



This chapter will take approximately 30 minutes to complete.

Standard Methods for Criteria Pollutants

OBJECTIVES

Terminal Learning Objective

At the end of this chapter, the student will be able to identify the standard methods for criteria pollutants.

Enabling Learning Objectives

- 7.1 Define NAAQS.
- 7.2 Identify the standard reference test methods for criteria pollutants.

7.1 Introduction

To protect the public health from harmful air pollution, the 1970 Amendments to the Clean Air Act (CAA) authorized the U.S. Environmental Protection Agency (EPA) to specify national ambient air quality standards (NAAQS). The NAAQS regulate ambient concentrations of criteria pollutants as outlined in “National Primary and Secondary Ambient Air Quality Standards,” Part 50 of Chapter 40 of the Code of Federal Regulations (40 CFR 50). States may choose to adopt either the NAAQS or more stringent standards.

To demonstrate compliance with the NAAQS, a network of air monitoring stations are operated nationwide. These stations test the ambient air and report the results to EPA. To ensure nationwide uniformity of these results, EPA established reference test methods for use in this network of stations. These methods are detailed in the appendices to 40 CFR 50.

7.2 Reference Method and Equivalent Method

A reference method uses a measurement principle specified in one of the appendices to 40 CFR 50. An equivalent method is a method which uses a different measurement principle, but which achieves a high degree of correlation to the reference method.

The responsibility for reviewing applications, designating reference and equivalent methods, and approving modifications resides with the Reference and Equivalent Methods (R&E) Program. Currently, this Program is part of the EPA’s Office of Research and Development of the National Exposure Research Laboratory (NERL).

Reference and equivalent methods designated by the R&E Program may be either manual or automated. If a manual method is to be considered for

equivalent designation, it must demonstrate a consistent relationship to the reference method when both methods are used to measure pollutant concentrations in a real atmosphere.

The distinction between automated reference and equivalent methods is based on the *measurement principle* that an instrument employs. For example, the reference measurement principle for automated methods for the detection of the oxides of nitrogen is based on the chemiluminescent reaction of nitric oxide with ozone. Any instrument, therefore, which meets the performance specification for automated methods and uses a chemiluminescent reaction of nitric oxide with ozone for detection is a reference method. Instruments using other measurement principles would be designated equivalent methods, provided they meet the performance specifications. The exception is PM_{2.5} methods, where certain parts of the sampling device must be identical to the Federal specifications in form and function, as well as performance.

This section is designed to provide a brief overview of the reference methods as they are described in the Code of Federal Regulations, and discuss potential problem areas and some quality assurance considerations from a practical standpoint. With the exception of sulfur dioxide (see below), equivalent methods are not discussed in detail in this section.

Criteria Pollutants and Measurement Methods

The United States has established National Ambient Air Quality Standards (NAAQS) for six pollutants. These standards have been promulgated by the US Environmental Protection Agency (EPA) to protect public health and welfare.

There are two types of NAAQS: primary and secondary. Primary standards are designed to protect public health, while secondary standards protect public welfare, including effects of air pollution on vegetation, materials, and visibility. These pollutants and standards are listed in Table 7-1.

Table 7-1. National Ambient Air Quality Standards (NAAQS).

Pollutant	Primary Standards		Secondary Standards		Reference Method/Principle	Typical Method/Principle
	Level	Avg. Time	Level	Avg. Time		
Carbon Monoxide	9 ppm (10 mg/m ³)	8-hour ⁽¹⁾	None		Nondispersive infrared photometry	same
	35 ppm (40 mg/m ³)	1-hour ⁽¹⁾				
Lead	1.5 µg/m ³	Quarterly Average	Same as Primary		High-volume sampling with AA analysis	same
Nitrogen Dioxide	0.053 ppm (100 µg/m ³)	Annual (Arithmetic Mean)	Same as Primary		Gas-phased chemiluminescence	same
Particulate Matter (PM ₁₀)	150 µg/m ³	24-hour ⁽²⁾	Same as Primary		High- or low-volume Sampling	same
Particulate Matter (PM _{2.5})	15.0 µg/m ³	Annual ⁽³⁾ (Arithmetic Mean)	Same as Primary		Low-volume sampling	same
	35 µg/m ³	24-hour ⁽⁴⁾	Same as Primary			
Ozone	0.075 ppm (2008)	8-hour ⁽⁵⁾	Same as Primary		Gas-phased chemiluminescence with ethylene	UV photometry
	0.08 ppm (1997)	8-hour ⁽⁶⁾	Same as Primary			
	0.12 ppm	1-hour ⁽⁷⁾ (Applies only in limited areas)	Same as Primary			
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm (1300 µg/m ³)	3-hour ⁽¹⁾	Pararosaniline method	UV fluorescence
	0.14 ppm	24-hour ⁽¹⁾				

⁽¹⁾ Not to be exceeded more than once per year.

