necessarily constraints of this reference method. Generally, the measurement system (analyzer) also requires means to reduce the effects of aromatic hydrocarbon species, and possibly other compounds, in the air sample to control measurement interferences from these compounds, which may be present in the ambient air. References 1 and 2 describe UVF method.

2.2 The measurement system is calibrated by referencing the instrumental fluorescence measurements to SO_2 standard concentrations traceable to a National Institute of Standards and Technology (NIST) primary standard for SO_2 (*see* Calibration Procedure below).

2.3 An analyzer implementing this measurement principle is shown schematically in Figure 1. Designs should include a measurement cell, a UV light source of appropriate wavelength, a UV detector system with appropriate wave length sensitivity, a pump and flow control system for sampling the ambient air and moving it into the measurement cell, sample air conditioning components as necessary to minimize measurement interferences, suitable control and measurement processing capability, and other apparatus as may be necessary. The analyzer must be designed to provide accurate, repeatable, and continuous measurements of SO_2 concentrations in ambient air, with measurement performance as specified in Subpart B of Part 53 of this chapter.

2.4 *Sampling considerations:* The use of a particle filter on the sample inlet line of a UVF SO_2 analyzer is required to prevent interference, malfunction, or damage due to particles in the sampled air.

3.0 INTERFERENCES

3.1 The effects of the principal potential interferences may need to be mitigated to meet the interference equivalent requirements of part 53 of this chapter. Aromatic hydrocarbons such as xylene and naphthalene can fluoresce and act as strong positive interferences. These gases can be removed by using a permeation type scrubber (hydrocarbon ''kicker''). Nitrogen oxide (NO) in high concentrations can also fluoresce and cause positive interference. Optical filtering can be employed to improve the rejection of interference from high NO. Ozone can absorb UV light given off by the SO_2 molecule and cause a measurement offset. This effect can be reduced by minimizing the measurement path length between the area where SO_2 fluorescence occurs and the photomultiplier tube detector (e.g., <5 cm). A hydrocarbon scrubber, optical filter and appropriate distancing of the measurement path length may be required method components to reduce interference.

4.0 CALIBRATION PROCEDURE

Atmospheres containing accurately known concentrations of sulfur dioxide are prepared using a compressed gas transfer standard diluted with accurately metered clean air flow rates.

4.1 *Apparatus:* Figure 2 shows a typical generic system suitable for diluting a SO_2 gas cylinder concentration standard with clean air through a mixing chamber to produce the desired calibration concentration standards. A valve may be used to conveniently divert the SO_2 from the sampling manifold to provide clean zero air at the output manifold for zero adjustment. The system may be made up using common laboratory components, or it may be a commercially manufactured system. In either case, the principle components are as follows:

4.1.1 SO_2 standard gas flow control and measurement devices (or a combined device) capable of regulating and maintaining the standard gas flow rate constant to within ±2 percent and measuring the gas flow rate accurate to within ±2, properly calibrated to a NIST-traceable standard.

4.1.2 Dilution air flow control and measurement devices (or a combined device) capable of regulating and maintaining the air flow rate constant to within ±2 percent and measuring the air flow rate accurate to within ±2, properly calibrated to a NIST-traceable standard.

4.1.3 Mixing chamber, of an inert material such as glass and of proper design to provide thorough mixing of pollutant gas and diluent air streams.

4.1.4 Sampling manifold, constructed of glass, polytetrafluoroethylene (PTFE Teflon™), or other suitably inert material and of sufficient diameter to insure a minimum pressure drop at the analyzer connection, with a vent designed to insure a minimum over-pressure (relative to ambient air pressure) at the analyzer connection and to prevent ambient air from entering the manifold.

4.1.5 Standard gas pressure regulator, of clean stainless steel with a stainless steel diaphragm, suitable for use with a high pressure SO_2 gas cylinder.

4.1.6 Reagents

4.1.6.1 SO_2 gas concentration transfer standard having a certified SO_2 concentration of not less than 10 ppm, in N_2, traceable to a NIST Standard Reference Material (SRM).

4.1.6.2 Clean zero air, free of contaminants that could cause a detectable response or a change in sensitivity of the analyzer. Since ultraviolet fluorescence analyzers may be sensitive to aromatic hydrocarbons and O_2-to-N_2 ratios, it is important that the clean zero air contains less than 0.1 ppm aromatic hydrocarbons and O_2 and N_2 percentages approximately the same as in ambient air. A procedure for generating zero air is given in reference 1.

4.2 Procedure

4.2.1 Obtain a suitable calibration apparatus, such as the one shown schematically in Figure 1, and verify that all materials in contact with the pollutant are of glass, Teflon™, or other suitably inert material and completely clean.

4.2.2 Purge the SO_2 standard gas lines and pressure regulator to remove any residual air.

4.2.3 Ensure that there are no leaks in the system and that the flow measuring devices are properly and accurately calibrated under the conditions of use against a reliable volume or flow rate standard such as a soap-bubble meter or a wet-test meter traceable to a NIST standard. All volumetric flow rates should be corrected to the same reference temperature and pressure by using the formula below:

$$F_c = F_m \frac{298.15P_m}{760(T_m + 273.15)}$$

Where:

F_c = corrected flow rate (L/min at 25 °C and 760 mm Hg),

F_m = measured flow rate, (at temperature, T_m and pressure, P_m),

P_m = measured pressure in mm Hg, (absolute), and

T_m = measured temperature in degrees Celsius.

4.2.4 Allow the SO_2 analyzer under calibration to sample zero air until a stable response is obtained, then make the proper zero adjustment.

4.2.5 Adjust the airflow to provide an SO_2 concentration of approximately 80 percent of the upper measurement range limit of the SO_2 instrument and verify that the total air flow of the calibration system exceeds the demand of all analyzers sampling from the output manifold (with the excess vented).

4.2.6 Calculate the actual SO_2 calibration concentration standard as:

$$[SO_2] = C\frac{F_p}{F_t}$$

Where:

C = the concentration of the SO_2 gas standard

F_p = the flow rate of SO_2 gas standard

F_t = the total air flow rate of pollutant and diluent gases

4.2.7 When the analyzer response has stabilized, adjust the SO_2 span control to obtain the desired response equivalent to the calculated standard concentration. If substantial adjustment of the span control is needed, it may be necessary to re-check the zero and span adjustments by repeating steps 4.2.4 through 4.2.7 until no further adjustments are needed.

4.2.8 Adjust the flow rate(s) to provide several other SO_2 calibration concentrations over the analyzer's measurement range. At least five different concentrations evenly spaced throughout the analyzer's range are suggested.

4.2.9 Plot the analyzer response (vertical or Y-axis) versus SO_2 concentration (horizontal or X-axis). Compute the linear regression slope and intercept and plot the regression line to verify that no point deviates from this line by more than 2 percent of the maximum concentration tested.

NOTE: Additional information on calibration and pollutant standards is provided in Section 12 of Reference 3.

5.0 FREQUENCY OF CALIBRATION

The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checking will vary by analyzer; however, the minimum frequency, acceptance criteria, and subsequent actions are specified in Reference 3, Appendix D: Measurement Quality Objectives and Validation Template for SO_2 (page 9 of 30). The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality control.

6.0 REFERENCES FOR SO_2 METHOD

1. H. Okabe, P. L. Splitstone, and J. J. Ball, "Ambient and Source SO_2 Detector Based on a Fluorescence Method", *Journal of the Air Control Pollution Association,* vol. 23, p. 514–516 (1973).
2. F. P. Schwarz, H. Okabe, and J. K. Whittaker, "Fluorescence Detection of Sulfur Dioxide in Air at the Parts per Billion Level," *Analytical Chemistry,* vol. 46, pp. 1024–1028 (1974).
3. *QA Handbook for Air Pollution Measurement Systems—Volume II. Ambient Air Quality Monitoring Programs.* U.S.

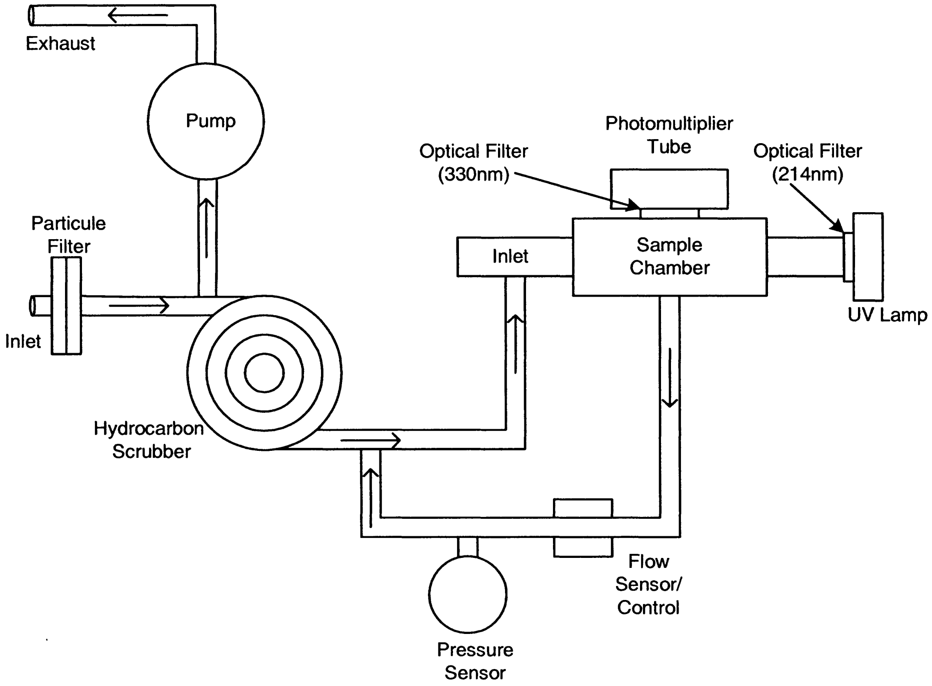

Figure 1. UVF SO_2 analyzer schematic diagram.

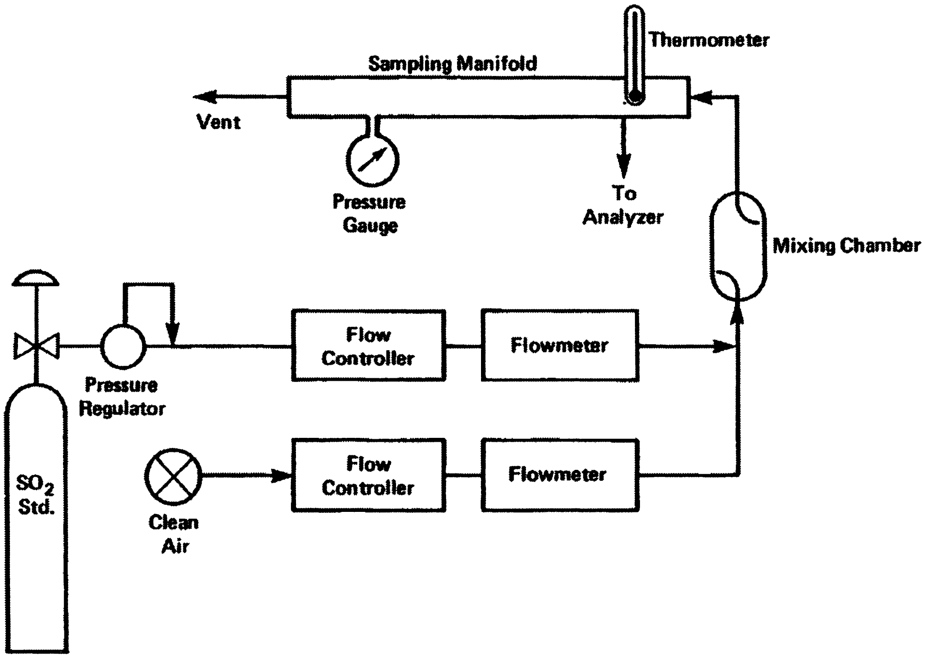

Figure 2. Calibration system using a compressed gas standard.

[75 FR 35593, June 22, 2010]

APPENDIX A–2 TO PART 50—REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1.0 *Applicability.*

1.1 This method provides a measurement of the concentration of sulfur dioxide (SO_2) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for sulfur oxides (sulfur dioxide) as specified in §50.4 and §50.5 of this chapter. The method is applicable to the measurement of ambient SO_2 concentrations using sampling periods ranging from 30 minutes to 24 hours. Additional quality assurance procedures and guidance are provided in part 58, appendixes A and B, of this chapter and in references 1 and 2.

2.0 *Principle.*

2.1 A measured volume of air is bubbled through a solution of 0.04 M potassium tetrachloromercurate (TCM). The SO_2 present in the air stream reacts with the TCM solution to form a stable monochlorosulfonatomercurate(*3*) complex. Once formed, this complex resists air oxidation(*4, 5*) and is stable in the presence of strong oxidants such as ozone and oxides of nitrogen. During subsequent analysis, the complex is reacted with acid-bleached pararosaniline dye and formaldehyde to form an intensely colored pararosaniline methyl sulfonic acid.

(*6*) The optical density of this species is determined spectrophotometrically at 548 nm and is directly related to the amount of SO_2 collected. The total volume of air sampled, corrected to EPA reference conditions (25 °C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of SO_2 in the ambient air is computed and expressed in micrograms per standard cubic meter (µg/std m^3).

3.0 *Range.*

3.1 The lower limit of detection of SO_2 in 10 mL of TCM is 0.75 µg (based on collaborative test results).(*7*) This represents a concentration of 25 μg SO_2/m^3 (0.01 ppm) in an air sample of 30 standard liters (short-term sampling) and a concentration of 13 μg SO_2/m^3 (0.005 ppm) in an air sample of 288 standard liters (long-term sampling). Concentrations less than 25 μg SO_2/m^3 can be measured by sampling larger volumes of ambient air; however, the collection efficiency falls off rapidly at low concentrations.(*8, 9*) Beer's law is adhered to up to 34 μg of SO_2 in 25 mL of final solution. This upper limit of the analysis range represents a concentration of 1,130 μg SO_2/m^3 (0.43 ppm) in an air sample of 30 standard liters and a concentration of 590 μg SO_2/m^3 (0.23 ppm) in an air sample of 288 standard liters. Higher concentrations can be measured by collecting a smaller volume of air, by increasing the volume of absorbing solution, or by diluting a suitable portion of the collected sample with absorbing solution prior to analysis.

4.0 *Interferences.*

4.1 The effects of the principal potential interferences have been minimized or eliminated in the following manner: Nitrogen oxides by the addition of sulfamic acid,(*10, 11*) heavy metals by the addition of ethylenediamine tetracetic acid disodium salt (EDTA) and phosphoric acid,(*10, 12*) and ozone by time delay.(*10*) Up to 60 μg Fe (III), 22 μg V (V), 10 μg Cu (II), 10 μg Mn (II), and 10 μg Cr (III) in 10 mL absorbing reagent can be tolerated in the procedure.(*10*) No significant interference has been encountered with 2.3 μg NH_3.(*13*)

5.0 *Precision and Accuracy.*

5.1 The precision of the analysis is 4.6 percent (at the 95 percent confidence level) based on the analysis of standard sulfite samples.(*10*)

5.2 Collaborative test results (*14*) based on the analysis of synthetic test atmospheres (SO_2 in scrubbed air) using the 24-hour sampling procedure and the sulfite-TCM calibration procedure show that:

- The replication error varies linearly with concentration from ±2.5 μg/m^3 at concentrations of 100 μg/m^3 to ±7 μg/m^3 at concentrations of 400 μg/m^3.
- The day-to-day variability within an individual laboratory (repeatability) varies linearly with concentration from ±18.1 μg/m^3 at levels of 100 μg/m^3 to ±50.9 μg/m^3 at levels of 400 μg/m^3.
- The day-to-day variability between two or more laboratories (reproducibility) varies linearly with concentration from ±36.9 μg/m^3 at levels of 100 μg/m^3 to ±103.5 μ g/m^3 at levels of 400 μg/m^3.
- The method has a concentration-dependent bias, which becomes significant at the 95 percent confidence level at the high concentration level. Observed values tend to be lower than the expected SO_2 concentration level.

6.0 *Stability.*

6.1 By sampling in a controlled temperature environment of 15° ±10 °C, greater than 98.9 percent of the SO_2–TCM complex is retained at the completion of sampling. (*15*) If kept at 5 °C following the completion of sampling, the collected sample has been found to be stable for up to 30 days. (*10*) The presence of EDTA enhances the stability of SO_2 in the TCM solution and the rate of decay is independent of the concentration of SO_2. (*16*)

7.0 *Apparatus.*

7.1 *Sampling.*

7.1.1 *Sample probe:* A sample probe meeting the requirements of section 7 of 40 CFR part 58, appendix E (Teflon® or glass with residence time less than 20 sec.) is used to transport ambient air to the sampling train location. The end of the probe should be designed or oriented to preclude the sampling of precipitation, large particles, etc. A suitable probe can be constructed from Teflon® tubing connected to an inverted funnel.

7.1.2 *Absorber—short-term sampling:* An all glass midget impinger having a solution capacity of 30 mL and a stem clearance of 4 ±1 mm from the bottom of the vessel is used for sampling periods of 30 minutes and 1 hour (or any period considerably less than 24 hours). Such an impinger is shown in Figure 1. These impingers are commercially available from distributors such as Ace Glass, Incorporated.

7.1.3 *Absorber—24-hour sampling:* A polypropylene tube 32 mm in diameter and 164 mm long (available from Bel Art Products, Pequammock, NJ) is used as the absorber. The cap of the absorber must be a polypropylene cap with two ports (rubber stoppers are unacceptable because the absorbing reagent can react with the stopper to yield erroneously high SO_2 concentrations). A glass impinger stem, 6 mm in diameter and 158 mm long, is inserted into one port of the absorber cap. The tip of the stem is tapered to a small diameter orifice (0.4 ±0.1 mm) such that a No. 79 jeweler's drill bit will pass through the opening but a No. 78 drill bit will not. Clearance from the bottom of the absorber to the tip of the stem must be 6 ±2 mm. Glass stems can be fabricated by any reputable glass blower or can be obtained from a scientific supply firm. Upon receipt, the orifice test should be performed to verify the orifice size. The 50 mL volume level should be permanently marked on the absorber. The assembled absorber is shown in Figure 2.

7.1.4 *Moisture trap:* A moisture trap constructed of a glass trap as shown in Figure 1 or a polypropylene tube as shown in Figure 2 is placed between the absorber tube and flow control device to prevent entrained liquid from reaching the flow control device. The tube is packed with indicating silica gel as shown in Figure 2. Glass wool may be substituted for silica gel when collecting short-term samples (1 hour or less) as shown in

Figure 1, or for long term (24 hour) samples if flow changes are not routinely encountered.

7.1.5 *Cap seals:* The absorber and moisture trap caps must seal securely to prevent leaks during use. Heat-shrink material as shown in Figure 2 can be used to retain the cap seals if there is any chance of the caps coming loose during sampling, shipment, or storage.

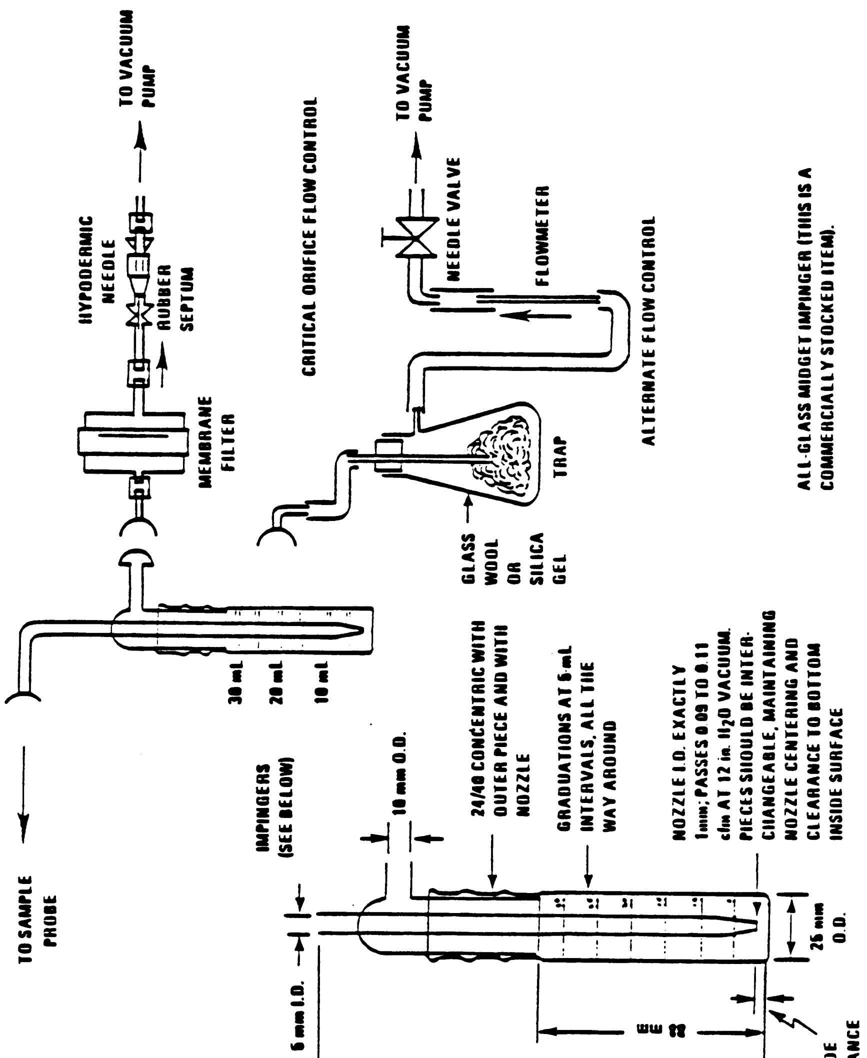

Figure 1. Short-term sampling train.

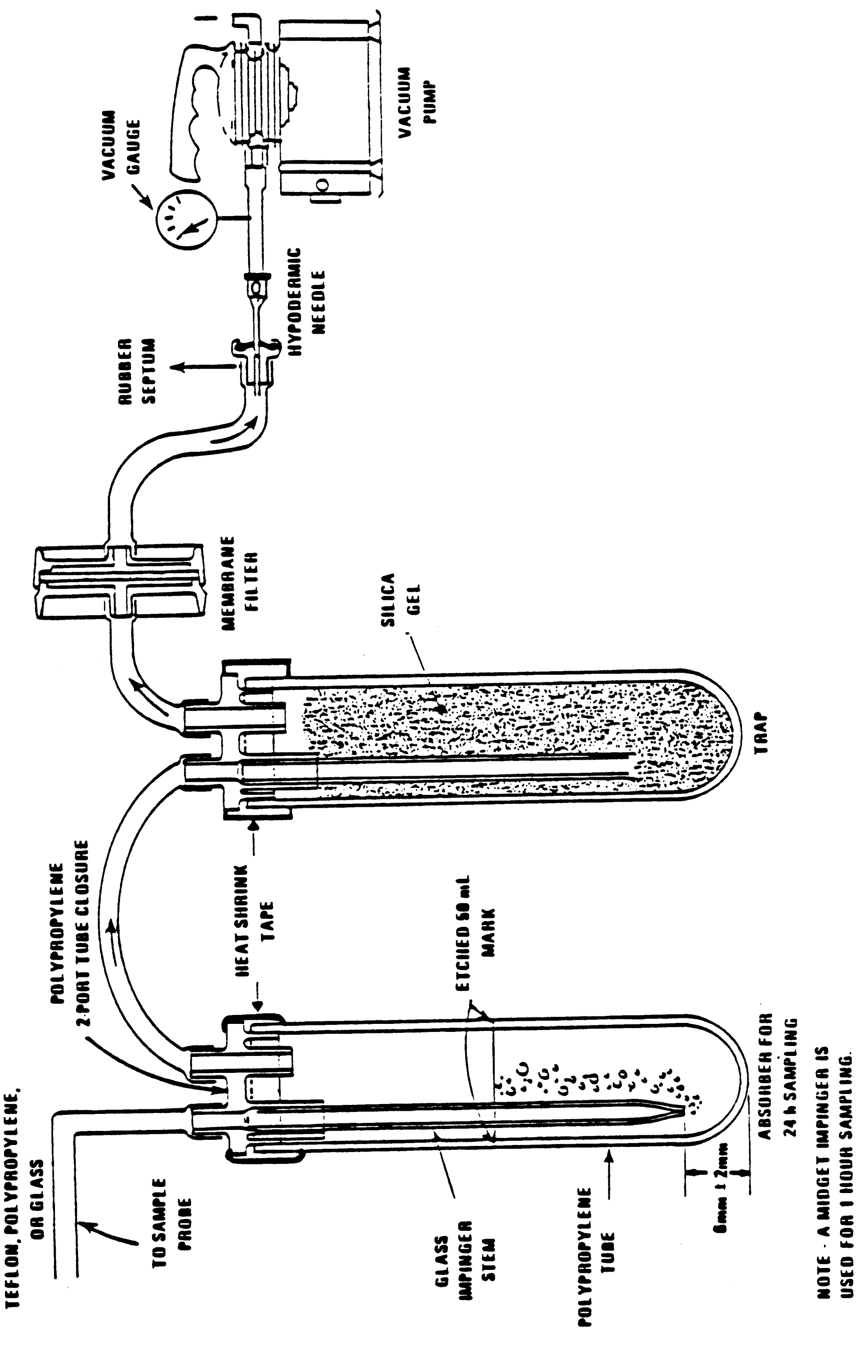

Figure 2. 24-Hour sampling system.

7.1.6 *Flow control device:* A calibrated rotameter and needle valve combination capable of maintaining and measuring air flow to within ±2 percent is suitable for short-term sampling but may not be used for long-term sampling. A critical orifice can be used for regulating flow rate for both long-term and short-term sampling. A 22-gauge hypodermic needle 25 mm long may be used as a critical orifice to yield a flow rate of approximately 1 L/min for a 30-minute sampling period. When sampling for 1 hour, a 23-gauge hypodermic needle 16 mm in length will provide a flow rate of approximately 0.5 L/min. Flow control for a 24-hour sample may be provided by a 27-gauge hypodermic needle critical orifice that is 9.5 mm in length. The flow rate should be in the range of 0.18 to 0.22 L/min.

7.1.7 *Flow measurement device:* Device calibrated as specified in 9.4.1 and used to measure sample flow rate at the monitoring site.

7.1.8 *Membrane particle filter:* A membrane filter of 0.8 to 2 µm porosity is used to protect the flow controller from particles during long-term sampling. This item is optional for short-term sampling.

7.1.9 *Vacuum pump:* A vacuum pump equipped with a vacuum gauge and capable of maintaining at least 70 kPa (0.7 atm) vacuum differential across the flow control device at the specified flow rate is required for sampling.

7.1.10 *Temperature control device:* The temperature of the absorbing solution during sampling must be maintained at 15° ±10 °C. As soon as possible following sampling and until analysis, the temperature of the collected sample must be maintained at 5° ±5 °C. Where an extended period of time may elapse before the collected sample can be moved to the lower storage temperature, a collection temperature near the lower limit of the 15 ±10 °C range should be used to minimize losses during this period. Thermoelectric coolers specifically designed for this temperature control are available commercially and normally operate in the range of 5° to 15 °C. Small refrigerators can be modified to provide the required temperature control; however, inlet lines must be insulated from the lower temperatures to prevent condensation when sampling under humid conditions. A small heating pad may be necessary when sampling at low temperatures (<7 °C) to prevent the absorbing solution from freezing.(*17*)

7.1.11 *Sampling train container:* The absorbing solution must be shielded from light during and after sampling. Most commercially available sampler trains are enclosed in a light-proof box.

7.1.12 *Timer:* A timer is recommended to initiate and to stop sampling for the 24-hour period. The timer is not a required piece of equipment; however, without the timer a technician would be required to start and stop the sampling manually. An elapsed time meter is also recommended to determine the duration of the sampling period.

7.2 *Shipping.*

7.2.1 *Shipping container:* A shipping container that can maintain a temperature of 5° ±5 °C is used for transporting the sample from the collection site to the analytical laboratory. Ice coolers or refrigerated shipping containers have been found to be satisfactory. The use of eutectic cold packs instead of ice will give a more stable temperature control. Such equipment is available from Cole-Parmer Company, 7425 North Oak Park Avenue, Chicago, IL 60648.

7.3 *Analysis.*

7.3.1 *Spectrophotometer:* A spectrophotometer suitable for measurement of absorbances at 548 nm with an effective spectral bandwidth of less than 15 nm is required for analysis. If the spectrophotometer reads out in transmittance, convert to absorbance as follows:

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

where:

A = absorbance, and
T = transmittance ($0 < \geq T < 1$).

A standard wavelength filter traceable to the National Bureau of Standards is used to verify the wavelength calibration according to the procedure enclosed with the filter. The wavelength calibration must be verified upon initial receipt of the instrument and after each 160 hours of normal use or every 6 months, whichever occurs first.

7.3.2 *Spectrophotometer cells:* A set of 1-cm path length cells suitable for use in the visible region is used during analysis. If the cells are unmatched, a matching correction factor must be determined according to Section 10.1.

7.3.3 *Temperature control device:* The color development step during analysis must be conducted in an environment that is in the range of 20° to 30 °C and controlled to ±1 °C. Both calibration and sample analysis must be performed under identical conditions (within 1 °C). Adequate temperature control may be obtained by means of constant temperature baths, water baths with manual temperature control, or temperature controlled rooms.

7.3.4 *Glassware:* Class A volumetric glassware of various capacities is required for preparing and standardizing reagents and standards and for dispensing solutions during analysis. These included pipets, volumetric flasks, and burets.

7.3.5 *TCM waste receptacle:* A glass waste receptacle is required for the storage of spent TCM solution. This vessel should be stoppered and stored in a hood at all times.

8.0 *Reagents.*

8.1 *Sampling.*

8.1.1 *Distilled water:* Purity of distilled water must be verified by the following procedure:(*18*)

- Place 0.20 mL of potassium permanganate solution (0.316 g/L), 500 mL of distilled water, and 1mL of concentrated sulfuric acid in a chemically resistant glass bottle, stopper the bottle, and allow to stand.
- If the permanganate color (pink) does not disappear completely after a period of 1 hour at room temperature, the water is suitable for use.
- If the permanganate color does disappear, the water can be purified by redistilling with one crystal each of barium hydroxide and potassium permanganate in an all glass still.

8.1.2 *Absorbing reagent* (0.04 M potassium tetrachloromercurate [TCM]): Dissolve 10.86 g mercuric chloride, 0.066 g EDTA, and 6.0 g potassium chloride in distilled water and dilute to volume with distilled water in a 1,000-mL volumetric flask. (*Caution:* Mercuric chloride is highly poisonous. If spilled on skin, flush with water immediately.) The pH of this reagent should be between 3.0 and 5.0 (*10*) Check the pH of the absorbing solution by using pH indicating paper or a pH meter. If the pH of the solution is not between 3.0 and 5.0, dispose of the solution according to one of the disposal techniques described in Section 13.0. The absorbing reagent is normally stable for 6 months. If a precipitate forms, dispose of the reagent according to one of the procedures described in Section 13.0.

8.2 *Analysis.*

8.2.1 *Sulfamic acid* (0.6%): Dissolve 0.6 g sulfamic acid in 100 mL distilled water. Perpare fresh daily.

8.2.2 *Formaldehyde* (0.2%): Dilute 5 mL formaldehyde solution (36 to 38 percent) to 1,000 mL with distilled water. Prepare fresh daily.

8.2.3 *Stock iodine solution* (0.1 N): Place 12.7 g resublimed iodine in a 250-mL beaker and add 40 g potassium iodide and 25 mL water. Stir until dissolved, transfer to a 1,000 mL volumetric flask and dilute to volume with distilled water.

8.2.4 *Iodine solution* (0.01 N): Prepare approximately 0.01 N iodine solution by diluting 50 mL of stock iodine solution (Section 8.2.3) to 500 mL with distilled water.

8.2.5 *Starch indicator solution:* Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with enough distilled water to form a paste. Add the paste slowly to 200 mL of boiling distilled water and continue boiling until clear. Cool and transfer the solution to a glass stopperd bottle.

8.2.6 *1 N hydrochloric acid:* Slowly and while stirring, add 86 mL of concentrated hydrochloric acid to 500 mL of distilled water. Allow to cool and dilute to 1,000 mL with distilled water.

8.2.7 *Potassium iodate solution:* Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate that has been previously dried at 180 °C for at least 3 hours and cooled in a dessicator. Dissolve, then dilute to volume in a 500-mL volumetric flask with distilled water.

8.2.8 *Stock sodium thiosulfate solution* (0.1 N): Prepare a stock solution by dissolving 25 g sodium thiosulfate ($Na_2 S_2 O_3 \div 5H_2 O$) in 1,000 mL freshly boiled, cooled, distilled water and adding 0.1 g sodium carbonate to the solution. Allow the solution to stand at least 1 day before standardizing. To standardize, accurately pipet 50 mL of potassium iodate solution (Section 8.2.7) into a 500-mL iodine flask and add 2.0 g of potassium iodide and 10 mL of 1 N HCl. Stopper the flask and allow to stand for 5 minutes. Titrate the solution with stock sodium thiosulfate solution (Section 8.2.8) to a pale yellow color. Add 5 mL of starch solution (Section 8.2.5) and titrate until the blue color just disappears. Calculate the normality (N_s) of the stock sodium thiosulfate solution as follows:

$$N_S = \frac{W}{M} \times 2.80 \qquad (2)$$

where:

M = volume of thiosulfate required in mL, and

W = weight of potassium iodate in g (recorded weight in Section 8.2.7).

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

8.2.9 *Working sodium thiosulfate titrant* (0.01 N): Accurately pipet 100 mL of stock sodium thiosulfate solution (Section 8.2.8) into a 1,000-mL volumetric flask and dilute to volume with freshly boiled, cooled, distilled water. Calculate the normality of the working sodium thiosulfate titrant (N_T) as follows:

$$N_T = N_S \times 0.100 \qquad (3)$$

8.2.10 *Standardized sulfite solution for the preparation of working sulfite-TCM solution:* Dissolve 0.30 g sodium metabisulfite ($Na_2 S_2 O_5$) or 0.40 g sodium sulfite ($Na_2 SO_3$) 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 μg SO_2/mL. 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 solution (Section 8.2.4) 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 stand for 5 minutes. Prepare the working sulfite-TCM solution (Section 8.2.11) immediately prior to adding the iodine solution to the flasks. Using a buret containing standardized 0.01 N thiosulfate titrant (Section 8.2.9), titrate the solution in each flask to a pale yellow color. Then add 5 mL starch solution (Section 8.2.5) and continue the titration until the blue color just disappears.

8.2.11 *Working sulfite-TCM solution:* Accurately pipet 5 mL of the standard sulfite solution (Section 8.2.10) into a 250-mL volumetric flask and dilute to volume with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution as follows:

$$C_{TCM/SO2}\left(\mu g\, SO_2/mL\right) = \frac{(A - B)\left(N_T\right)(32{,}000)}{25} \times 0.02 \qquad (4)$$

where:

A = volume of thiosulfate titrant required for the blank, mL;

B = volume of thiosulfate titrant required for the sample, mL;

N_T = normality of the thiosulfate titrant, from equation (3);

32,000 = milliequivalent weight of SO_2, μg;

25 = volume of standard sulfite solution, mL; and

0.02 = dilution factor.

This solution is stable for 30 days if kept at 5 °C. (16) If not kept at 5 °C, prepare fresh daily.

8.2.12 *Purified pararosaniline (PRA) stock solution* (0.2% nominal):

8.2.12.1 *Dye specifications*—

- The dye must have a maximum absorbance at a wavelength of 540 nm when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid;
- The absorbance of the reagent blank, which is temperature sensitive (0.015 absorbance unit/ °C), must not exceed 0.170 at 22 °C with a 1-cm optical path length when the blank is prepared according to the specified procedure;
- The calibration curve (Section 10.0) must have a slope equal to 0.030 ±0.002 absorbance unit/μg SO_2 with a 1-cm optical path length when the dye is pure and the sulfite solution is properly standardized.

8.2.12.2 *Preparation of stock PRA solution*—A specially purified (99 to 100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco Co.). Alternatively, the dye may be purified, a stock solution prepared, and then assayed according to the procedure as described below.*(10)*

8.2.12.3 *Purification procedure for PRA*—

1. Place 100 mL each of 1-butanol and 1 N HCl in a large separatory funnel (250-mL) and allow to equilibrate. Note: Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Before using, check by placing 20 mL of 1-butanol and 5 mL of 20 percent potassium iodide (KI) solution in a 50-mL separatory funnel and shake thoroughly. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide and collect the middle fraction or purchase a new supply of 1-butanol.

2. Weigh 100 mg of pararosaniline hydrochloride dye (PRA) in a small beaker. Add 50 mL of the equilibrated acid (drain in acid from the bottom of the separatory funnel in 1.) to the beaker and let stand for several minutes. Discard the remaining acid phase in the separatory funnel.

3. To a 125-mL separatory funnel, add 50 mL of the equilibrated 1-butanol (draw the 1-butanol from the top of the separatory funnel in 1.). Transfer the acid solution (from 2.) containing the dye to the funnel and shake carefully to extract. The violet impurity will transfer to the organic phase.

4. Transfer the lower aqueous phase into another separatory funnel, add 20 mL of equilibrated 1-butanol, and extract again.

5. Repeat the extraction procedure with three more 10-mL portions of equilibrated 1-butanol.

6. After the final extraction, filter the acid phase through a cotton plug into a 50-mL volumetric flask and bring to volume with 1 N HCl. This stock reagent will be a yellowish red.

7. To check the purity of the PRA, perform the assay and adjustment of concentration (Section 8.2.12.4) and prepare a reagent blank (Section 11.2); the absorbance of this reagent blank at 540 nm should be less than 0.170 at 22 °C. If the absorbance is greater than 0.170 under these conditions, further extractions should be performed.

8.2.12.4 *PRA assay procedure*—The concentration of pararosaniline hydrochloride (PRA) need be assayed only once after purification. It is also recommended that commercial solutions of pararosaniline be assayed when first purchased. The assay procedure is as follows:*(10)*

1. Prepare 1 M acetate-acetic acid buffer stock solution with a pH of 4.79 by dissolving

13.61 g of sodium acetate trihydrate in distilled water in a 100-mL volumetric flask. Add 5.70 mL of glacial acetic acid and dilute to volume with distilled water.

2. Pipet 1 mL of the stock PRA solution obtained from the purification process or from a commercial source into a 100-mL volumetric flask and dilute to volume with distilled water.

3. Transfer a 5–mL aliquot of the diluted PRA solution from 2. into a 50–mL volumetric flask. Add 5mL of 1 M acetate-acetic acid buffer solution from 1. and dilute the mixture to volume with distilled water. Let the mixture stand for 1 hour.

4. Measure the absorbance of the above solution at 540 nm with a spectrophotometer against a distilled water reference. Compute the percentage of nominal concentration of PRA by

$$\%\mathrm{PRA} = \frac{\mathrm{A} \times \mathrm{K}}{\mathrm{W}} \qquad (5)$$

where:

A = measured absorbance of the final mixture (absorbance units);

W = weight in grams of the PRA dye used in the assay to prepare 50 mL of stock solution (for example, 0.100 g of dye was used to prepare 50 mL of solution in the purification procedure; when obtained from commercial sources, use the stated concentration to compute W; for 98% PRA, W = .098 g.); and

K = 21.3 for spectrophotometers having a spectral bandwidth of less than 15 nm and a path length of 1 cm.

8.2.13 *Pararosaniline reagent:* To a 250–mL volumetric flask, add 20 mL of stock PRA solution. Add an additional 0.2 mL of stock solution for each percentage that the stock assays below 100 percent. Then add 25 mL of 3 M phosphoric acid and dilute to volume with distilled water. The reagent is stable for at least 9 months. Store away from heat and light.

9.0 *Sampling Procedure.*

9.1 *General Considerations.* Procedures are described for short-term sampling (30-minute and 1-hour) and for long-term sampling (24-hour). Different combinations of absorbing reagent volume, sampling rate, and sampling time can be selected to meet special needs. For combinations other than those specifically described, the conditions must be adjusted so that linearity is maintained between absorbance and concentration over the dynamic range. Absorbing reagent volumes less than 10 mL are not recommended. The collection efficiency is above 98 percent for the conditions described; however, the efficiency may be substantially lower when sampling concentrations below 25 $\mu\gamma SO_2/m^3$.(*8,9*)

9.2 *30-Minute and 1-Hour Sampling.* Place 10 mL of TCM absorbing reagent in a midget impinger and seal the impinger with a thin film of silicon stopcock grease (around the ground glass joint). Insert the sealed impinger into the sampling train as shown in Figure 1, making sure that all connections between the various components are leak tight. Greaseless ball joint fittings, heat shrinkable Teflon® tubing, or Teflon® tube fittings may be used to attain leakfree conditions for portions of the sampling train that come into contact with air containing SO_2. Shield the absorbing reagent from direct sunlight by covering the impinger with aluminum foil or by enclosing the sampling train in a light-proof box. Determine the flow rate according to Section 9.4.2. Collect the sample at 1 ±0.10 L/min for 30-minute sampling or 0.500 ±0.05 L/min for 1-hour sampling. Record the exact sampling time in minutes, as the sample volume will later be determined using the sampling flow rate and the sampling time. Record the atmospheric pressure and temperature.