⁽²⁾ Not to be exceeded more than once per year on average over 3 years.

⁽³⁾ To attain this standard, the 3-year average of the weighted annual mean PM_{2.5} concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m³.

⁽⁴⁾ To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35µg/m³ (effective December 17, 2006).

⁽⁵⁾ To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm (effective May 27, 2008).

⁽⁶⁾ (a) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.

(b) The 1997 standard—and the implementation rules for that standard—will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.

⁽⁷⁾ (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1 .

(b) As of June 15, 2005, EPA revoked the 1-hour ozone standard in all areas except the 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

The national monitoring networks used to determine compliance with these NAAQS must use methods approved through the R&E Program. Following is a brief discussion regarding each of these pollutants and its associated reference method.

Particulate Matter

PM_{2.5}

The reference method for PM_{2.5} provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 μm in ambient air. The method requires sampling over a 24-hour period for purposes of determining whether the primary and secondary NAAQS are met.

An electrically powered air sampler draws ambient air at a constant volumetric flow rate into a specially shaped inlet and through an inertial particle size separator (impactor) where the suspended particulate matter in the PM_{2.5} range is separated for collection on a polytetrafluoroethylene (PTFE) filter over the specified sampling period. Alternatively, the Very Sharp Cut Cyclone (VSCC) particle size separator may be used in place of the inertial impactor. Samplers which utilized the VSCC were initially designated as equivalent methods. In recent years they have been re-designated with reference method status.

Each filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net gain due to collected PM_{2.5}. The total volume of air sampled is determined by the sampler from the measured flow rate (at actual ambient temperature and pressure) and the sampling time. The mass concentration of PM_{2.5} in the ambient air is computed as the total mass of collected particles in the PM_{2.5} size range divided by the actual volume of air sampled, and is expressed in micrograms per cubic meter of air ($\mu\text{g}/\text{m}^3$).

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, and timing errors.

A more detailed discussion of PM_{2.5} samplers can be found in Chapters 4 and 5 of this manual.

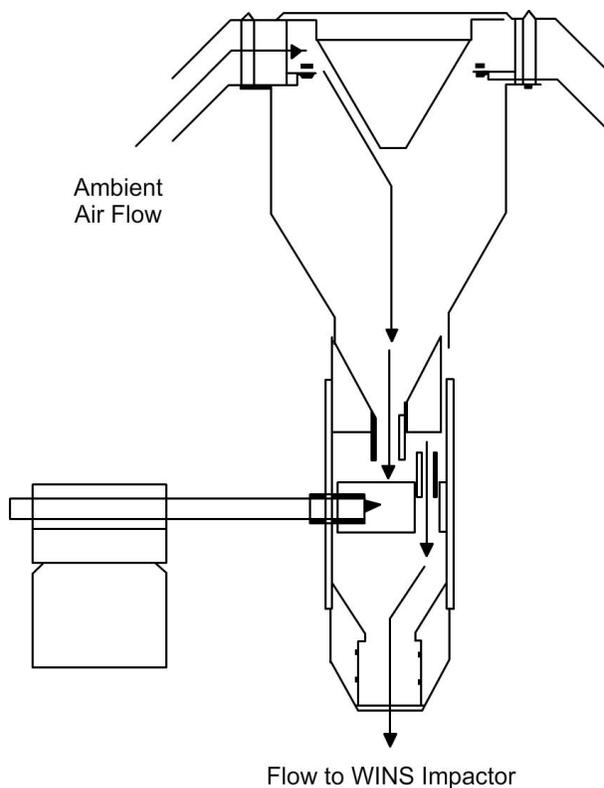


Figure 7-1. Schematic image of PM_{2.5} sampler utilizing a WINS impactor.