9.3 *24-Hour Sampling.* Place 50 mL of TCM absorbing solution in a large absorber, close the cap, and, if needed, apply the heat shrink material as shown in Figure 3. Verify that the reagent level is at the 50 mL mark on the absorber. Insert the sealed absorber into the sampling train as shown in Figure 2. At this time verify that the absorber temperature is controlled to 15 ±10 °C. During sampling, the absorber temperature must be controlled to prevent decomposition of the collected complex. From the onset of sampling until analysis, the absorbing solution must be protected from direct sunlight. Determine the flow rate according to Section 9.4.2. Collect the sample for 24 hours from midnight to midnight at a flow rate of 0.200 ±0.020 L/min. A start/stop timer is helpful for initiating and stopping sampling and an elapsed time meter will be useful for determining the sampling time.

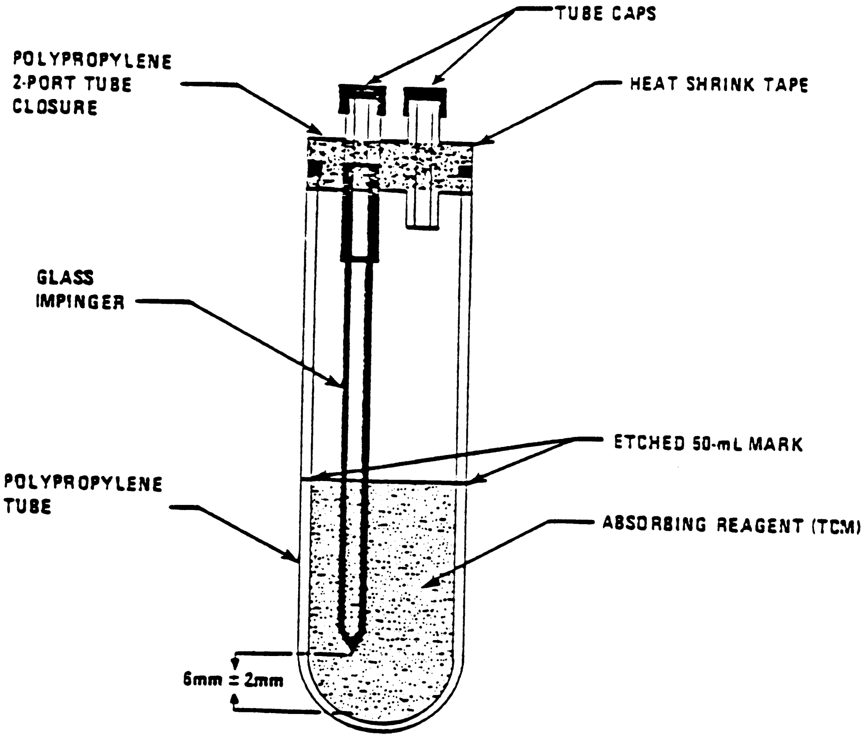

Figure 3. An absorber (24-hour sample) filled and assembled for shipment.

9.4 *Flow Measurement.*

9.4.1 *Calibration:* Flow measuring devices used for the on-site flow measurements required in 9.4.2 must be calibrated against a reliable flow or volume standard such as an NBS traceable bubble flowmeter or calibrated wet test meter. Rotameters or critical orifices used in the sampling train may be calibrated, if desired, as a quality control check, but such calibration shall not replace the on-site flow measurements required by 9.4.2. In-line rotameters, if they are to be calibrated, should be calibrated in situ, with the appropriate volume of solution in the absorber.

9.4.2 *Determination of flow rate at sampling site:* For short-term samples, the standard flow rate is determined at the sampling site at the initiation and completion of sample collection with a calibrated flow measuring device connected to the inlet of the absorber. For 24-hour samples, the standard flow rate is determined at the time the absorber is placed in the sampling train and again when the absorber is removed from the train for shipment to the analytical laboratory with a calibrated flow measuring device connected to the inlet of the sampling train. The flow rate determination must be made with all components of the sampling system in operation (e.g., the absorber temperature controller and any sample box heaters must also be operating). Equation 6 may be used to determine the standard flow rate when a calibrated positive displacement meter is used as the flow measuring device. Other types of calibrated flow measuring devices may also be used to determine the flow rate at the sampling site provided that the user applies any appropriate corrections to devices for which output is dependent on temperature or pressure.

$$Q_{std} = Q_{act} \times \frac{P_b - (1 - RH)P_{H_2O}}{P_{std}} \times \frac{298.16.}{\left(T_{meter} + 273.16\right).} \qquad (6)$$

where:

Q_{std} = flow rate at standard conditions, std L/min (25 °C and 760 mm Hg);

Q_{act} = flow rate at monitoring site conditions, L/min;

P_b = barometric pressure at monitoring site conditions, mm Hg or kPa;

RH = fractional relative humidity of the air being measured;

P_{H_2O} = vapor pressure of water at the temperature of the air in the flow or volume standard, in the same units as P_b, (for wet volume standards only, i.e., bubble flowmeter or wet test meter; for dry standards, i.e., dry test meter, P_{H_2O} = 0);

P_{std} = standard barometric pressure, in the same units as P_b (760 mm Hg or 101 kPa); and

T_{meter} = temperature of the air in the flow or volume standard, °C (e.g., bubble flowmeter).

If a barometer is not available, the following equation may be used to determine the barometric pressure:

$$P_b = 760 - .076(H)\,\text{mm Hg, or } P_b = 101 - .01(H)\,\text{kPa} \qquad (7)$$

where:

H = sampling site elevation above sea level in meters.

If the initial flow rate (Q_i) differs from the flow rate of the critical orifice or the flow rate indicated by the flowmeter in the sampling train (Q_c) by more than 5 percent as determined by equation (8), check for leaks and redetermine Q_i.

$$\%\ \text{Diff} = \frac{Q_i - Q_c}{Q_c} \times 100 \qquad (8)$$

Invalidate the sample if the difference between the initial (Q_i) and final (Q_f) flow rates is more than 5 percent as determined by equation (9):

$$\%\ \text{Diff} = \frac{Q_i - Q_f}{Q_f} \times 100 \qquad (9)$$

9.5 *Sample Storage and Shipment.* Remove the impinger or absorber from the sampling train and stopper immediately. Verify that the temperature of the absorber is not above 25 °C. Mark the level of the solution with a temporary (e.g., grease pencil) mark. If the sample will not be analyzed within 12 hours of sampling, it must be stored at 5° ±5 °C until analysis. Analysis must occur within 30 days. If the sample is transported or shipped for a period exceeding 12 hours, it is recommended that thermal coolers using eutectic ice packs, refrigerated shipping containers, etc., be used for periods up to 48 hours. (*17*) Measure the temperature of the absorber solution when the shipment is received. Invalidate the sample if the temperature is above 10 °C. Store the sample at 5° ±5 °C until it is analyzed.

10.0 *Analytical Calibration.*

10.1 *Spectrophotometer Cell Matching.* If unmatched spectrophotometer cells are used, an absorbance correction factor must be determined as follows:

1. Fill all cells with distilled water and designate the one that has the lowest absorbance at 548 nm as the reference. (This reference cell should be marked as such and continually used for this purpose throughout all future analyses.)
2. Zero the spectrophotometer with the reference cell.
3. Determine the absorbance of the remaining cells (A_c) in relation to the reference cell and record these values for future use. Mark all cells in a manner that adequately identifies the correction.

The corrected absorbance during future analyses using each cell is determining as follows:

$$A = A_{obs} - A_c \qquad (10)$$

where:

A = corrected absorbance,

A_{obs} = uncorrected absorbance, and

A_c = cell correction.

10.2 *Static Calibration Procedure* (Option 1). Prepare a dilute working sulfite-TCM solution by diluting 10 mL of the working sulfite-TCM solution (Section 8.2.11) to 100 mL with TCM absorbing reagent. Following the table below, accurately pipet the indicated volumes of the sulfite-TCM solutions into a series of 25-mL volumetric flasks. Add TCM absorbing reagent as indicated to bring the volume in each flask to 10 mL.

Sulfite-TCM solution	Volume of sulfite-TCM solution	Volume of TCM, mL	Total µg SO_2 (approx.*
Working	4.0	6.0	28.8
Working	3.0	7.0	21.6
Working	2.0	8.0	14.4
Dilute working	10.0	0.0	7.2
Dilute working	5.0	5.0	3.6
	0.0	10.0	0.0

*Based on working sulfite-TCM solution concentration of 7.2 µg SO_2/mL; the actual total µg SO_2 must be calculated using equation 11 below.

To each volumetric flask, add 1 mL 0.6% sulfamic acid (Section 8.2.1), accurately pipet 2 mL 0.2% formaldehyde solution (Section 8.2.2), then add 5 mL pararosaniline solution (Section 8.2.13). Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with recently boiled and cooled distilled water and mix thoroughly. The color must be developed (during the 30-minute period) in a temperature environment in the range of 20° to 30 °C, which is controlled to ±1 °C. For increased precision, a constant temperature bath is recommended during the color development step. After 30 minutes, determine the corrected absorbance of each standard at 548 nm against a distilled water reference (Section 10.1). Denote this absorbance as (A). Distilled water is used in the reference cell rather than the reagant blank because of the temperature sensitivity of the reagent blank. Calculate the total micrograms SO_2 in each solution:

$$\mu g\ SO_2 = V_{TCM/SO2} \times C_{TCM/SO2} \times D \qquad (11)$$

where:

$V_{TCM/SO}2$ = volume of sulfite-TCM solution used, mL;

$C_{TCM/SO}2$ = concentration of sulfur dioxide in the working sulfite-TCM, µg SO_2/mL (from equation 4); and

D = dilution factor (D = 1 for the working sulfite-TCM solution; D = 0.1 for the diluted working sulfite-TCM solution).

A calibration equation is determined using the method of linear least squares (Section 12.1). The total micrograms SO_2 contained in each solution is the x variable, and the corrected absorbance (eq. 10) associated with each solution is the y variable. For the calibration to be valid, the slope must be in the range of 0.030 ±0.002 absorbance unit/µg SO_2, the intercept as determined by the least squares method must be equal to or less than 0.170 absorbance unit when the color is developed at 22 °C (add 0.015 to this 0.170 specification for each °C above 22 °C) and the correlation coefficient must be greater than 0.998. If these criteria are not met, it may be the result of an impure dye and/or an improperly standardized sulfite-TCM solution. A calibration factor (B_s) is determined by calculating the reciprocal of the slope and is subsequently used for calculating the sample concentration (Section 12.3).

10.3 *Dynamic Calibration Procedures* (Option 2). Atmospheres containing accurately known concentrations of sulfur dioxide are prepared using permeation devices. In the systems for generating these atmospheres, the permeation device emits gaseous SO_2 at a known, low, constant rate, provided the temperature of the device is held constant (±0.1 °C) and the device has been accurately calibrated at the temperature of use. The SO_2 permeating from the device is carried by a low flow of dry carrier gas to a mixing chamber where it is diluted with SO_2-free air to the desired concentration and supplied to a vented manifold. A typical system is shown schematically in Figure 4 and this system and other similar systems have been described in detail by O'Keeffe and Ortman; (*19*) Scaringelli, Frey, and Saltzman, (*20*) and Scaringelli, O'Keeffe, Rosenberg, and Bell. (*21*) Permeation devices may be prepared or purchased and in both cases must be traceable either to a National Bureau of Standards (NBS) Standard Reference Material (SRM 1625, SRM 1626, SRM 1627) or to an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 22, and a list of CRM sources is available from the address shown for Reference 22. A recommended protocol for certifying a permeation device to an NBS SRM or CRM is given in Section 2.0.7 of Reference 2. Device permeation rates of 0.2 to 0.4 µg/min, inert gas flows of about 50 mL/min, and dilution air flow rates from 1.1 to 15 L/min conveniently yield standard atmospheres in the range of 25 to 600 µg SO_2/m^3 (0.010 to 0.230 ppm).

10.3.1 *Calibration Option 2A* (30-minute and 1-hour samples): Generate a series of six standard atmospheres of SO_2 (e.g., 0, 50, 100, 200, 350, 500, 750 µg/m^3) by adjusting the dilution flow rates appropriately. The concentration of SO_2 in each atmosphere is calculated as follows:

$$C_a = \frac{P_r \times 10^3}{Q_d + Q_p} \qquad (12)$$

where:

C_a = concentration of SO_2 at standard conditions, µg/m^3;

P_r = permeation rate, µg/min;

Q_d = flow rate of dilution air, std L/min; and

Q_p = flow rate of carrier gas across permeation device, std L/min.

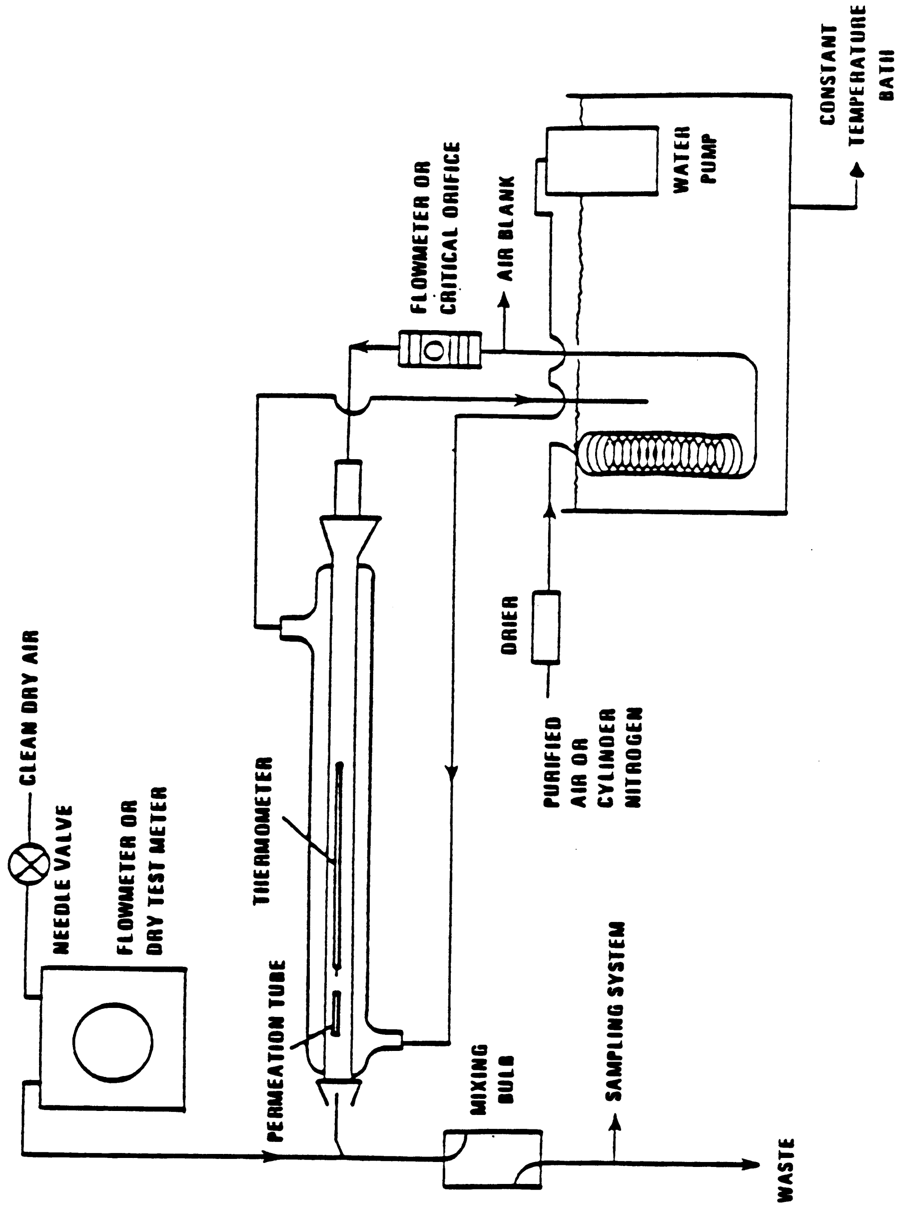

Figure 4. Permeation tube schematic for laboratory use.

Be sure that the total flow rate of the standard exceeds the flow demand of the sample train, with the excess flow vented at atmospheric pressure. Sample each atmosphere using similar apparatus as shown in Figure 1 and under the same conditions as field sampling (*i.e.*, use same absorbing reagent volume and sample same volume of air at an equivalent flow rate). Due to the length of the sampling periods required, this method is not recommended for 24-hour sampling. At the completion of sampling, quantitatively transfer the contents of each impinger to one of a series of 25-mL volumetric flasks (if 10 mL of absorbing solution was used) using small amounts of distilled water for rinse (<5mL). If >10 mL of absorbing solution was used, bring the absorber solution in each impinger to orginal volume with distilled H_2 O and pipet 10-mL portions from each impinger into a series of 25-mL volumetric flasks. If the color development steps are not to be started within 12 hours of sampling, store the solutions at 5° ±5 °C. Calculate the total micrograms SO_2 in each solution as follows:

$$\mu gSO_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \qquad (13)$$

where:

C_a = concentration of SO_2 in the standard atmosphere, µg/m^3;

O_s = sampling flow rate, std L/min;

t = sampling time, min;

V_a = volume of absorbing solution used for color development (10 mL); and

V_b = volume of absorbing solution used for sampling, mL.

Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate a calibration equation and a calibration factor (B_g) according to Section 10.2, adhering to all the specified criteria.

10.3.2 Calibration Option 2B (24-hour samples): Generate a standard atmosphere containing approximately 1,050 µg SO_2/m^3 and calculate the exact concentration according to equation 12. Set up a series of six absorbers according to Figure 2 and connect to a common manifold for sampling the standard atmosphere. Be sure that the total flow rate of the standard exceeds the flow demand at the sample manifold, with the excess flow vented at atmospheric pressure. The absorbers are then allowed to sample the atmosphere for varying time periods to yield solutions containing 0, 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2 µg SO_2/mL solution. The sampling times required to attain these solution concentrations are calculated as follows:

$$t = \frac{V_b \times C_s}{C_a \times Q_s \times 10^{-3}} \qquad (14)$$

where:

t = sampling time, min;

V_b = volume of absorbing solution used for sampling (50 mL);

C_s = desired concentration of SO_2 in the absorbing solution, µg/mL;

C_a = concentration of the standard atmosphere calculated according to equation 12, µg/m^3; and

Q_s = sampling flow rate, std L/min.

At the completion of sampling, bring the absorber solutions to original volume with distilled water. Pipet a 10-mL portion from each absorber into one of a series of 25-mL volumetric flasks. If the color development steps are not to be started within 12 hours of sampling, store the solutions at 5° ±5 °C. Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate the total µg SO_2 in each standard as follows:

$$\mu gSO_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \qquad (15)$$

where:

V_a = volume of absorbing solution used for color development (10 mL).

All other parameters are defined in equation 14.

Calculate a calibration equation and a calibration factor (B_t) according to Section 10.2 adhering to all the specified criteria.

11.0 *Sample Preparation and Analysis.*

11.1 *Sample Preparation.* Remove the samples from the shipping container. If the shipment period exceeded 12 hours from the completion of sampling, verify that the temperature is below 10 °C. Also, compare the solution level to the temporary level mark on the absorber. If either the temperature is above 10 °C or there was significant loss (more than 10 mL) of the sample during shipping, make an appropriate notation in the record and invalidate the sample. Prepare the samples for analysis as follows:

1. For 30-minute or 1-hour samples: Quantitatively transfer the entire 10 mL amount of absorbing solution to a 25-mL volumetric flask and rinse with a small amount (<5 mL) of distilled water.

2. For 24-hour samples: If the volume of the sample is less than the original 50-mL volume (permanent mark on the absorber), adjust the volume back to the original volume with distilled water to compensate for water lost to evaporation during sampling. If the final volume is greater than the original volume, the volume must be measured using a graduated cylinder. To analyze, pipet 10 mL

of the solution into a 25-mL volumetric flask.

11.2 *Sample Analysis.* For each set of determinations, prepare a reagent blank by adding 10 mL TCM absorbing solution to a 25-mL volumetric flask, and two control standards containing approximately 5 and 15 µg SO_2, respectively. The control standards are prepared according to Section 10.2 or 10.3. The analysis is carried out as follows:

1. Allow the sample to stand 20 minutes after the completion of sampling to allow any ozone to decompose (if applicable).
2. To each 25-mL volumetric flask containing reagent blank, sample, or control standard, add 1 mL of 0.6% sulfamic acid (Section 8.2.1) and allow to react for 10 min.
3. Accurately pipet 2 mL of 0.2% formaldehyde solution (Section 8.2.2) and then 5 mL of pararosaniline solution (Section 8.2.13) into each flask. Start a laboratory timer set at 30 minutes.
4. Bring each flask to volume with recently boiled and cooled distilled water and mix thoroughly.
5. During the 30 minutes, the solutions must be in a temperature controlled environment in the range of 20° to 30 °C maintained to ±1 °C. This temperature must also be within 1 °C of that used during calibration.
6. After 30 minutes and before 60 minutes, determine the corrected absorbances (equation 10) of each solution at 548 nm using 1-cm optical path length cells against a distilled water reference (Section 10.1). (*Distilled water is used as a reference instead of the reagent blank because of the sensitivity of the reagent blank to temperature.)*
7. Do not allow the colored solution to stand in the cells because a film may be deposited. Clean the cells with isopropyl alcohol after use.
8. The reagent blank must be within 0.03 absorbance units of the intercept of the calibration equation determined in Section 10.

11.3 *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 the absorbance redetermined within 5 minutes. Solutions with higher absorbances can be diluted up to sixfold with the reagent blank in order to obtain scale readings of less than 1.0 absorbance unit. However, it is recommended that a smaller portion (<10 mL) of the original sample be reanalyzed (if possible) if the sample requires a dilution greater than 1:1.

11.4 *Reagent disposal.* All reagents containing mercury compounds must be stored and disposed of using one of the procedures contained in Section 13. Until disposal, the discarded solutions can be stored in closed glass containers and should be left in a fume hood.

12.0 *Calculations.*

12.1 *Calibration Slope, Intercept, and Correlation Coefficient.* The method of least squares is used to calculate a calibration equation in the form of:

$$y = mx + b \qquad (16)$$

where:

y = corrected absorbance,
m = slope, absorbance unit/µg SO_2,
x = micrograms of SO_2,
b = y intercept (absorbance units).

The slope (m), intercept (b), and correlation coefficient (r) are calculated as follows:

$$m = \frac{n\sum xy - (\sum x)(\sum y)}{n\sum x^2 - (\sum x)^2} \qquad (17)$$

$$b = \frac{\sum y - m\sum x}{n} \qquad (18)$$

$$r = \sqrt{\frac{m(\sum xy - \sum x \sum y / n)}{\sum y^2 - (\sum y)^2 / n}} \qquad (19)$$

where n is the number of calibration points.

A data form (Figure 5) is supplied for easily organizing calibration data when the slope, intercept, and correlation coefficient are calculated by hand.

12.2 *Total Sample Volume.* Determine the sampling volume at standard conditions as follows:

$$V_{std} = \frac{Q_i + Q_f}{2} \times t \qquad (20)$$

where:

V_{std} = sampling volume in std L,
Q_i = standard flow rate determined at the initiation of sampling in std L/min,
Q_f = standard flow rate determined at the completion of sampling is std L/min, and
t = total sampling time, min.

12.3 *Sulfur Dioxide Concentration.* Calculate and report the concentration of each sample as follows:

$$\mu g\ SO_2/m^3 = \frac{(A - A_o)(B_x)(10^3)}{V_{std}} \times \frac{V_b}{V_a} \qquad (21)$$

where:

A = corrected absorbance of the sample solution, from equation (10);
A_o = corrected absorbance of the reagent blank, using equation (10);
B_X = calibration factor equal to B_s, B_g, or B_t depending on the calibration procedure used, the reciprocal of the slope of the calibration equation;
V_a = volume of absorber solution analyzed, mL;
V_b = total volume of solution in absorber (see 11.1–2), mL; and
V_{std} = standard air volume sampled, std L (from Section 12.2).

DATA FORM

[For hand calculations]

Calibration point no.	Micrograms So_2	Absorbance units			
	(x)	(y)	x^2	xy	y^2
1	....	....	....	....	....
2	....	....	....	....	....
3	....	....	....	....	....
4	....	....	....	....	....
5	....	....	....	....	....
6	....	....	....	....	....

Σ x=______ Σ y=______ Σ x^2=______ Σxy______ Σy^2______

n=______ (number of pairs of coordinates.)

FIGURE 5. Data form for hand calculations.

12.4 Control Standards. Calculate the analyzed micrograms of SO_2 in each control standard as follows:

$$C_q = \left(A - A_o\right) \times B_x \tag{22}$$

where:

C_q = analyzed µg SO_2 in each control standard,

A = corrected absorbance of the control standard, and

A_o = corrected absorbance of the reagent blank.

The difference between the true and analyzed values of the control standards must not be greater than 1 µg. If the difference is greater than 1 µg, the source of the discrepancy must be identified and corrected.

12.5 Conversion of µg/m^3 to ppm (v/v). If desired, the concentration of sulfur dioxide at reference conditions can be converted to ppm SO_2 (v/v) as follows:

$$\text{ppm } SO_2 = \frac{\mu g\ SO_2}{m^3} \times 3.82 \times 10^{-4} \tag{23}$$

13.0 The TCM absorbing solution and any reagents containing mercury compounds must be treated and disposed of by one of the methods discussed below. Both methods remove greater than 99.99 percent of the mercury.

13.1 *Disposal of Mercury-Containing Solutions.*

13.2 *Method for Forming an Amalgam.*

1. Place the waste solution in an uncapped vessel in a hood.
2. For each liter of waste solution, add approximately 10 g of sodium carbonate until neutralization has occurred (NaOH may have to be used).
3. Following neutralization, add 10 g of granular zinc or magnesium.
4. Stir the solution in a hood for 24 hours. Caution must be exercised as hydrogen gas is evolved by this treatment process.
5. After 24 hours, allow the solution to stand without stirring to allow the mercury amalgam (solid black material) to settle to the bottom of the waste receptacle.
6. Upon settling, decant and discard the supernatant liquid.
7. Quantitatively transfer the solid material to a container and allow to dry.
8. The solid material can be sent to a mercury reclaiming plant. It must not be discarded.

13.3 *Method Using Aluminum Foil Strips.*

1. Place the waste solution in an uncapped vessel in a hood.
2. For each liter of waste solution, add approximately 10 g of aluminum foil strips. If all the aluminum is consumed and no gas is evolved, add an additional 10 g of foil. Repeat until the foil is no longer consumed and allow the gas to evolve for 24 hours.
3. Decant the supernatant liquid and discard.
4. Transfer the elemental mercury that has settled to the bottom of the vessel to a storage container.
5. The mercury can be sent to a mercury reclaiming plant. It must not be discarded.

14.0 *References for SO_2 Method.*

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[47 FR 54899, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983. Redesignated at 75 FR 35595, June 22, 2010]

APPENDIX B TO PART 50—REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATE MATTER IN THE ATMOSPHERE (HIGH-VOLUME METHOD)

1.0 *Applicability.*

1.1 This method provides a measurement of the mass concentration of total suspended particulate matter (TSP) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for particulate matter as specified in §50.6 and §50.7 of this chapter. The measurement process is nondestructive, and the size of the sample collected is usually adequate for subsequent chemical analysis. Quality assurance procedures and guidance are provided in part 58, appendixes A and B, of this chapter and in References 1 and 2.

2.0 *Principle.*

2.1 An air sampler, properly located at the measurement site, draws a measured quantity of ambient air into a covered housing and through a filter during a 24-hr (nominal) sampling period. The sampler flow rate and the geometry of the shelter favor the collection of particles up to 25–50 μm (aerodynamic diameter), depending on wind speed and direction.(*3*) The filters used are specified to have a minimum collection efficiency of 99 percent for 0.3 μm (DOP) particles (see Section 7.1.4).

2.2 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (25 °C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter (μg/std m^3). For samples collected at temperatures and pressures significantly different than standard conditions, these corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations. The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period.

3.0 *Range.*

3.1 The approximate concentration range of the method is 2 to 750 μg/std m^3. The upper limit is determined by the point at which the sampler can no longer maintain the specified flow rate due to the increased pressure drop of the loaded filter. This point is affected by particle size distribution, moisture content of the collected particles, and variability from filter to filter, among other things. The lower limit is determined by the sensitivity of the balance (see Section 7.10) and by inherent sources of error (see Section 6).

3.2 At wind speeds between 1.3 and 4.5 m/sec (3 and 10 mph), the high-volume air sampler has been found to collect particles up to 25 to 50 µm, depending on wind speed and direction.(*3*) For the filter specified in Section 7.1, there is effectively no lower limit on the particle size collected.

4.0 *Precision.*

4.1 Based upon collaborative testing, the relative standard deviation (coefficient of variation) for single analyst precision (repeatability) of the method is 3.0 percent. The corresponding value for interlaboratory precision (reproducibility) is 3.7 percent.(*4*)

5.0 *Accuracy.*

5.1 The absolute accuracy of the method is undefined because of the complex nature of atmospheric particulate matter and the difficulty in determining the ''true'' particulate matter concentration. This method provides a measure of particulate matter concentration suitable for the purpose specified under Section 1.0, Applicability.

6.0 *Inherent Sources of Error.*

6.1 *Airflow variation.* The weight of material collected on the filter represents the (integrated) sum of the product of the instantaneous flow rate times the instantaneous particle concentration. Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period. The error resulting from a nonconstant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration. Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period. Use of a contant flow controller is recommended.*

6.2 *Air volume measurement.* If the flow rate changes substantially or nonuniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the presampling and postsampling flow rates. Greater air volume measurement accuracy may be achieved by (1) equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period,* (2) using a calibrated, continuous flow rate recording device to record the actual flow rate during the samping period and integrating the flow rate over the period, or (3) any other means that will accurately measure the total air volume sampled during the sampling period. Use of a continuous flow recorder is recommended, particularly if the sampler is not equipped with a constant flow controller.

6.3 *Loss of volatiles.* Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the postsampling weighing.(*5*) Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as practical.

6.4 *Artifact particulate matter.* Artifact particulate matter can be formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher than true TSP determination.(*6 7*) This effect usually occurs early in the sample period and is a function of the filter pH and the presence of acid gases. It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant where relatively small particulate weights are collected.

6.5 *Humidity.* Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can be hygroscopic.(*8*) The moisture conditioning procedure minimizes but may not completely eliminate error due to moisture.

6.6 *Filter handling.* Careful handling of the filter between the presampling and postsampling weighings is necessary to avoid errors due to loss of fibers or particles from the filter. A filter paper cartridge or cassette used to protect the filter can minimize handling errors. (See Reference 2, Section 2).

6.7 *Nonsampled particulate matter.* Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. (*9*) It is recommended that errors from this source be minimized by an automatic mechanical device that keeps the filter covered during nonsampling periods, or by timely installation and retrieval of filters to minimize the nonsampling periods prior to and following operation.

6.8 *Timing errors.* Samplers are normally controlled by clock timers set to start and stop the sampler at midnight. Errors in the nominal 1,440-min sampling period may result from a power interruption during the sampling period or from a discrepancy between the start or stop time recorded on the filter information record and the actual start or stop time of the sampler. Such discrepancies may be caused by (1) poor resolution of the timer set-points, (2) timer error due to power interruption, (3) missetting of

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*At elevated altitudes, the effectiveness of automatic flow controllers may be reduced because of a reduction in the maximum sampler flow.

the timer, or (4) timer malfunction. In general, digital electronic timers have much better set-point resolution than mechanical timers, but require a battery backup system to maintain continuity of operation after a power interruption. A continuous flow recorder or elapsed time meter provides an indication of the sampler run-time, as well as indication of any power interruption during the sampling period and is therefore recommended.

6.9 *Recirculation of sampler exhaust.* Under stagnant wind conditions, sampler exhaust air can be resampled. This effect does not appear to affect the TSP measurement substantially, but may result in increased carbon and copper in the collected sample. (*10*) This problem can be reduced by ducting the exhaust air well away, preferably downwind, from the sampler.

7.0 *Apparatus.*

(See References 1 and 2 for quality assurance information.)

NOTE: Samplers purchased prior to the effective date of this amendment are not subject to specifications preceded by (†).

7.1 *Filter.* (Filters supplied by the Environmental Protection Agency can be assumed to meet the following criteria. Additional specifications are required if the sample is to be analyzed chemically.)

7.1.1 *Size:* 20.3 ±0.2 × 25.4 ±0.2 cm (nominal 8 × 10 in).

7.1.2 *Nominal exposed area:* 406.5 cm^2 (63 in^2).

7.1.3. *Material:* Glass fiber or other relatively inert, nonhygroscopic material. (*8*)

7.1.4 *Collection efficiency:* 99 percent minimum as measured by the DOP test (ASTM–2986) for particles of 0.3 μm diameter.

7.1.5 *Recommended pressure drop range:* 42–54 mm Hg (5.6–7.2 kPa) at a flow rate of 1.5 std m^3/min through the nominal exposed area.

7.1.6 *pH:* 6 to 10. (*11*)

7.1.7 *Integrity:* 2.4 mg maximum weight loss. (*11*)

7.1.8 *Pinholes:* None.

7.1.9 *Tear strength:* 500 g minimum for 20 mm wide strip cut from filter in weakest dimension. (See ASTM Test D828–60).

7.1.10 *Brittleness:* No cracks or material separations after single lengthwise crease.

7.2 *Sampler.* The air sampler shall provide means for drawing the air sample, via reduced pressure, through the filter at a uniform face velocity.

7.2.1 The sampler shall have suitable means to:

a. Hold and seal the filter to the sampler housing.

b. Allow the filter to be changed conveniently.

c. Preclude leaks that would cause error in the measurement of the air volume passing through the filter.

d. (†) Manually adjust the flow rate to accommodate variations in filter pressure drop and site line voltage and altitude. The adjustment may be accomplished by an automatic flow controller or by a manual flow adjustment device. Any manual adjustment device must be designed with positive detents or other means to avoid unintentional changes in the setting.

7.2.2 *Minimum sample flow rate, heavily loaded filter:* 1.1 m^3/min (39 ft^3/min).‡

7.2.3 *Maximum sample flow rate, clean filter:* 1.7 m^3/min (60 ft^3/min).‡

7.2.4 *Blower Motor:* The motor must be capable of continuous operation for 24-hr periods.

7.3 *Sampler shelter.*

7.3.1 The sampler shelter shall:

a. Maintain the filter in a horizontal position at least 1 m above the sampler supporting surface so that sample air is drawn downward through the filter.

b. Be rectangular in shape with a gabled roof, similar to the design shown in Figure 1.

c. Cover and protect the filter and sampler from precipitation and other weather.

d. Discharge exhaust air at least 40 cm from the sample air inlet.

e. Be designed to minimize the collection of dust from the supporting surface by incorporating a baffle between the exhaust outlet and the supporting surface.

7.3.2 The sampler cover or roof shall overhang the sampler housing somewhat, as shown in Figure 1, and shall be mounted so as to form an air inlet gap between the cover and the sampler housing walls. † This sample air inlet should be approximately uniform on all sides of the sampler. † The area of the sample air inlet must be sized to provide an effective particle capture air velocity of between 20 and 35 cm/sec at the recommended operational flow rate. The capture velocity is the sample air flow rate divided by the inlet area measured in a horizontal plane at the lower edge of the cover. † Ideally, the inlet area and operational flow rate should be selected to obtain a capture air velocity of 25 ±2 cm/sec.

7.4 *Flow rate measurement devices.*

7.4.1 The sampler shall incorporate a flow rate measurement device capable of indicating the total sampler flow rate. Two common types of flow indicators covered in the calibration procedure are (1) an electronic mass flowmeter and (2) an orifice or orifices

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(†) See note at beginning of Section 7 of this appendix.

‡ These specifications are in actual air volume units; to convert to EPA standard air volume units, multiply the specifications by $(P_b/P_{std})(298/T)$ where P_b and T are the barometric pressure in mm Hg (or kPa) and the temperature in K at the sampler, and P_{std} is 760 mm Hg (or 101 kPa).

located in the sample air stream together with a suitable pressure indicator such as a manometer, or aneroid pressure gauge. A pressure recorder may be used with an orifice to provide a continuous record of the flow. Other types of flow indicators (including rotameters) having comparable precision and accuracy are also acceptable.

7.4.2 † The flow rate measurement device must be capable of being calibrated and read in units corresponding to a flow rate which is readable to the nearest 0.02 std m^3/min over the range 1.0 to 1.8 std m^3/min.

7.5 *Thermometer*, to indicate the approximate air temperature at the flow rate measurement orifice, when temperature corrections are used.

7.5.1 *Range:* −40° to + 50 °C (223–323 K).

7.5.2 *Resolution:* 2 °C (2 K).

7.6 *Barometer*, to indicate barometric pressure at the flow rate measurement orifice, when pressure corrections are used.

7.6.1 *Range:* 500 to 800 mm Hg (66–106 kPa).

7.6.2 *Resolution:* ±5 mm Hg (0.67 kPa).

7.7 *Timing/control device.*

7.7.1 The timing device must be capable of starting and stopping the sampler to obtain an elapsed run-time of 24 hr ±1 hr (1,440 ±60 min).

7.7.2 *Accuracy of time setting:* ±30 min, or better. (See Section 6.8).

7.8 *Flow rate transfer standard*, traceable to a primary standard. (See Section 9.2.)

7.8.1 *Approximate range:* 1.0 to 1.8 m^3/min.

7.8.2 *Resolution:* 0.02 m^3/min.

7.8.3 *Reproducibility:* ±2 percent (2 times coefficient of variation) over normal ranges of ambient temperature and pressure for the stated flow rate range. (See Reference 2, Section 2.)

7.8.4 *Maximum pressure drop at 1.7 std m^3/ min;* 50 cm H_2O (5 kPa).

7.8.5 The flow rate transfer standard must connect without leaks to the inlet of the sampler and measure the flow rate of the total air sample.

7.8.6 The flow rate transfer standard must include a means to vary the sampler flow rate over the range of 1.0 to 1.8 m^3/min (35–64 ft^3/min) by introducing various levels of flow resistance between the sampler and the transfer standard inlet.

7.8.7 The conventional type of flow transfer standard consists of: An orifice unit with adapter that connects to the inlet of the sampler, a manometer or other device to measure orifice pressure drop, a means to vary the flow through the sampler unit, a thermometer to measure the ambient temperature, and a barometer to measure ambient pressure. Two such devices are shown in Figures 2a and 2b. Figure 2a shows multiple fixed resistance plates, which necessitate disassembly of the unit each time the flow resistance is changed. A preferable design, illustrated in Figure 2b, has a variable flow restriction that can be adjusted externally without disassembly of the unit. Use of a conventional, orifice-type transfer standard is assumed in the calibration procedure (Section 9). However, the use of other types of transfer standards meeting the above specifications, such as the one shown in Figure 2c, may be approved; see the note following Section 9.1.

7.9 *Filter conditioning environment*

7.9.1 *Controlled temperature:* between 15° and 30 °C with less than ±3 °C variation during equilibration period.

7.9.2 *Controlled humidity:* Less than 50 percent relative humidity, constant within ±5 percent.

7.10 *Analytical balance.*

7.10.1 *Sensitivity:* 0.1 mg.

7.10.2 Weighing chamber designed to accept an unfolded 20.3 × 25.4 cm (8 × 10 in) filter.

7.11 *Area light source*, similar to X-ray film viewer, to backlight filters for visual inspection.

7.12 *Numbering device*, capable of printing identification numbers on the filters before they are placed in the filter conditioning environment, if not numbered by the supplier.

8.0 *Procedure.*

(See References 1 and 2 for quality assurance information.)

8.1 Number each filter, if not already numbered, near its edge with a unique identification number.

8.2 Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.

8.3 Equilibrate each filter in the conditioning environment for at least 24-hr.

8.4 Following equilibration, weigh each filter to the nearest milligram and record this tare weight (W_i) with the filter identification number.

8.5 Do not bend or fold the filter before collection of the sample.

8.6 Open the shelter and install a numbered, preweighed filter in the sampler, following the sampler manufacturer's instructions. During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter. Filter cassettes that can be loaded and unloaded in the laboratory may be used to minimize this problem (See Section 6.6).

8.7 Close the shelter and run the sampler for at least 5 min to establish run-temperature conditions.

8.8 Record the flow indicator reading and, if needed, the barometric pressure (P^3_3) and the ambient temperature (T^3_3) see NOTE following step 8.12). Stop the sampler. Determine the sampler flow rate (see Section 10.1); if it is outside the acceptable range (1.1 to 1.7 m^3/min [39–60 ft^3/min]), use a different filter, or adjust the sampler flow rate. Warning: Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.

8.9 Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).

8.10 Set the timer to start and stop the sampler such that the sampler runs 24-hrs, from midnight to midnight (local time).