PM₁₀

The reference method for PM₁₀ provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 10 micrometers in ambient air. The method requires sampling over a 24-hour period for purposes of determining whether the primary and secondary NAAQS are met.

An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM₁₀ size range. Each size fraction in the PM₁₀ size range is then collected on a separate filter over the specified sampling period. Some PM₁₀ samplers use particle size separators which differ from the configuration shown in Figure 7-2 and are designated as reference methods. These include high- and low-volume samplers which use various inlet configurations (see 40 CFR 50, Appendix L for descriptions of these inlet configurations) based on inertial impaction and instruments known as dichotomous samplers which separate particle sizes using “virtual” impaction.

Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM₁₀. The total volume of air sampled, corrected to EPA reference conditions (25°C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM₁₀ in the ambient air is computed as the total mass of

collected particles in the PM₁₀ size range divided by the total volume of air sampled, and is expressed in micrograms per standard cubic meter (µg/std m³).

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, and timing errors.

A more detailed discussion of PM₁₀ samplers can be found in Chapters 4 and 5 of this manual.

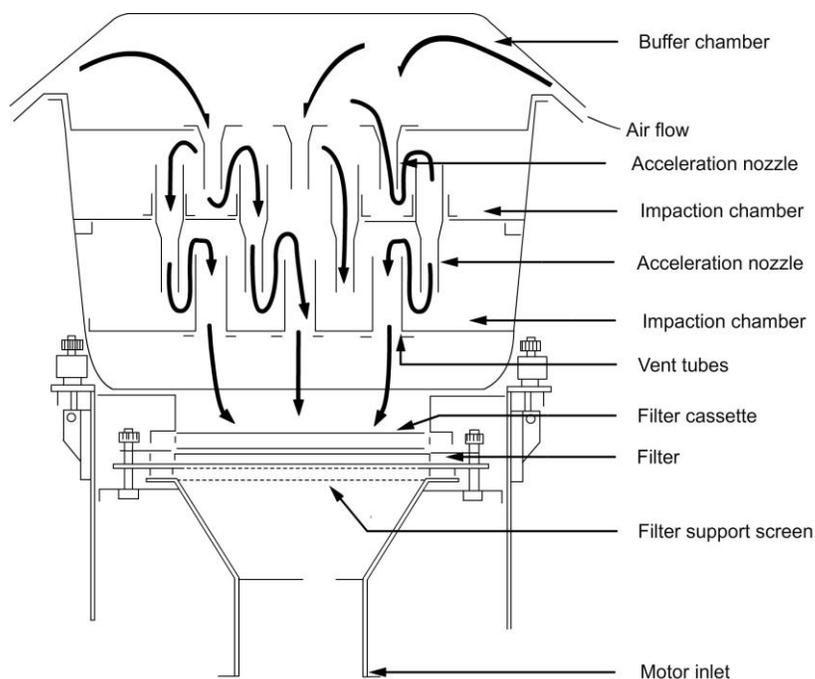


Figure 7-2. Schematic of PM₁₀ sampler.

Ozone

The reference measurement principle for the measurement of ozone is the gas-phase chemiluminescence resulting from the reaction of ozone with ethylene. Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with ethylene to emit light, which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

The unstable nature of ozone requires that ozone be generated *in situ* in order to calibrate ozone monitors. Ultraviolet (UV) photometry has been designated as the calibration procedure. A schematic of a typical UV photometric calibration system is shown in Figure 7-3.

Ozone monitoring locations now use the equivalent method, which is an ultraviolet method.