8.11 As soon as practical following the sampling period, run the sampler for at least 5 min to again establish run-temperature conditions.

8.12 Record the flow indicator reading and, if needed, the barometric pressure ($P^3{}_3$) and the ambient temperature ($T^3{}_3$).

NOTE: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration (see step 9.3.9). For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site *during the sampling period* should be estimated from weather bureau or other available data.

8.13 Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter. See the precautions in step 8.6.

8.14 Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).

8.15 Record the ending time or elapsed time on the filter information record, either from the stop set-point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1,440 ±60 min. for a valid sample.

8.16 Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement. If the sample is known to be defective, void it at this time.

8.17 Equilibrate the exposed filter in the conditioning environment for at least 24-hrs.

8.18 Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number. See Section 10 for TSP concentration calculations.

9.0 *Calibration.*

9.1 Calibration of the high volume sampler's flow indicating or control device is necessary to establish traceability of the field measurement to a primary standard via a flow rate transfer standard. Figure 3a illustrates the certification of the flow rate transfer standard and Figure 3b illustrates its use in calibrating a sampler flow indicator. Determination of the corrected flow rate from the sampler flow indicator, illustrated in Figure 3c, is addressed in Section 10.1

NOTE: The following calibration procedure applies to a conventional orifice-type flow transfer standard and an orifice-type flow indicator in the sampler (the most common types). For samplers using a pressure recorder having a square-root scale, 3 other acceptable calibration procedures are provided in Reference 12. Other types of transfer standards may be used if the manufacturer or user provides an appropriately modified calibration procedure that has been approved by EPA under Section 2.8 of appendix C to part 58 of this chapter.

9.2 *Certification of the flow rate transfer standard.*

9.2.1 *Equipment required:* Positive displacement standard volume meter traceable to the National Bureau of Standards (such as a Roots meter or equivalent), stop-watch, manometer, thermometer, and barometer.

9.2.2 Connect the flow rate transfer standard to the inlet of the standard volume meter. Connect the manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice manometer to the pressure tap on the transfer standard. Connect a high-volume air pump (such as a high-volume sampler blower) to the outlet side of the standard volume meter. See Figure 3a.

9.2.3 Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other suitable means. Start the high-volume air pump and note any change in the standard volume meter reading. The reading should remain constant. If the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

9.2.4 After satisfactorily completing the leak check as described above, unclamp both manometer lines and zero both manometers.

9.2.5 Achieve the appropriate flow rate through the system, either by means of the variable flow resistance in the transfer standard or by varying the voltage to the air pump. (Use of resistance plates as shown in Figure 1a is discouraged because the above leak check must be repeated each time a new resistance plate is installed.) At least five different but constant flow rates, evenly distributed, with at least three in the specified flow rate interval (1.1 to 1.7 m^3/min [39–60 ft^3/min]), are required.

9.2.6 Measure and record the certification data on a form similar to the one illustrated in Figure 4 according to the following steps.

9.2.7 Observe the barometric pressure and record as P_1 (item 8 in Figure 4).

9.2.8 Read the ambient temperature in the vicinity of the standard volume meter and record it as T_1 (item 9 in Figure 4).

9.2.9 Start the blower motor, adjust the flow, and allow the system to run for at least 1 min for a constant motor speed to be attained.

9.2.10 Observe the standard volume meter reading and simultaneously start a stopwatch. Record the initial meter reading (V_i) in column 1 of Figure 4.

9.2.11 Maintain this constant flow rate until at least 3 m^3 of air have passed through the standard volume meter. Record the standard volume meter inlet pressure manometer reading as ΔP (column 5 in Figure 4), and the orifice manometer reading as ΔH (column 7 in Figure 4). Be sure to indicate the correct units of measurement.

9.2.12 After at least 3 m^3 of air have passed through the system, observe the standard volume meter reading while simultaneously stopping the stopwatch. Record the final meter reading (V_f) in column 2 and the elapsed time (t) in column 3 of Figure 4.

9.2.13 Calculate the volume measured by the standard volume meter at meter conditions of temperature and pressures as $V_m = V_f - V_i$. Record in column 4 of Figure 4.

9.2.14 Correct this volume to standard volume (std m^3) as follows:

$$V_{std} = V_m \frac{P_1 - \Delta P}{P_{std}} \frac{T_{std}}{T_1}$$

where:

V_{std} = standard volume, std m^3;

V_m = actual volume measured by the standard volume meter;

P_1 = barometric pressure during calibration, mm Hg or kPa;

ΔP = differential pressure at inlet to volume meter, mm Hg or kPa;

P_{std} = 760 mm Hg or 101 kPa;

T_{std} = 298 K;

T_1 = ambient temperature during calibration, K.

Calculate the standard flow rate (std m^3/min) as follows:

$$Q_{std} = \frac{V_{std}}{t}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min

t = elapsed time, minutes.

Record Q_{std} to the nearest 0.01 std m^3/min in column 6 of Figure 4.

9.2.15 Repeat steps 9.2.9 through 9.2.14 for at least four additional constant flow rates, evenly spaced over the approximate range of 1.0 to 1.8 std m^3/min (35–64 ft^3/min).

9.2.16 For each flow, compute

$\sqrt{\Delta\Delta H}\ (P_1/P_{std})(298/T_1)$

(column 7a of Figure 4) and plot these value against Q_{std} as shown in Figure 3a. Be sure to use consistent units (mm Hg or kPa) for barometric pressure. Draw the orifice transfer standard certification curve or calculate the linear least squares slope (m) and intercept (b) of the certification curve:

$\sqrt{\Delta\Delta H}\ (P_1/P_{std})(298/T_1)$

$= mQ_{std} + b$. See Figures 3 and 4. A certification graph should be readable to 0.02 std m^3/min.

9.2.17 Recalibrate the transfer standard annually or as required by applicable quality control procedures. (See Reference 2.)

9.3 *Calibration of sampler flow indicator.*

NOTE: For samplers equipped with a flow controlling device, the flow controller must be disabled to allow flow changes during calibration of the sampler's flow indicator, or the alternate calibration of the flow controller given in 9.4 may be used. For samplers using an orifice-type flow indicator downstream of the motor, do not vary the flow rate by adjusting the voltage or power supplied to the sampler.

9.3.1 A form similar to the one illustrated in Figure 5 should be used to record the calibration data.

9.3.2 Connect the transfer standard to the inlet of the sampler. Connect the orifice manometer to the orifice pressure tap, as illustrated in Figure 3b. Make sure there are no leaks between the orifice unit and the sampler.

9.3.3 Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration.

9.3.4 Measure and record the ambient temperature, T_2, and the barometric pressure, P_2, during calibration.

9.3.5 Adjust the variable resistance or, if applicable, insert the appropriate resistance plate (or no plate) to achieve the desired flow rate.

9.3.6 Let the sampler run for at least 2 min to re-establish the run-temperature conditions. Read and record the pressure drop across the orifice (ΔH) and the sampler flow rate indication (I) in the appropriate columns of Figure 5.

9.3.7 Calculate $\sqrt{\Delta\Delta H}(P_2/P_{std})(298/T_2)$ and determine the flow rate at standard conditions (Q_{std}) either graphically from the certification curve or by calculating Q_{std} from the least square slope and intercept of the transfer standard's transposed certification curve:

$Q_{std} = 1/m\ \sqrt{\Delta H (P_2/P_{std})(298/T_2)} - b$. Record the value of Q_{std} on Figure 5.

9.3.8 Repeat steps 9.3.5, 9.3.6, and 9.3.7 for several additional flow rates distributed over a range that includes 1.1 to 1.7 std m^3/min.

9.3.9 Determine the calibration curve by plotting values of the appropriate expression involving I, selected from table 1, against Q_{std}. The choice of expression from table 1 depends on the flow rate measurement device used (see Section 7.4.1) and also on whether the calibration curve is to incorporate geographic average barometric pressure (P_a) and seasonal average temperature (T_a) for the site to approximate actual pressure and temperature. Where P_a and T_a can be determined for a site for a seasonal period such that the actual barometric pressure and temperature at the site do not vary by more than ±60 mm Hg (8 kPa) from P_a or ±15 °C from T_a, respectively, then using P_a and T_a avoids the need for subsequent pressure and temperature calculation when the sampler is used. The geographic average barometric pressure (P_a) may be estimated from an altitude-pressure table or by making an (approximate) elevation correction of −26 mm Hg (−3.46 kPa) for each 305 m (1,000 ft) above sea level (760 mm Hg or 101 kPa). The seasonal average temperature (T_a) may be estimated from weather station or other records. Be sure to use consistent units (mm Hg or kPa) for barometric pressure.

9.3.10 Draw the sampler calibration curve or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve: [Expression from table 1]= $mQ_{std} + b$. See Figures 3 and 5. Calibration curves should be readable to 0.02 std m^3/min.

9.3.11 For a sampler equipped with a flow controller, the flow controlling mechanism should be re-enabled and set to a flow near the lower flow limit to allow maximum control range. The sample flow rate should be verified at this time with a clean filter installed. Then add two or more filters to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced.

9.4 Alternate calibration of flow-controlled samplers. A flow-controlled sampler may be calibrated solely at its controlled flow rate, provided that previous operating history of the sampler demonstrates that the flow rate is stable and reliable. In this case, the flow indicator may remain uncalibrated but should be used to indicate any relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of samples because of controller malfunction.

9.4.1 Set the flow controller for a flow near the lower limit of the flow range to allow maximum control range.

9.4.2 Install a clean filter in the sampler and carry out steps 9.3.2, 9.3.3, 9.3.4, 9.3.6, and 9.3.7.

9.4.3 Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes where the flow control range may be reduced.

TABLE 1. EXPRESSIONS FOR PLOTTING SAMPLER CALIBRATION CURVES

Type of sampler flow rate measuring device	Expression	
	For actual pressure and temperature corrections	For incorporation of geographic average pressure and seasonal average temperature
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

TABLE 2. EXPRESSIONS FOR DETERMINING FLOW RATE DURING SAMPLER OPERATION

Type of sampler flow rate measuring device	Expression	
	For actual pressure and temperature corrections	For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	$\sqrt{I}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	I

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

10.0 *Calculations of TSP Concentration.*

10.1 Determine the average sampler flow rate during the sampling period according to either 10.1.1 or 10.1.2 below.

10.1.1 For a sampler without a continuous flow recorder, determine the appropriate expression to be used from table 2 corresponding to the one from table 1 used in step 9.3.9. Using this appropriate expression, determine Q_{std} for the initial flow rate from the sampler calibration curve, either graphically or from the transposed regression equation:

Q_{std} =

1/m ([Appropriate expression from table 2]−b)

Similarly, determine Q_{std} from the final flow reading, and calculate the average flow Q_{std} as one-half the sum of the initial and final flow rates.

10.1.2 For a sampler with a continuous flow recorder, determine the average flow rate device reading, I, for the period. Determine the appropriate expression from table 2 corresponding to the one from table 1 used in step 9.3.9. Then using this expression and the average flow rate reading, determine Q_{std} from the sampler calibration curve, either graphically or from the transposed regression equation:

Q_{std} =

1/m ([Appropriate expression from table 2] − b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining Q_{std}.

10.2 Calculate the total air volume sampled as:

$V - Q_{std} \times t$

where:

V = total air volume sampled, in standard volume units, std m³/;

Q_{std} = average standard flow rate, std m³/min;

t = sampling time, min.

10.3 Calculate and report the particulate matter concentration as:

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

where:

TSP = mass concentration of total suspended particulate matter, µg/std m³;

W_i = initial weight of clean filter, g;

W_f = final weight of exposed filter, g;

V = air volume sampled, converted to standard conditions, std m³,

10^6 = conversion of g to µg.

10.4 If desired, the actual particulate matter concentration (see Section 2.2) can be calculated as follows:

$(TSP)_a = TSP\ (P_3/P_{std})(298/T_3)$

where:

$(TSP)_a$ = actual concentration at field conditions, µg/m³;

TSP = concentration at standard conditions, µg/std m³;

P_3 = average barometric pressure during sampling period, mm Hg;

P_{std} = 760 mn Hg (or 101 kPa);

T_3 = average ambient temperature during sampling period, K.

11.0 *References.*

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles. EPA–600/9–76–005, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1976.

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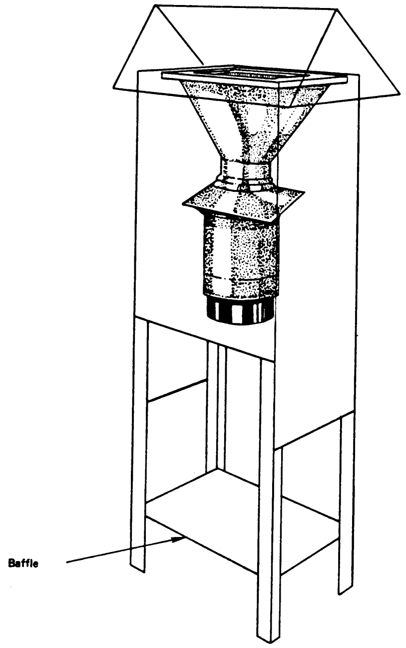
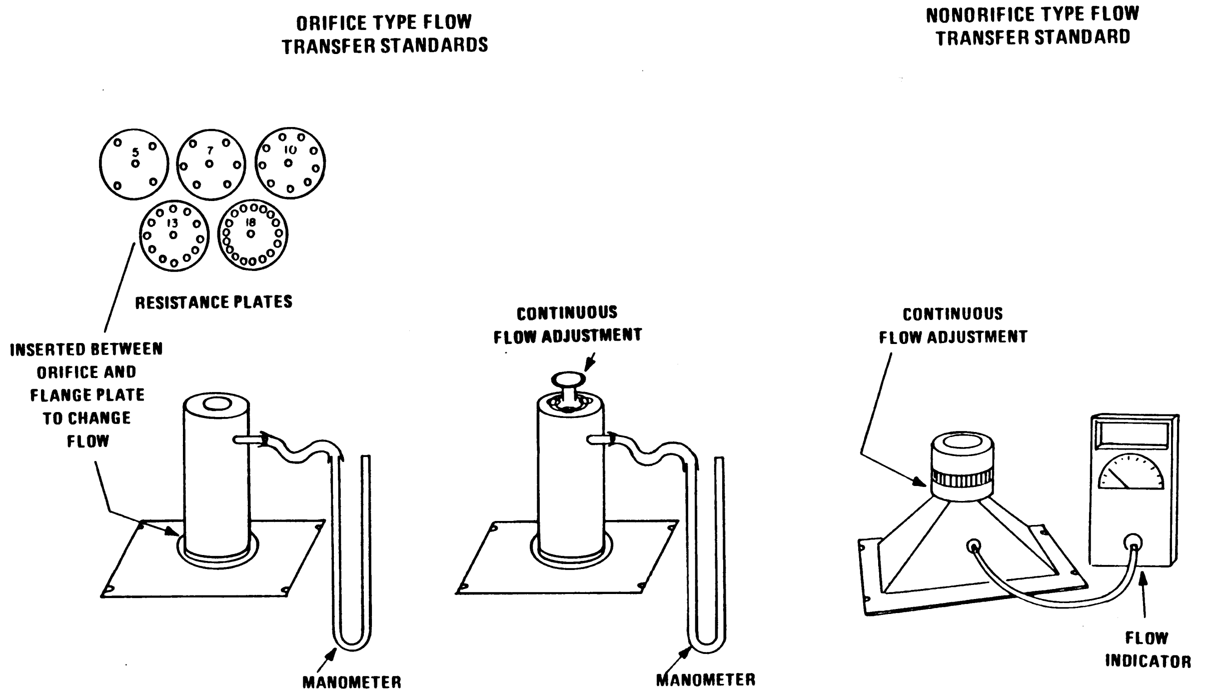


Figure 1. High-volume sampler in shelter.



2a. ORIFICE UNIT USING FIXED RESISTANCE PLATES.

2b. PREFERABLE ORIFICE UNIT WITH EXTERNALLY ADJUSTABLE RESISTANCE.

2c. ELECTRONIC FLOWMETER WITH EXTERNALLY ADJUSTABLE RESISTANCE.

Figure 2. Various types of flow transfer standards. Note that all devices are designed to mount to the filter inlet area of the sampler.

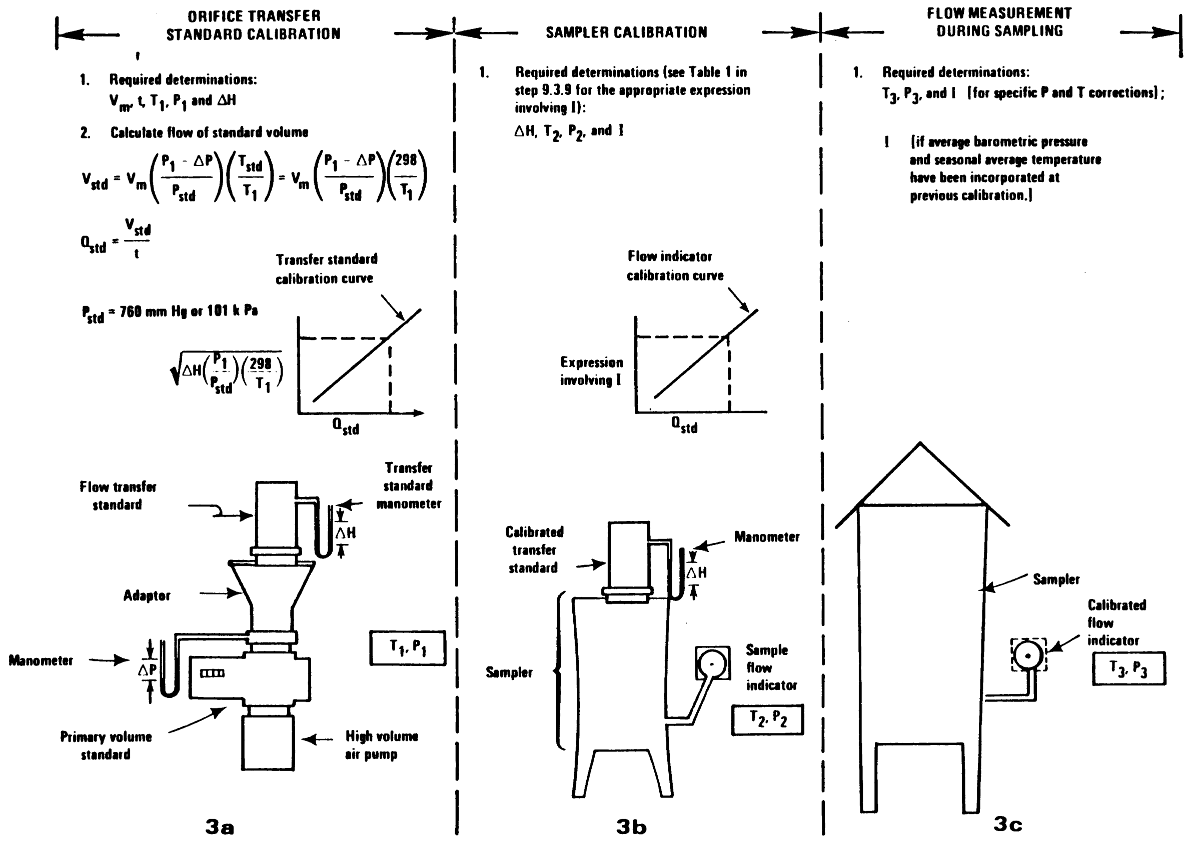


Figure 3. Illustration of the 3 steps in the flow measurement process.

ORIFICE TRANSFER STANDARD CERTIFICATION WORKSHEET

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(7a)
Run No.	Meter reading start V_i (m^3)	Meter reading stop V_f (m^3)	Sampling time t (min)	Volume measured V_m (m^3)	Differential pressure (at inlet to volume meter) ΔP (mm Hg or kPa)	(X) Flow rate Q_{std} (std m^3/min)	Pressure drop across orifice ΔH ☐ (in) or ☐ (cm) of water	(Y) $\sqrt{\Delta H\left(\frac{P_1}{P_{std}}\right)\left(\frac{298}{T_1}\right)}$
1								
2								
3								
4								
5								
6								

RECORDED CALIBRATION DATA

Standard volume meter no. ______________________

Transfer standard type: ☐ orifice ☐ other

Model No. ______________ Serial No. ______________

(8) P_1: ______________ mm Hg (or kPa) (10) P_{std}: 760 mm Hg (or 101 kPa)

(9) T_1: ______________ K (11) T_{std}: 298 K

Calibration performed by: ______________________

Date: ______________

CALCULATION EQUATIONS

(1) $V_m = V_f - V_i$

(2) $V_{std} = V_m\left(\frac{P_1 - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_1}\right)$

(3) $Q_{std} = \frac{V_{std}}{t}$

LEAST SQUARES CALCULATIONS

Linear ($Y = mX + b$) regression equation of $Y = \sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ on $X = Q_{std}$ for Orifice Calibration Unit (i.e., $\sqrt{\Delta H(P_1/P_{std})(298/T_1)} = mQ_{std} + b$)

Slope (m) = ____________ Intercept (b) = ____________ Correlation coefficient (r) = ____________

To use for subsequent calibration: $X = \frac{1}{m}(Y-b)$; $\boxed{Q_{std} = \frac{1}{m}\left(\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)} - b\right)}$

Figure 4. Example of orifice transfer standard certification worksheet.