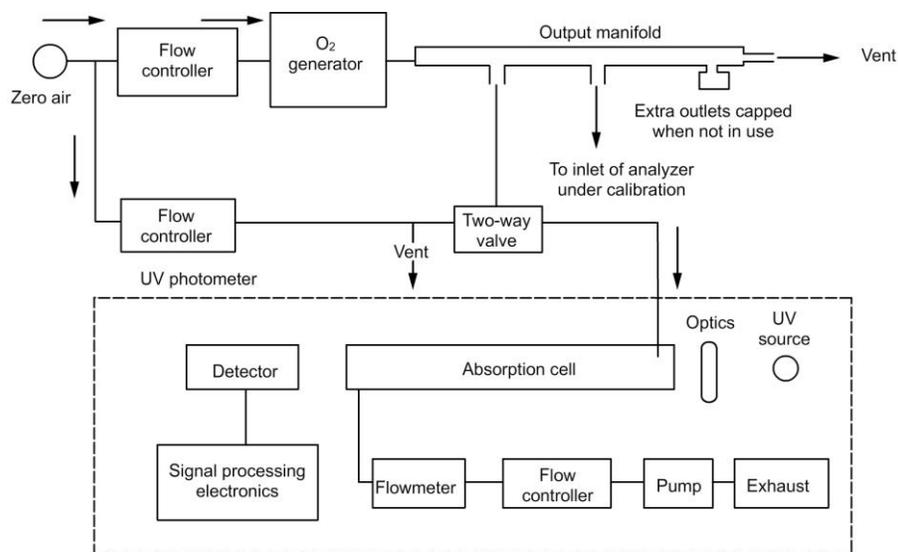


Figure 7-3. Schematic diagram of a typical photometric calibration system.

A more detailed discussion of ozone monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Carbon Monoxide

The reference measurement principle used to measure ambient levels of carbon monoxide is nondispersive infrared (NDIR) photometry. A signal is produced as a result of the infrared absorption of carbon monoxide which can be related to the absolute CO concentration by calibrating the photometer as specified in Appendix C of 40 CFR 50.

The problem areas associated with this method are the broad band absorption of carbon dioxide and water vapor. These two compounds' absorption results in an interference. The techniques of "negative filtering" or gas filter correlation alleviate these problems.

A more detailed discussion of carbon monoxide monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Nitrogen Dioxide

The reference measurement principle for the determination of nitrogen dioxide is the gas-phase chemiluminescence reaction of nitric oxide with ozone (Eq. 7-1).

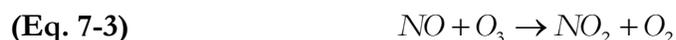


Nitrogen dioxide is measured indirectly by measuring total oxides of nitrogen ($\text{NO}_x = \text{NO}_2 + \text{NO}$) and electronically subtracting the nitric oxide concentration (NO), yielding a nitrogen dioxide determination (NO_2). A measure

of the total oxides of nitrogen is obtained by passing the sample across a catalytic converter, which reduces nitrogen dioxide to nitric oxide (Eq. 7-2).



The calibration of the NO and NO_x channels of the instrument is accomplished by diluting a pressurized tank of NO. The calibration of the NO₂ channel is accomplished with a permeation device or the gas-phase titration of an NO standard gas with ozone. The gas-phase titration involves the following reaction (Eq. 7-3):



This produces a known amount of nitrogen dioxide which allows one to calibrate the NO₂ channel of the monitor. The other calibration procedure specified in Appendix F, 40 CFR 50, uses a dynamic dilution system in combination with a permeation device to produce a known amount of NO₂.

The problem areas associated with this method are interferences such as peroxyacetyl nitrate (PAN) and other nitrogen-containing compounds. In periods of high photochemical activity, corrections for these interferences may be necessary.

The chemical composition of the atmosphere plays an important role in determining the validity of the nitrogen dioxide measurements obtained using a reference method analyzer. For most ambient air measurements, however, interferences such as the ones mentioned previously are minimal. The frequency of calibration and other maintenance (e.g., replacement of ozone filter, check of converter efficiency, etc.) are important quality assurance considerations.

A more detailed discussion of nitrogen dioxide monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Sulfur Dioxide

The reference method for the measurement of dioxide in ambient air is a manual wet-chemical method – the pararosaniline method. Sulfur dioxide is bubbled through a solution of potassium tetrachloromercurate (TCM) which forms a monochlorosulfonatomercurate complex. This complex forms an intensely colored solution upon addition of pararosaniline dye and formaldehyde. The concentration of sulfur dioxide can be determined spectrophotometrically by measuring the absorbance of the colored solution.

The potential problems associated with interferences are minimized by the procedures listed in Table 7-2.

Table 7-2. Parasiline interferences.

Interference	Corrective procedure
Ozone	Time delay
Heavy metals	Addition of EDTA and phosphoric acid
Oxides of nitrogen	Addition of sulfamic acid

Other precautions to be considered related to the sampling train (Figure 7-4) and to sampling conditions. The inner diameter of the tip of the impinger stem should be checked to make sure that a No. 79 jeweler’s drill bit will pass through, but a No. 78 jeweler’s drill bit will not. The temperature instability of the monochlorosulfonatomercurate complex during sampling also poses potential problems. This is minimized by using a temperature control device to maintain a temperature of $15^{\circ} \pm 10^{\circ}\text{C}$ during sampling. Collected samples must be kept at a temperature of $5^{\circ} \pm 5^{\circ}\text{C}$. Since this method involves a laboratory analysis of the sample after collection in the field, care should be taken in handling the sample once it has been collected to avoid contamination.