HIGH-VOLUME AIR SAMPLER CALIBRATION WORKSHEET

Site Location: ____________________

Date: ____________ Barometric Pressure, P_2 mm Hg (or kPa) ____________

Calibrated By: ____________ Temperature, T_2 (K) ____________

Sampler No. ____________ Serial No. ____________

Transfer std. type: ____________ Serial No. ____________

P_{std} = 760 mm Hg (or 101 kPa)

Optional: Average barometric pressure: P_a = ____________

Seasonal average temperature: T_a = ____________

					(Y)	
No.	ΔH Pressure drop across orifice ☐(in) or ☐(cm) of water	$\sqrt{\Delta H\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	(X) Q_{std} (from orifice certification) std m³/min	I Sampler flow rate indication (arbitrary)	For specific pressure and temperature corrections (see Table 1) ☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	For incorporation of average pressure and seasonal average temperature (see Table 1) ☐ I or ☐ $\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$ or ☐ $I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
1						
2						
3						
4						
5						
6						

LEAST SQUARES CALCULATIONS

Linear regression of Y on X: $Y = mX + b$; Y = appropriate expression from Table 1; $X = Q_{std}$.

Slope (m) = ____ Intercept (b) = ____ Correlation Coeff. (r) = ________

To determine subsequent flow rate during use: $X = \frac{1}{m}(Y-b)$; $\boxed{Q_{std} = \frac{1}{m}(\text{[appropriate expression from Table 2]} - b)}$

Figure 5. Example of high-volume air sampler calibration worksheet.

[47 FR 54912, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983]

APPENDIX C TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED PHOTOMETRY)

1.0 APPLICABILITY

1.1 This non-dispersive infrared photometry (NDIR) Federal Reference Method (FRM) provides measurements of the concentration of carbon monoxide (CO) in ambient air for determining compliance with the primary and secondary National Ambient Air Quality Standards (NAAQS) for CO as specified in §50.8 of this chapter. The method is applicable to continuous sampling and measurement of ambient CO concentrations suitable for determining 1-hour or longer average measurements. The method may also provide measurements of shorter averaging times, subject to specific analyzer performance limitations. Additional CO monitoring quality assurance procedures and guidance are provided in part 58, appendix A, of this chapter and in reference 1 of this appendix C.

2.0 MEASUREMENT PRINCIPLE

2.1 Measurements of CO in ambient air are based on automated measurement of the absorption of infrared radiation by CO in an ambient air sample drawn into an analyzer employing non-wavelength-dispersive, infrared photometry (NDIR method). Infrared energy from a source in the photometer is passed through a cell containing the air sample to be analyzed, and the quantitative absorption of energy by CO in the sample cell is measured by a suitable detector. The photometer is sensitized specifically to CO by employing CO gas in a filter cell in the optical path, which, when compared to a differential optical path without a CO filter cell, limits the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs. However, to meet measurement performance requirements, various optical filters, reference cells, rotating gas filter cells, dual-beam configurations, moisture traps, or other means may also be used to further enhance sensitivity and stability of the photometer and to minimize potential measurement interference from water vapor, carbon dioxide (CO_2), or other species. Also, various schemes may be used to provide a suitable zero reference for the photometer, and optional automatic compensation may be provided for the actual pressure and temperature of the air sample in the measurement cell. The measured infrared absorption, converted to a digital reading or an electrical output signal, indicates the measured CO concentration.

2.2 The measurement system is calibrated by referencing the analyzer's CO measurements to CO concentration standards traceable to a National Institute of Standards and Technology (NIST) primary standard for CO, as described in the associated calibration procedure specified in section 4 of this reference method.

2.3 An analyzer implementing this measurement principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.

2.4 Sampling *considerations*. The use of a particle filter in the sample inlet line of a CO FRM analyzer is optional and left to the discretion of the user unless such a filter is specified or recommended by the analyzer manufacturer in the analyzer's associated operation or instruction manual.

3.0 INTERFERENCES

3.1 The NDIR measurement principle is potentially susceptible to interference from water vapor and CO_2, which have some infrared absorption at wavelengths in common with CO and normally exist in the atmosphere. Various instrumental techniques can be used to effectively minimize these interferences.

4.0 CALIBRATION PROCEDURES

4.1 *Principle*. Either of two methods may be selected for dynamic multipoint calibration of FRM CO analyzers, using test gases of accurately known CO concentrations obtained from one or more compressed gas cylinders certified as CO transfer standards:

4.1.1 Dilution *method:* A single certified standard cylinder of CO is quantitatively diluted as necessary with zero air to obtain the various calibration concentration standards needed.

4.1.2 Multiple-*cylinder method:* Multiple, individually certified standard cylinders of CO are used for each of the various calibration concentration standards needed.

4.1.3 Additional information on calibration may be found in Section 12 of reference 1.

4.2 Apparatus. The major components and typical configurations of the calibration systems for the two calibration methods are shown in Figures 1 and 2. Either system may be made up using common laboratory components, or it may be a commercially manufactured system. In either case, the principal components are as follows:

4.2.1 CO standard gas flow control and measurement devices (or a combined device) capable of regulating and maintaining the standard gas flow rate constant to within ±2 percent and measuring the gas flow rate accurate to within ±2 percent, properly calibrated to a NIST-traceable standard.

4.2.2 For the dilution method (Figure 1), dilution air flow control and measurement devices (or a combined device) capable of regulating and maintaining the air flow rate constant to within ±2 percent and measuring the air flow rate accurate to within ±2 percent, properly calibrated to a NIST-traceable standard.

4.2.3 Standard gas pressure regulator(s) for the standard CO cylinder(s), suitable for use with a high-pressure CO gas cylinder and having a non-reactive diaphragm and internal parts and a suitable delivery pressure.

4.2.4 Mixing chamber for the dilution method of an inert material and of proper design to provide thorough mixing of CO standard gas and diluent air streams.

4.2.5 Output sampling manifold, constructed of an inert material and of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure nearly atmospheric pressure at the analyzer connection port and to prevent ambient air from entering the manifold.

4.3 Reagents

4.3.1 CO gas concentration transfer standard(s) of CO in air, containing an appropriate concentration of CO suitable for the selected operating range of the analyzer under calibration and traceable to a NIST standard reference material (SRM). If the CO analyzer has significant sensitivity to CO_2, the CO standard(s) should also contain 350 to 400 ppm CO_2 to replicate the typical CO_2 concentration in ambient air. However, if the zero air dilution ratio used for the dilution method is not less than 100:1 and the zero air contains ambient levels of CO_2, then the CO standard may be contained in nitrogen and need not contain CO_2.

4.3.2 For the dilution method, clean zero air, free of contaminants that could cause a detectable response on or a change in sensitivity of the CO analyzer. The zero air should contain <0.1 ppm CO.

4.4 Procedure Using the Dilution Method

4.4.1 Assemble or obtain a suitable dynamic dilution calibration system such as the one shown schematically in Figure 1. Generally, all calibration gases including zero air must be introduced into the sample inlet of the analyzer. However, if the analyzer has special, approved zero and span inlets and automatic valves to specifically allow introduction of calibration standards at near atmospheric pressure, such inlets may be used for calibration in lieu of the sample inlet. For specific operating instructions, refer to the manufacturer's manual.

4.4.2 Ensure that there are no leaks in the calibration system and that all flowmeters are properly and accurately calibrated, under the conditions of use, if appropriate, against a reliable volume or flow rate standard such as a soap-bubble meter or wet-test meter traceable to a NIST standard. All volumetric flow rates should be corrected to the same temperature and pressure such as 298.15 K (25 °C) and 760 mm Hg (101 kPa), using a correction formula such as the following:

$$F_c = F_m \frac{298.15 \times P_m}{760(T_m + 273.15)} \quad (1)$$

Where:

F_c = corrected flow rate (L/min at 25 °C and 760 mm Hg),

F_m = measured flow rate (at temperature T_m and pressure P_m),

P_m = measured pressure in mm Hg (absolute), and

T_m = measured temperature in degrees Celsius.

4.4.3 Select the operating range of the CO analyzer to be calibrated. Connect the measurement signal output of the analyzer to an appropriate readout instrument to allow the analyzer's measurement output to be continuously monitored during the calibration. Where possible, this readout instrument should be the same one used to record routine monitoring data, or, at least, an instrument that is as closely representative of that system as feasible.

4.4.4 Connect the inlet of the CO analyzer to the output-sampling manifold of the calibration system.

4.4.5 Adjust the calibration system to deliver zero air to the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until a stable response is obtained. After the response has stabilized, adjust the analyzer zero reading.

4.4.6 Adjust the zero air flow rate and the CO gas flow rate from the standard CO cylinder to provide a diluted CO concentration of approximately 80 percent of the measurement upper range limit (URL) of the operating range of the analyzer. The total air flow rate must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. The exact CO concentration is calculated from:

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_{CO}} \quad (2)$$

Where:

$[CO]_{OUT}$ = diluted CO concentration at the output manifold (ppm),

$[CO]_{STD}$ = concentration of the undiluted CO standard (ppm),

F_{CO} = flow rate of the CO standard (L/min), and

F_D = flow rate of the dilution air (L/min).

Sample this CO concentration until a stable response is obtained. Adjust the analyzer span control to obtain the desired analyzer response reading equivalent to the calculated standard concentration. If substantial adjustment of the analyzer span control is required, it may be necessary to recheck the zero and span adjustments by repeating steps 4.4.5 and 4.4.6. Record the CO concentration and the analyzer's final response.

4.4.7 Generate several additional concentrations (at least three evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{CO} or increasing F_D. Be sure the total flow exceeds the analyzer's total flow demand. For each concentration generated, calculate the exact CO concentration using equation (2). Record the concentration and the analyzer's stable response for each concentration. Plot the analyzer responses (vertical or y-axis) versus the corresponding CO concentrations (horizontal or x-axis). Calculate the linear regression slope and intercept of the calibration curve and verify that no point deviates from this line by more than 2 percent of the highest concentration tested.

4.5 Procedure *Using the Multiple-Cylinder Method*. Use the procedure for the dilution method with the following changes:

4.5.1 Use a multi-cylinder, dynamic calibration system such as the typical one shown in Figure 2.

4.5.2 The flowmeter need not be accurately calibrated, provided the flow in the output manifold can be verified to exceed the analyzer's flow demand.

4.5.3 The various CO calibration concentrations required in Steps 4.4.5, 4.4.6, and 4.4.7 are obtained without dilution by selecting zero air or the appropriate certified standard cylinder.

4.6 Frequency *of Calibration*. The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checking, will vary by analyzer. However, the minimum frequency, acceptance criteria, and subsequent actions are specified in reference 1, appendix D, ''Measurement Quality Objectives and Validation Template for CO'' (page 5 of 30). The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of CO analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality control.

5.0 REFERENCE

1. *QA Handbook for Air Pollution Measurement Systems—Volume II. Ambient Air Quality Monitoring Program*. U.S. EPA. EPA–454/B–08–003 (2008).

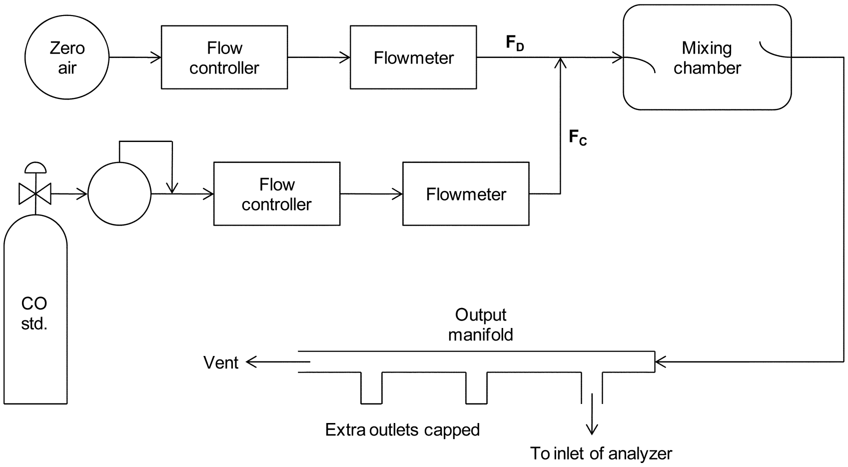


Figure 1. Dilution method for calibration of CO analyzers.

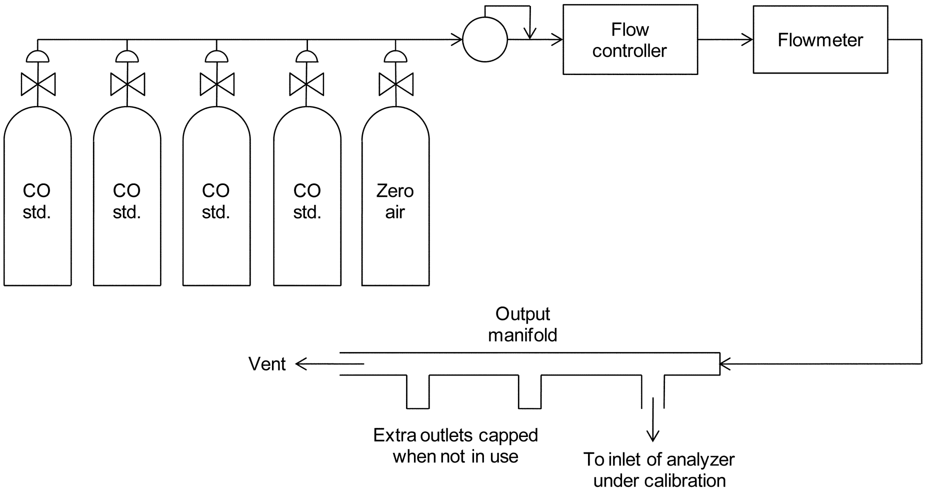


Figure 2. Multiple cylinder method for calibration of CO analyzers.

[76 FR 54323, Aug. 31, 2011]

APPENDIX D TO PART 50—REFERENCE MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF OZONE IN THE ATMOSPHERE (CHEMILUMINESCENCE METHOD)

1.0 *Applicability.*

1.1 This chemiluminescence method provides reference measurements of the concentration of ozone (O_3) in ambient air for determining compliance with the national primary and secondary ambient air quality standards for O_3 as specified in 40 CFR part 50. This automated method is applicable to the measurement of ambient O_3 concentrations using continuous (real-time) sampling and analysis. Additional quality assurance procedures and guidance are provided in 40 CFR part 58, appendix A, and in Reference 14.

2.0 *Measurement Principle.*

2.1 This reference method is based on continuous automated measurement of the intensity of the characteristic chemiluminescence released by the gas phase reaction of O_3 in sampled air with either ethylene (C_2H_4) or nitric oxide (NO) gas. An ambient air sample stream and a specific flowing concentration of either C_2H_4 (ET–CL method) or NO (NO–CL method) are mixed in a measurement cell, where the resulting chemiluminescence is quantitatively measured by a sensitive photo-detector. References 8–11 describe the chemiluminescence measurement principle.

2.2 The measurement system is calibrated by referencing the instrumental chemiluminescence measurements to certified O_3 standard concentrations generated in a dynamic flow system and assayed by photometry to be traceable to a National Institute of Standards and Technology (NIST) standard reference photometer for O_3 (see Section 4, Calibration Procedure, below).

2.3 An analyzer implementing this measurement principle is shown schematically in Figure 1. Designs implementing this measurement principle must include: an appropriately designed mixing and measurement cell; a suitable quantitative photometric measurement system with adequate sensitivity and wavelength specificity for O_3; a pump, flow control, and sample conditioning system for sampling the ambient air and moving it into and through the measurement cell; a sample air dryer as necessary to meet the water vapor interference limit requirement specified in subpart B of part 53 of this chapter; a means to supply, meter, and mix a constant, flowing stream of either C_2H_4 or NO gas of fixed concentration with the sample air flow in the measurement cell; suitable electronic control and measurement processing capability; and other associated apparatus as may be necessary. The analyzer must be designed and constructed to provide accurate, repeatable, and continuous measurements of O_3 concentrations in ambient air, with measurement performance that meets the requirements specified in subpart B of part 53 of this chapter.

2.4 An analyzer implementing this measurement principle and calibration procedure will be considered a federal reference method (FRM) only if it has been designated as a reference method in accordance with part 53 of this chapter.

2.5 *Sampling considerations.* The use of a particle filter on the sample inlet line of a chemiluminescence O_3 FRM analyzer is required to prevent buildup of particulate matter in the measurement cell and inlet components. This filter must be changed weekly (or at least often as specified in the manufacturer's operation/instruction manual), and the sample inlet system used with the analyzer must be kept clean, to avoid loss of O_3 in the O_3 sample air prior to the concentration measurement.

3.0 *Interferences.*

3.1 Except as described in 3.2 below, the chemiluminescence measurement system is inherently free of significant interferences from other pollutant substances that may be present in ambient air.

3.2 A small sensitivity to variations in the humidity of the sample air is minimized by a sample air dryer. Potential loss of O_3 in the inlet air filter and in the air sample handling components of the analyzer and associated exterior air sampling components due to buildup of airborne particulate matter is minimized by filter replacement and cleaning of the other inlet components.

4.0 *Calibration Procedure.*

4.1 *Principle.* The calibration procedure is based on the photometric assay of O_3 concentrations in a dynamic flow system. The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient (α) of O_3 at 254 nm, (2) the optical path length (l) through the sample, (3) the transmittance of the sample at a nominal wavelength of 254 nm, and (4) the temperature (T) and pressure (P) of the sample. The transmittance is defined as the ratio I/I_0, where I is the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O_3 sample, and I_0 is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_0. The quantities defined above are related by the Beer-Lambert absorption law,

$$\text{Transmitance} = \frac{I}{I_0} = e^{-\alpha c l} \qquad (1)$$

Where:

α = absorption coefficient of O_3 at 254 nm = 308 ±4 atm−1 cm−1 at 0 °C and 760 torr,[1 2 3 4 5 6 7]

c = O_3 concentration in atmospheres, and

l = optical path length in cm.

A stable O_3 generator is used to produce O_3 concentrations over the required calibration concentration range. Each O_3 concentration is determined from the measurement of the transmittance (I/I_0) of the sample at 254 nm with a photometer of path length l and calculated from the equation,

$$c(\text{atm}) = -\frac{1}{\alpha l}\left(\ln\frac{I}{I_0}\right) \qquad (2a)$$

or

$$c(\text{ppm}) = -\frac{10^6}{\alpha l}\left(\ln\frac{I}{I_0}\right). \qquad (2b)$$

The calculated O_3 concentrations must be corrected for O_3 losses, which may occur in the photometer, and for the temperature and pressure of the sample.

4.2 *Applicability.* This procedure is applicable to the calibration of ambient air O_3 analyzers, either directly or by means of a transfer standard certified by this procedure. Transfer standards must meet the requirements and specifications set forth in Reference 12.

4.3 *Apparatus.* A complete UV calibration system consists of an O_3 generator, an output port or manifold, a photometer, an appropriate source of zero air, and other components as necessary. The configuration must provide a stable O_3 concentration at the system output and allow the photometer to accurately assay the output concentration to the precision specified for the photometer (4.3.1). Figure 2 shows a commonly used configuration and serves to illustrate the calibration procedure, which follows. Other configurations may require appropriate variations in the procedural steps. All connections between components in the calibration system downstream of the O_3 generator must be of glass, Teflon, or other relatively inert materials. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 13. For certification of transfer standards which provide their own source of O_3, the transfer standard may replace the O_3 generator and possibly other components shown in Figure 2; see Reference 12 for guidance.

4.3.1 *UV photometer.* The photometer consists of a low-pressure mercury discharge lamp, (optional) collimation optics, an absorption cell, a detector, and signal-processing electronics, as illustrated in Figure 2. It must be capable of measuring the transmittance, I/I_0, at a wavelength of 254 nm with sufficient precision such that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3% of the concentration. Because the low-pressure mercury lamp radiates at several wavelengths, the photometer must incorporate suitable means to assure that no O_3 is generated in the cell by the lamp, and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%. In addition, the cell and associated plumbing must be designed to minimize loss of O_3 from contact with cell walls and gas handling components. See Reference 13 for additional information.

4.3.2 *Air flow controllers.* Air flow controllers are devices capable of regulating air flows as necessary to meet the output stability and photometer precision requirements.

4.3.3 *Ozone generator.* The ozone generator used must be capable of generating stable levels of O_3 over the required concentration range.

4.3.4 *Output manifold.* The output manifold must be constructed of glass, Teflon, or other relatively inert material, and should be of sufficient diameter to insure a negligible pressure drop at the photometer connection and other output ports. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

4.3.5 *Two-way valve.* A manual or automatic two-way valve, or other means is used to switch the photometer flow between zero air and the O_3 concentration.

4.3.6 *Temperature indicator.* A device to indicate temperature must be used that is accurate to ±1 °C.

4.3.7 *Barometer or pressure indicator.* A device to indicate barometric pressure must be used that is accurate to ±2 torr.

4.4 *Reagents.*

4.4.1 *Zero air.* The zero air must be free of contaminants which would cause a detectable response from the O_3 analyzer, and it must be free of NO, C_2H_4, and other species which react with O_3. A procedure for generating suitable zero air is given in Reference 13. As shown in Figure 2, the zero air supplied to the photometer cell for the I_0 reference measurement must be derived from the same source as the zero air used for generation of the O_3 concentration to be assayed (I measurement). When using the photometer to certify a transfer standard having its own source of O_3, see Reference 12 for guidance on meeting this requirement.

4.5 *Procedure.*

4.5.1 *General operation.* The calibration photometer must be dedicated exclusively to use as a calibration standard. It must always be used with clean, filtered calibration gases, and never used for ambient air sampling. A number of advantages are realized by locating the calibration photometer in a clean laboratory where it can be stationary, protected from the physical shock of transportation, operated by a responsible analyst, and used as a common standard for all field calibrations via transfer standards.

4.5.2 *Preparation.* Proper operation of the photometer is of critical importance to the accuracy of this procedure. Upon initial operation of the photometer, the following steps must be carried out with all quantitative results or indications recorded in a chronological record, either in tabular form or plotted on a graphical chart. As the performance and stability record of the photometer is established, the frequency of these steps may be reduced to be consistent with the documented stability of the photometer and the guidance provided in Reference 12.

4.5.2.1 *Instruction manual.* Carry out all set up and adjustment procedures or checks as described in the operation or instruction manual associated with the photometer.

4.5.2.2 *System check.* Check the photometer system for integrity, leaks, cleanliness, proper flow rates, etc. Service or replace filters and zero air scrubbers or other consumable materials, as necessary.

4.5.2.3 *Linearity*. Verify that the photometer manufacturer has adequately established that the linearity error of the photometer is less than 3%, or test the linearity by dilution as follows: Generate and assay an O_3 concentration near the upper range limit of the system or appropriate calibration scale for the instrument, then accurately dilute that concentration with zero air and reassay it. Repeat at several different dilution ratios. Compare the assay of the original concentration with the assay of the diluted concentration divided by the dilution ratio, as follows

$$E = \frac{A_1 - A_2/R}{A_1} \times 100\% \qquad (3)$$

Where:

E = linearity error, percent
A_1 = assay of the original concentration
A_2 = assay of the diluted concentration
R = dilution ratio = flow of original concentration divided by the total flow

The linearity error must be less than 5%. Since the accuracy of the measured flowrates will affect the linearity error as measured this way, the test is not necessarily conclusive. Additional information on verifying linearity is contained in Reference 13.

4.5.2.4 *Inter-comparison*. The photometer must be inter-compared annually, either directly or via transfer standards, with a NIST standard reference photometer (SRP) or calibration photometers used by other agencies or laboratories.

4.5.2.5 *Ozone losses*. Some portion of the O_3 may be lost upon contact with the photometer cell walls and gas handling components. The magnitude of this loss must be determined and used to correct the calculated O_3 concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 13.

4.5.3 *Assay of O_3 concentrations*. The operator must carry out the following steps to properly assay O_3 concentrations.

4.5.3.1 Allow the photometer system to warm up and stabilize.

4.5.3.2 Verify that the flow rate through the photometer absorption cell, F, allows the cell to be flushed in a reasonably short period of time (2 liter/min is a typical flow). The precision of the measurements is inversely related to the time required for flushing, since the photometer drift error increases with time.

4.5.3.3 Ensure that the flow rate into the output manifold is at least 1 liter/min greater than the total flow rate required by the photometer and any other flow demand connected to the manifold.

4.5.3.4 Ensure that the flow rate of zero air, Fz, is at least 1 liter/min greater than the flow rate required by the photometer.

4.5.3.5 With zero air flowing in the output manifold, actuate the two-way valve to allow the photometer to sample first the manifold zero air, then Fz. The two photometer readings must be equal ($I = I_0$).

NOTE: In some commercially available photometers, the operation of the two-way valve and various other operations in section 4.5.3 may be carried out automatically by the photometer.

4.5.3.6 Adjust the O_3 generator to produce an O_3 concentration as needed.

4.5.3.7 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the stable measured value of Io.

4.5.3.8 Actuate the two-way valve to allow the photometer to sample the O_3 concentration until the absorption cell is thoroughly flushed and record the stable measured value of I.

4.5.3.9 Record the temperature and pressure of the sample in the photometer absorption cell. (See Reference 13 for guidance.)

4.5.3.10 Calculate the O_3 concentration from equation 4. An average of several determinations will provide better precision.

$$[O_3]_{OUT} = \left(\frac{-1}{\alpha l}\ln\frac{I}{I_0}\right)\left(\frac{T}{273}\right)\left(\frac{760}{P}\right) \times \frac{10^6}{L} \qquad (4)$$

Where:

$[O_3]_{OUT}$ = O_3 concentration, ppm
α = absorption coefficient of O_3 at 254 nm = 308 atm−1 cm−1 at 0 °C and 760 torr
l = optical path length, cm
T = sample temperature, K
P = sample pressure, torr
L = correction factor for O_3 losses from 4.5.2.5 = (1−fraction of O_3 lost).

NOTE: Some commercial photometers may automatically evaluate all or part of equation 4. It is the operator's responsibility to verify that all of the information required for equation 4 is obtained, either automatically by the photometer or manually. For "automatic" photometers which evaluate the first term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O_3 levels. See the photometer instruction manual and Reference 13 for guidance.

4.5.3.11 Obtain additional O_3 concentration standards as necessary by repeating steps 4.5.3.6 to 4.5.3.10 or by Option 1.

4.5.4 *Certification of transfer standards.* A transfer standard is certified by relating the output of the transfer standard to one or more O_3 calibration standards as determined according to section 4.5.3. The exact procedure varies depending on the nature and design of the transfer standard. Consult Reference 12 for guidance.

4.5.5 *Calibration of ozone analyzers.* Ozone analyzers must be calibrated as follows, using O_3 standards obtained directly according to section 4.5.3 or by means of a certified transfer standard.

4.5.5.1 Allow sufficient time for the O_3 analyzer and the photometer or transfer standard to warm-up and stabilize.

4.5.5.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and then adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift (if any). Record the stable zero air response as "Z".

4.5.5.3 Generate an O_3 concentration standard of approximately 80% of the desired upper range limit (URL) of the O_3 analyzer. Allow the O_3 analyzer to sample this O_3 concentration standard until a stable response is obtained.

4.5.5.4 Adjust the O_3 analyzer's span control to obtain the desired response equivalent to the calculated standard concentration. Record the O_3 concentration and the corresponding analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 4.5.5.2 to 4.5.5.4.

4.5.5.5 Generate additional O_3 concentration standards (a minimum of 5 are recommended) over the calibration scale of the O_3 analyzer by adjusting the O_3 source or by Option 1. For each O_3 concentration standard, record the O_3 concentration and the corresponding analyzer response.

4.5.5.6 Plot the O_3 analyzer responses (vertical or Y-axis) versus the corresponding O_3 standard concentrations (horizontal or X-axis). Compute the linear regression slope and intercept and plot the regression line to verify that no point deviates from this line by more than 2 percent of the maximum concentration tested.

4.5.5.7 *Option 1:* The various O_3 concentrations required in steps 4.5.3.11 and 4.5.5.5 may be obtained by dilution of the O_3 concentration generated in steps 4.5.3.6 and 4.5.5.3. With this option, accurate flow measurements are required. The dynamic calibration system may be modified as shown in Figure 3 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flow rate through the O_3 generator (Fo) and the dilution air flow rate (FD) are measured with a flow or volume standard that is traceable to a NIST flow or volume calibration standard. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_O}{F_O+F_D}\right) \qquad (5)$$

Where:

$[O_3]'_{OUT}$ = diluted O_3 concentration, ppm
FO = flow rate through the O_3 generator, liter/min
FD = diluent air flow rate, liter/min

NOTE: Additional information on calibration and pollutant standards is provided in Section 12 of Reference 14.

5.0 *Frequency of Calibration.*

5.1 The frequency of calibration, as well as the number of points necessary to establish the calibration curve, and the frequency of other performance checking will vary by analyzer; however, the minimum frequency, acceptance criteria, and subsequent actions are specified in Appendix D of Reference 14: Measurement Quality Objectives and Validation Templates. The user's quality control program shall provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality control.

6.0 *References.*

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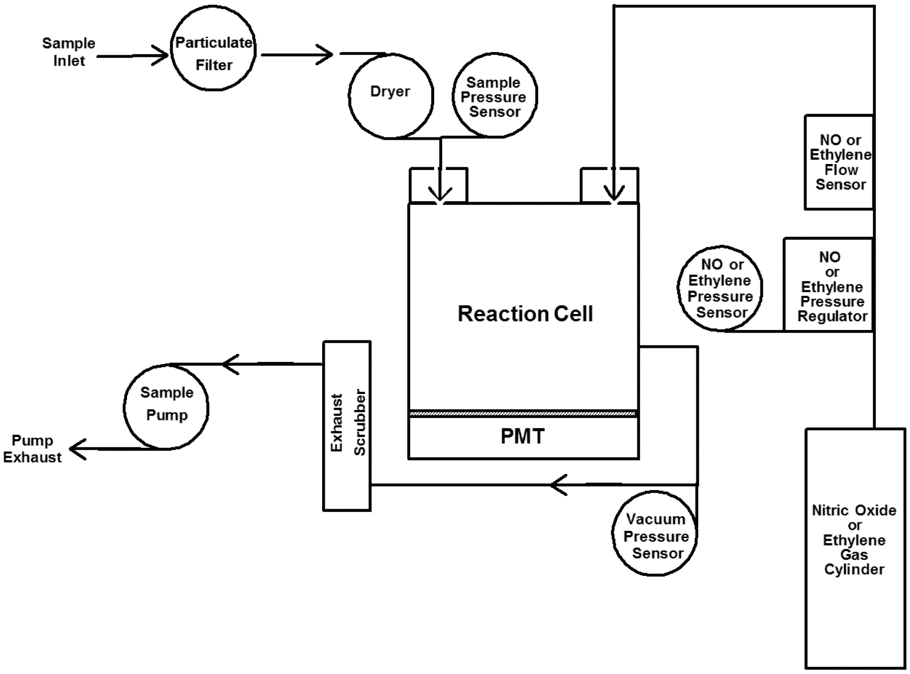

Figure 1. Gas-phase chemiluminescence analyzer schematic diagram, where PMT means photomultiplier tube.

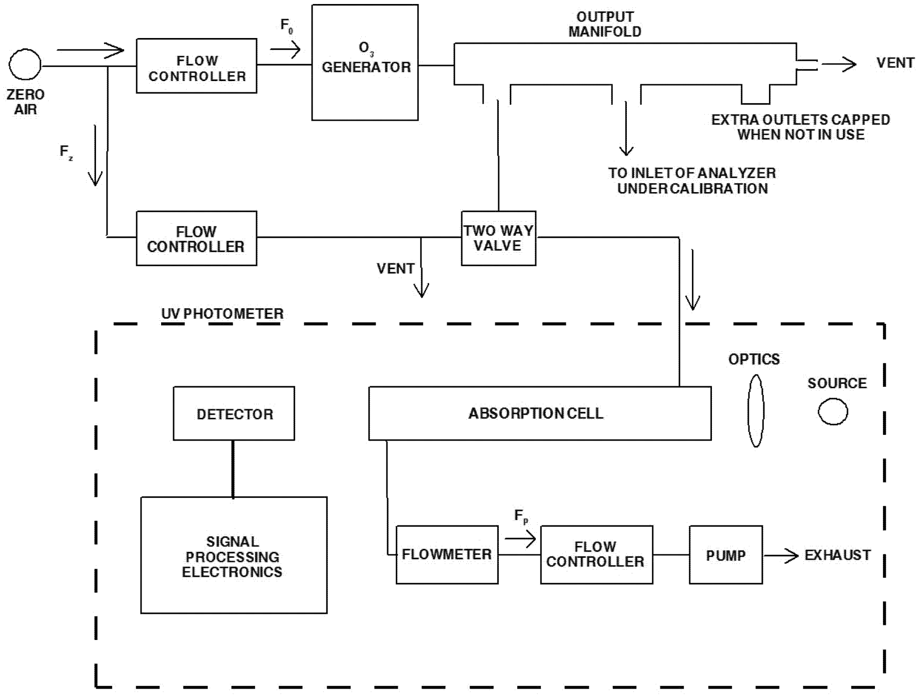

Figure 2. Schematic diagram of a typical UV photometric calibration system.

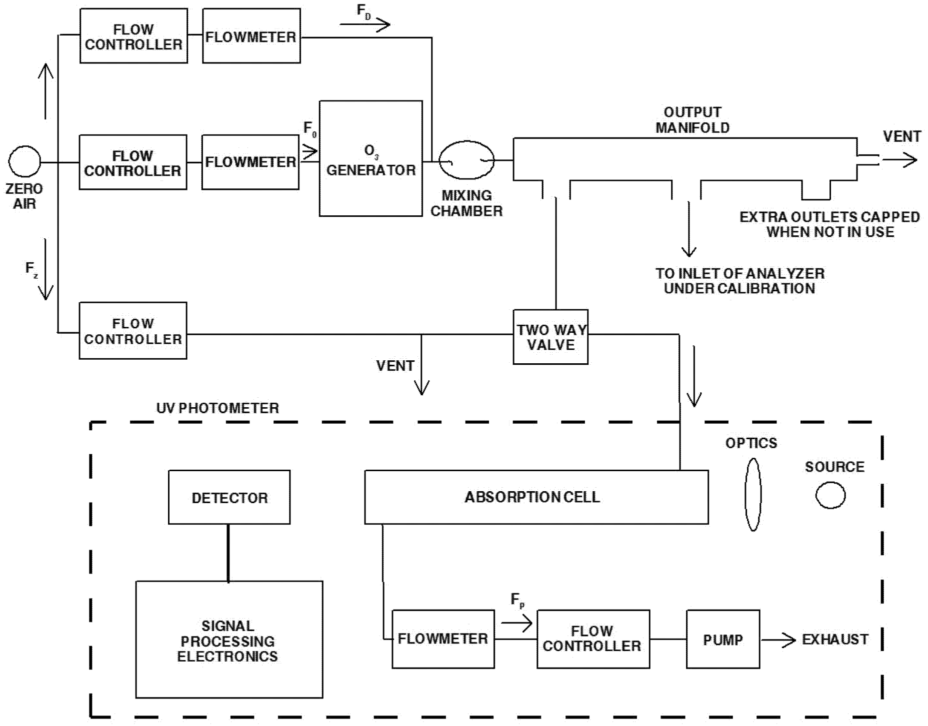

Figure 3. Schematic diagram of a typical UV photometric calibration system (Option 1).

[80 FR 65453, Oct. 26, 2015]

APPENDIX E TO PART 50 [RESERVED]

APPENDIX F TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF NITROGEN DIOXIDE IN THE ATMOSPHERE (GAS PHASE CHEMILUMINESCENCE)

PRINCIPLE AND APPLICABILITY

1. Atmospheric concentrations of nitrogen dioxide (NO_2) are measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nanometers, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). (*1,2,3*) NO_2 is first quantitatively reduced to NO(*4,5,6*) by means of a converter. NO, which commonly exists in ambient air together with NO_2, passes through the converter unchanged causing a resultant total NO_X concentration equal to NO + NO_2. A sample of the input air is also measured without having passed through the converted. This latter NO measurement is subtracted from the former measurement (NO + NO_2) to yield the final NO_2 measurement. The NO and NO + NO_2 measurements may be made concurrently with dual systems, or cyclically with the same system provided the cycle time does not exceed 1 minute.

2. *Sampling considerations.*

2.1 Chemiluminescence NO/NO_X/NO_2 analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. (*7*) Atmospheric concentrations of these potential interferences are generally low relative to NO_2 and valid NO_2 measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known or suspected to be high relative to NO_2, the use of an equivalent method for the measurement of NO_2 is recommended.

2.2 The use of integrating flasks on the sample inlet line of chemiluminescence NO/

NO_X/NO_2 analyzers is optional and left to couraged. The sample residence time between the sampling point and the analyzer should be kept to a minimum to avoid erroneous NO_2 measurements resulting from the reaction of ambient levels of NO and O_3 in the sampling system.

2.3 The use of particulate filters on the sample inlet line of chemiluminescence NO/NO_X/NO_2 analyzers is optional and left to the discretion of the user or the manufacturer.

Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO_2 measurements and therefore filters should be changed frequently.

3. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.

CALIBRATION

1. *Alternative A*—Gas phase titration (GPT) of an NO standard with O_3.

Major equipment required: Stable O_3 generator. Chemiluminescence NO/NO_X/NO_2 analyzer with strip chart recorder(s). NO concentration standard.

1.1 *Principle*. This calibration technique is based upon the rapid gas phase reaction between NO and O_3 to produce stoichiometric quantities of NO_2 in accordance with the following equation: (*8*)

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO/NO_X/NO_2 analyzer is used as an indicator of changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated may be varied by adding variable amounts of O_3 from a stable uncalibrated O_3 generator. (*9*)

1.2 *Apparatus*. Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be of glass, Teflon®, or other non-reactive material.

1.2.1 *Air flow controllers*. Devices capable of maintaining constant air flows within ±2% of the required flowrate.

1.2.2 *NO flow controller*. A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO should be of a non-reactive material.

1.2.3 *Air flowmeters*. Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

1.2.4 *NO flowmeter*. A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

1.2.5 *Pressure regulator for standard NO cylinder*. This regulator must have a nonreactive diaphragm and internal parts and a suitable delivery pressure.

1.2.6 *Ozone generator*. The generator must be capable of generating sufficient and stable levels of O_3 for reaction with NO to generate NO_2 concentrations in the range required. Ozone generators of the electric discharge type may produce NO and NO_2 and are not recommended.

1.2.7 *Valve*. A valve may be used as shown in Figure 1 to divert the NO flow when zero air is required at the manifold. The valve should be constructed of glass, Teflon®, or other nonreactive material.

1.2.8 *Reaction chamber*. A chamber, constructed of glass, Teflon®, or other nonreactive material, for the quantitative reaction of O_3 with excess NO. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) meets the requirements specified in 1.4. For practical reasons, t_R should be less than 2 minutes.

1.2.9 *Mixing chamber*. A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specification given in 1.4 is met.

1.2.10 *Output manifold*. The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

1.3 *Reagents*.

1.3.1 *NO concentration standard*. Gas cylinder standard containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. This standard must be traceable to a National Bureau of Standards (NBS) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684), an NBS NO_2 Standard Reference Material (SRM 1629), or an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 14, and a list of CRM sources is available from the address shown for Reference 14. A recommended protocol for certifying NO gas cylinders against either an NO SRM or CRM is given in section 2.0.7 of Reference 15. Reference 13 gives procedures for certifying an NO gas cylinder against an NBS NO_2 SRM and for determining the amount of NO_2 impurity in an NO cylinder.

1.3.2 *Zero air.* Air, free of contaminants which will cause a detectable response on the $NO/NO_X/NO_2$ analyzer or which might react with either NO, O_3, or NO_2 in the gas phase titration. A procedure for generating zero air is given in reference 13.