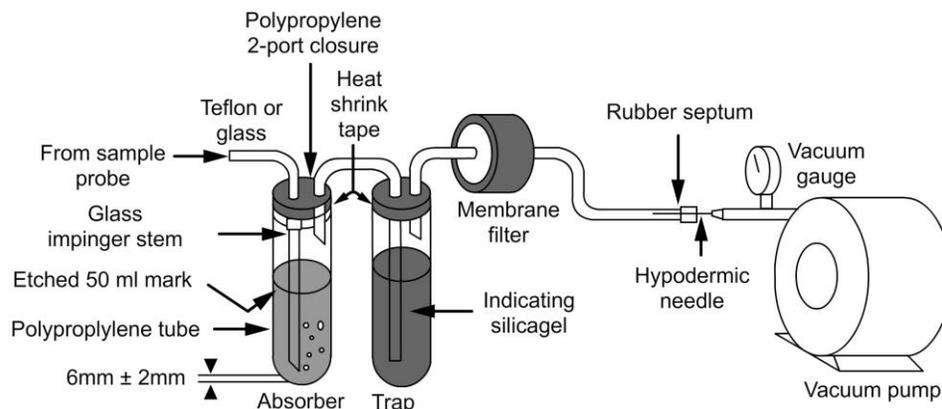


Figure 7-4. SO₂ sampling train for 24-hour sampling.

Current monitoring sites do not use the reference method for sulfur dioxide sampling. A continuous equivalent method based on ultraviolet (UV) fluorescence is used nearly exclusively today. A signal is produced as a result of a SO₂ molecule emitting a characteristic wave length of light (fluorescence) as it returns to a lower “energy state” after having been “electronically excited” by radiation of UV energy. The fluorescence emissions are measured by a detector and processed electronically to yield the concentration of SO₂ in the sample air.

The problem areas associated with UV fluorescence are related primarily to the quenching effects of O₂, N₂, CO₂, and water vapor. For ambient monitoring, the levels of O₂, N₂, and, for the most part, CO₂ and water vapor are constant; thus the

quenching effect is fairly constant. Hydrocarbons may also interfere, but all equivalent method analyzers are equipped with a hydrocarbon scrubber (i.e., “kicker” or “cutter”) to eliminate this potential problem.

A more detailed discussion of sulfur dioxide monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Lead

The reference method for lead consists of measuring the lead content of particulate matter collected by the total suspended particulate reference method's high-volume sampling procedure as described below. After sample collection, lead is acid-extracted from the particulate matter of a ¾ in. x 8 in. strip of the high-volume filter. Finally, the lead content of the resulting solution is determined by atomic absorption spectrometry.

In the high-volume method, air is drawn through a filter composed of glass fibers or other relatively inert, nonhygroscopic material, and the amount of particulate matter collected is determined gravimetrically. A flow rate measurement device for the sampler is calibrated against actual air flow with a flow rate transfer standard, which is first calibrated against a positive displacement standard volume meter.

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, timing errors, recirculation of sampler exhaust, and the wind direction sensitivity of the sampler.

Potential problems exist in the analysis portion of the method as well. In addition to the sampling problems associated with the high-volume method, lead may be distributed nonuniformly across the filter. The problem can be alleviated by analyzing a larger portion of the filter. Chemical and light-scattering interferences may be encountered during the atomic absorption spectrophotometric analysis. Chemical interferences can be overcome using the method of standard additions. Light-scattering interferences can be corrected using a dual-channel atomic absorption spectrophotometer equipped with a continuum light source, by using a nonabsorbing wavelength that is near the lead analytical wavelength, or by using a chelating agent to chemically isolate potential interferences during the analysis so that they do not interfere. Furthermore, for accurate particulate lead analyses, it is necessary that the variation of lead content from filter to filter within a given batch of blank filters be small.

A more detailed discussion of lead monitors can be found in Chapters 4, 5, and 8 of this manual.

References

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