1.4 *Dynamic parameter specification.*

1.4.1 The O_3 generator air flowrate (F_0) and NO flowrate (F_{NO}) (see Figure 1) must be adjusted such that the following relationship holds:

$$P_R = [\text{NO}]_{RC} \times t_R \; 2.75 \text{ ppm-minutes} \quad (2)$$

$$[\text{NO}]_{RC} = [\text{NO}]_{\text{STD}} \left(\frac{F_{\text{NO}}}{F_{\text{O}} + F_{\text{NO}}} \right) \quad (3)$$

$$t_R = \frac{V_{RC}}{F_O + F_{\text{NO}}} < 2 \text{ minutes} \quad (4)$$

where:

P_R = dynamic parameter specification, determined empirically, to insure complete reaction of the available O_3, ppm-minute

$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm

$_R$ = residence time of the reactant gases in the reaction chamber, minute

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_{NO} = NO flowrate, scm³/min

F_O = O_3 generator air flowrate, scm³/min

V_{RC} = volume of the reaction chamber, scm³

1.4.2 The flow conditions to be used in the GPT system are determined by the following procedure:

(a) Determine F_T, the total flow required at the output manifold (F_T = analyzer demand plus 10 to 50% excess).

(b) Establish $[NO]_{OUT}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ should be approximately equivalent to 90% of the upper range limit (*URL*) of the NO_2 concentration range to be covered.

(c) Determine F_{NO} as

$$F_{\text{NO}} = \frac{[NO]_{\text{OUT}} \times F_{\text{T}}}{[NO]_{\text{STD}}} \quad (5)$$

(d) Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 200 to 500 scm³.

(e) Compute FO as

$$F_{\text{O}} = \sqrt{\frac{[\text{NO}]_{\text{STD}} \times F_{\text{NO}} \times V_{\text{RC}}}{2.75}} - F_{\text{NO}} \quad (6)$$

(f) Compute t_R as

$$t_R = \frac{V_{RC}}{F_{\text{O}} + F_{\text{NO}}} \quad (7)$$

Verify that t_R <2 minutes. If not, select a reaction chamber with a smaller V_{RC}.

(g) Compute the diluent air flowrate as

$$F_D = F_T' \; F_O' \; F_{\text{NO}} \quad (8)$$

where:

F_D = diluent air flowrate, scm³/min

(h) If F_O turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_O and F_D.

NOTE: A dynamic parameter lower than 2.75 ppm-minutes may be used if it can be determined empirically that quantitative reaction of O_3 with NO occurs. A procedure for making this determination as well as a more detailed discussion of the above requirements and other related considerations is given in reference 13.

1.5 *Procedure.*

1.5.1 Assemble a dynamic calibration system such as the one shown in Figure 1.

1.5.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25 °C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

1.5.3 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

1.5.4 Select the operating range of the $NO/NO_X/NO_2$ analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NO_X channels on higher ranges is desired, subsequent recalibration of the NO and NO_X channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NO_X, and NO_2 during operation of the analyzer.

1.5.5 Connect the recorder output cable(s) of the NO/NO_X/NO_2 analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

1.5.6 Determine the GPT flow conditions required to meet the dynamic parameter specification as indicated in 1.4.

1.5.7 Adjust the diluent air and O_3 generator air flows to obtain the flows determined in section 1.4.2. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_X, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: Some analyzers may have separate zero controls for NO, NO_X, and NO_2. Other analyzers may have separate zero controls only for NO and NO_X, while still others may have only one zero control common to all three channels.

Offsetting the analyzer zero adjustments to + 5 percent of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, Z_{NOX}, and Z_{NO2}.

1.5.8 *Preparation of NO and NO_X calibration curves.*

1.5.8.1 *Adjustment of NO span control.* Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80 percent of the upper range limit (*URL*) of the NO range. This exact NO concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad (9)$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

Sample this NO concentration until the NO and NO_X responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

recorder response (percent scale) =

$$\left(\frac{[NO]_{OUT}}{URL} \times 100\right) + Z_{NO} \qquad (10)$$

where:

URL = nominal upper range limit of the NO channel, ppm

NOTE: Some analyzers may have separate span controls for NO, NO_X, and NO_2. Other analyzers may have separate span controls only for NO and NO_X, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.1. Record the NO concentration and the analyzer's NO response.

1.5.8.2 *Adjustment of NO_X span control.* When adjusting the analyzer's NO_X span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the standard NO cylinder are given in reference 13. The exact NO_X concentration is calculated from:

$$[NO_X]_{OUT} = \frac{F_{NO} \times \left([NO]_{STD} + [NO_2]_{IMP}\right)}{F_{NO} + F_O + F_D} \qquad (11)$$

where:

$[NO_X]_{OUT}$ = diluted NO_X concentration at the output manifold, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

Adjust the NO_X span control to obtain a recorder response as indicated below:

recorder response (% scale) =

$$\left(\frac{[NO_X]_{OUT}}{URL} \times 100\right) + Z_{NO_X} \qquad (12)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NO_X.

If substantial adjustment of the NO_X span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.2. Record the NO_X concentration and the analyzer's NO_X response.

1.5.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_X concentrations using equations (9) and (11) respectively. Record the analyzer's NO and NO_X responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_X concentrations and draw or calculate the NO and NO_X calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero air point and NO and NO_X concentrations of approximately 80% of the *URL*.

1.5.9 *Preparation of NO_2 calibration curve.*

1.5.9.1 Assuming the NO_2 zero has been properly adjusted while sampling zero air in step 1.5.7, adjust F_O and F_D as determined in section 1.4.2. Adjust F_{NO} to generate an NO concentration near 90% of the *URL* of the NO range. Sample this NO concentration until the NO and NO_X responses have stabilized. Using the NO calibration curve obtained in section 1.5.8, measure and record the NO concentration as $[NO]_{orig}$. Using the NO_X calibration curve obtained in section 1.5.8, measure and record the NO_X concentration as $[NO_X]_{orig}$.

1.5.9.2 Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in the NO concentration equivalent to approximately 80% of the URL of the NO_2 range. The decrease must not exceed 90% of the NO concentration determined in step 1.5.9.1. After the analyzer responses have stabilized, record the resultant NO and NO_X concentrations as $[NO]_{rem}$ and $[NO_X]_{rem}$.

1.5.9.3 Calculate the resulting NO_2 concentration from:

$$[NO_2]_{OUT} = [NO]_{orig} - [NO]_{rem} + \frac{F_{NO} \times [NO_2]_{IMP}}{F_{NO} + F_O + F_D} \qquad (13)$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

$[NO]_{orig}$ = original NO concentration, prior to addition of O_3, ppm

$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm

Adjust the NO_2 span control to obtain a recorder response as indicated below:

recorder response (% scale) =

$$\left(\frac{[NO_2]_{OUT}}{URL} \times 100\right) + Z_{NO_2} \qquad (14)$$

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_X channels and no further adjustment is made here for NO_2.

If substantial adjustment of the NO_2 span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.9.3. Record the NO_2 concentration and the corresponding analyzer NO_2 and NO_X responses.

1.5.9.4 Maintaining the same F_{NO}, F_O, and F_D as in section 1.5.9.1, adjust the ozone generator to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using equation (13) and record the corresponding analyzer NO_2 and NO_X responses. Plot the analyzer's NO_2 responses versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

1.5.10 *Determination of converter efficiency.*

1.5.10.1 For each NO_2 concentration generated during the preparation of the NO_2 calibration curve (see section 1.5.9) calculate the concentration of NO_2 converted from:

$$\left[NO_2\right]_{CONV} = \left[NO_2\right]_{OUT}{'} \left(\left[NO_X\right]_{orig}{'} \left[NO_X\right]_{rem}\right) \qquad (15)$$

where:

$[NO_2]_{CONV}$ = concentration of NO_2 converted, ppm

$[NO_X]_{orig}$ = original NO_X concentration prior to addition of O_3, ppm

$[NO_X]_{rem}$ = NO_X concentration remaining after addition of O_3, ppm

NOTE: Supplemental information on calibration and other procedures in this method are given in reference 13.

Plot $[NO_2]_{CONV}$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency, E_C The average converter efficiency must be greater than 96%; if it is less than 96%, replace or service the converter.

2. *Alternative B*—NO_2 permeation device.

Major equipment required:

Stable O_3 generator.

Chemiluminescence NO/NO_X/NO_2 analyzer with strip chart recorder(s).

NO concentration standard.

NO_2 concentration standard.

2.1 *Principle.* Atmospheres containing accurately known concentrations of nitrogen dioxide are generated by means of a permeation device. (*10*) The permeation device emits NO_2 at a known constant rate provided the temperature of the device is held constant (±0.1 °C) and the device has been accurately calibrated at the temperature of use. The NO_2 emitted from the device is diluted with zero air to produce NO_2 concentrations suitable for calibration of the NO_2 channel of the $NO/NO_X/NO_2$ analyzer. An NO concentration standard is used for calibration of the NO and NO_X channels of the analyzer.

2.2 *Apparatus.* A typical system suitable for generating the required NO and NO_2 concentrations is shown in Figure 2. All connections between components downstream from the permeation device should be of glass, Teflon®, or other non-reactive material.

2.2.1 *Air flow controllers.* Devices capable of maintaining constant air flows within ±2% of the required flowrate.

2.2.2 *NO flow controller.* A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO must be of a non-reactive material.

2.2.3 *Air flowmeters.* Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

2.2.4 *NO flowmeter.* A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.2.5 *Pressure regulator for standard NO cylinder.* This regulator must have a non-reactive diaphragm and internal parts and a suitable delivery pressure.

2.2.6 *Drier.* Scrubber to remove moisture from the permeation device air system. The use of the drier is optional with NO_2 permeation devices not sensitive to moisture. (Refer to the supplier's instructions for use of the permeation device.)

2.2.7 *Constant temperature chamber.* Chamber capable of housing the NO_2 permeation device and maintaining its temperature to within ±0.1 °C.

2.2.8 *Temperature measuring device.* Device capable of measuring and monitoring the temperature of the NO_2 permeation device with an accuracy of ±0.05 °C.

2.2.9 *Valves.* A valve may be used as shown in Figure 2 to divert the NO_2 from the permeation device when zero air or NO is required at the manifold. A second valve may be used to divert the NO flow when zero air or NO_2 is required at the manifold.

The valves should be constructed of glass, Teflon®, or other nonreactive material.

2.2.10 *Mixing chamber.* A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of pollutant gas streams and diluent air.

2.2.11 *Output manifold.* The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.3 *Reagents.*

2.3.1 *Calibration standards.* Calibration standards are required for both NO and NO_2. The reference standard for the calibration may be either an NO or NO_2 standard, and must be traceable to a National Bureau of Standards (NBS) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684), and NBS NO_2 Standard Reference Material (SRM 1629), or an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 14, and a list of CRM sources is available from the address shown for Reference 14. Reference 15 gives recommended procedures for certifying an NO gas cylinder against an NO SRM or CRM and for certifying an NO_2 permeation device against an NO_2 SRM. Reference 13 contains procedures for certifying an NO gas cylinder against an NO_2 SRM and for certifying an NO_2 permeation device against an NO SRM or CRM. A procedure for determining the amount of NO_2 impurity in an NO cylinder is also contained in Reference 13. The NO or NO_2 standard selected as the reference standard must be used to certify the other standard to ensure consistency between the two standards.

2.3.1.1 *NO_2 Concentration standard.* A permeation device suitable for generating NO_2 concentrations at the required flow-rates over the required concentration range. If the permeation device is used as the reference standard, it must be traceable to an SRM or CRM as specified in 2.3.1. If an NO cylinder is used as the reference standard, the NO_2 permeation device must be certified against the NO standard according to the procedure given in Reference 13. The use of the permeation device should be in strict accordance with the instructions supplied with the device. Additional information regarding the use of permeation devices is given by Scaringelli et al. (11) and Rook et al. (12).

2.3.1.2 *NO Concentration standard.* Gas cylinder containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. If this cylinder is used as the reference standard, the cylinder must be traceable to an SRM or CRM as specified in 2.3.1. If an NO_2 permeation device is used as the reference standard, the NO cylinder must be certified against the NO_2 standard according to the procedure given in Reference 13. The cylinder should be recertified on a regular basis as determined by the local quality control program.

2.3.3 *Zero air.* Air, free of contaminants which might react with NO or NO_2 or cause a detectable response on the $NO/NO_X/NO_2$ analyzer. When using permeation devices that are sensitive to moisture, the zero air passing across the permeation device must be dry to avoid surface reactions on the device. (Refer to the supplier's instructions for use of the permeation device.) A procedure for generating zero air is given in reference 13.

2.4 *Procedure.*

2.4.1 Assemble the calibration apparatus such as the typical one shown in Figure 2.

2.4.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25 °C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

2.4.3 Install the permeation device in the constant temperature chamber. Provide a small fixed air flow (200–400 scm^3/min) across the device. The permeation device should always have a continuous air flow across it to prevent large buildup of NO_2 in the system and a consequent restabilization period. Record the flowrate as FP. Allow the device to stabilize at the calibration temperature for at least 24 hours. The temperature must be adjusted and controlled to within ±0.1 °C or less of the calibration temperature as monitored with the temperature measuring device.

2.4.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by

(1) Carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve;

(2) Thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve;

(3) Not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

2.4.5 Select the operating range of the NO/ NO_X NO_2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NO_X channels on higher ranges is desired, subsequent recalibration of the NO and NO_X channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NO_X, and NO_2 during operation of the analyzer.

2.4.6 Connect the recorder output cable(s) of the $NO/NO_X/NO_2$ analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

2.4.7 Switch the valve to vent the flow from the permeation device and adjust the diluent air flowrate, F_D, to provide zero air at the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_X, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: Some analyzers may have separate zero controls for NO, NO_X, and NO_2. Other analyzers may have separate zero controls only for NO and NO_X, while still others may have only one zero common control to all three channels.

Offsetting the analyzer zero adjustments to + 5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, Z_{NOX}, and Z_{NO2}.

2.4.8 *Preparation of NO and NO_X calibration curves.*

2.4.8.1 *Adjustment of NO span control.* Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the upper range limit (URL) of the NO range. The exact NO concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_D} \qquad (16)$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

F_{NO} = NO flowrate, scm^3/min

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_D = diluent air flowrate, scm^3/min

Sample this NO concentration until the NO and NO_X responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

recorder response (% scale) =

$$= \left(\frac{[NO]_{OUT}}{URL} \times 100 \right) + Z_{NO} \qquad (17)$$

$$= \left(\frac{[NO_X]_{OUT}}{URL} \times 100 \right) + Z_{NO_X} \qquad (19)$$

where:

URL = nominal upper range limit of the NO channel, ppm

NOTE: Some analyzers may have separate span controls for NO, NO_X, and NO_2. Other analyzers may have separate span controls only for NO and NO_X, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.1. Record the NO concentration and the analyzer's NO response.

2.4.8.2 *Adjustment of NO_X span control.* When adjusting the analyzer's NO_X span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the standard NO cylinder are given in reference 13. The exact NO_X concentration is calculated from:

$$[NO_X]_{OUT} = \frac{F_{NO} \times \left([NO]_{STD} + [NO_2]_{IMP}\right)}{F_{NO} + F_D} \quad (18)$$

where:

$[NO_X]_{OUT}$ = diluted NO_X cencentration at the output manifold, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

Adjust the NO_X span control to obtain a convenient recorder response as indicated below:

recorder response (% scale)

$$= \left(\frac{[NO_X]_{OUT}}{URL} \times 100\right) + Z_{NO_X} \quad (19)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NO_X.

If substantial adjustment of the NO_X span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.2. Record the NO_X concentration and the analyzer's NO_X response.

2.4.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_X concentrations using equations (16) and (18) respectively. Record the analyzer's NO and NO_X responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_X concentrations and draw or calculate the NO and NO_X calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero point and NO and NO_X concentrations of approximately 80 percent of the URL.

2.4.9 *Preparation of NO_2 calibration curve.*

2.4.9.1 Remove the NO flow. Assuming the NO_2 zero has been properly adjusted while sampling zero air in step 2.4.7, switch the valve to provide NO_2 at the output manifold.

2.4.9.2 Adjust F_D to generate an NO_2 concentration of approximately 80 percent of the *URL* of the NO_2 range. The total air flow must exceed the demand of the analyzer(s) under calibration. The actual concentration of NO_2 is calculated from:

$$[NO_2]_{OUT} = \frac{R \times K}{F_P + F_D} \quad (20)$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

R = permeation rate, μg/min

K = 0.532 μl NO_2/μg NO_2 (at 25 °C and 760 mm Hg)

F_P = air flowrate across permeation device, scm³/min

F_D = diluent air flowrate, scm³/min

Sample this NO_2 concentration until the NO_X and NO_2 responses have stabilized. Adjust the NO_2 span control to obtain a recorder response as indicated below:

recorder response (% scale)

$$= \left(\frac{[NO_2]_{OUT}}{URL} \times 100\right) + Z_{NO2} \quad (21)$$

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_X channels and no further adjustment is made here for NO_2.

If substantial adjustment of the NO_2 span control is necessary it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.9.2. Record the NO_2 concentration and the analyzer's NO_2 response. Using the NO_X calibration curve obtained in step 2.4.8, measure and record the NO_X concentration as $[NO_X]_M$.

2.4.9.3 Adjust F_D to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using equation (20) and record the corresponding analyzer NO_2 and NO_X responses. Plot the analyzer's NO_2 responses versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

2.4.10 *Determination of converter efficiency.*

2.4.10.1 Plot $[NO_X]_M$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency,

E_C. The average converter efficiency must be greater than 96 percent; if it is less than 96 percent, replace or service the converter.

NOTE: Supplemental information on calibration and other procedures in this method are given in reference 13.

3. *Frequency of calibration.* The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checks, will vary from one analyzer to another. The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, and quality control.

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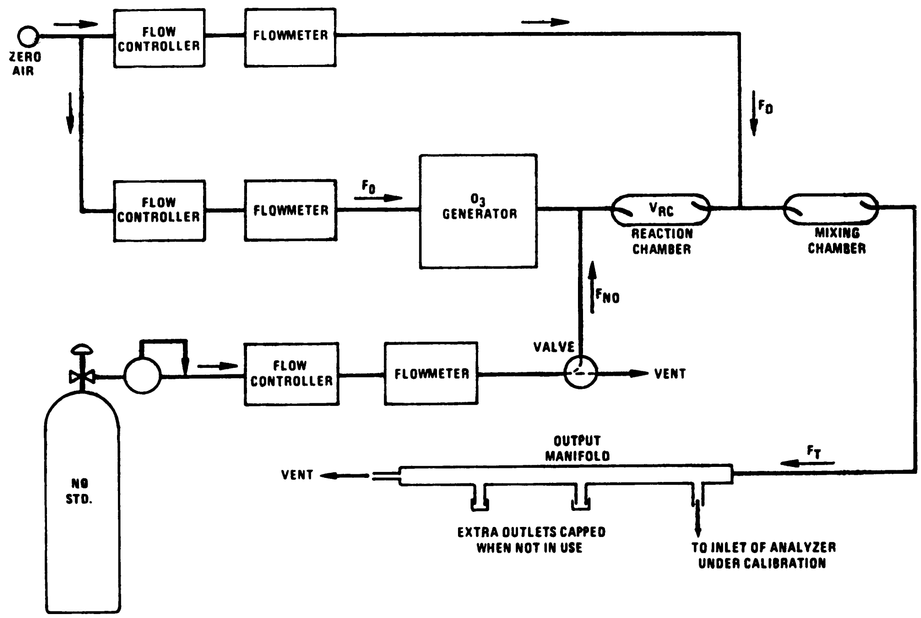

Figure 1. Schematic diagram of a typical GPT calibration system.

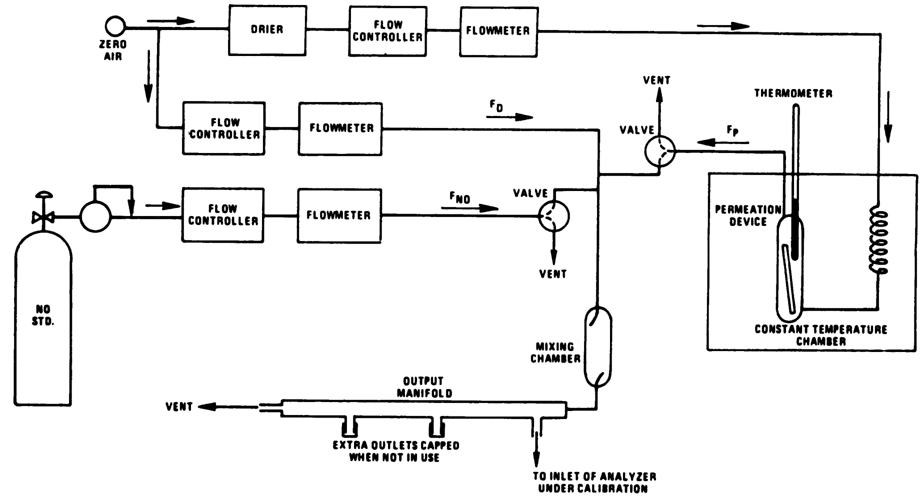

Figure 2. Schematic diagram of a typical calibration apparatus using an NO_2 permeation device.

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