



Air Resources Board

State of California



Office Environmental Health
Hazard Assessment

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Review of the California Ambient Air Quality Standard For Nitrogen Dioxide

Technical Support Document

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California Environmental Protection Agency

Air Resources Board

and

Office of Environmental Health and Hazard Assessment

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California Environmental Protection Agency

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3 Measurement of Nitrogen Dioxide

3.1 Introduction

NO₂ gas is formed in ambient air through the oxidation of nitric oxide (NO). The sum of the concentrations of NO and NO₂ in ambient air is generally defined as the concentration of nitrogen oxides (NO_x).

The recommended methodology to quantify hourly NO₂ concentrations for California's ambient air monitoring network is gas-phase chemiluminescence. Ambient concentrations of NO and NO_x are determined directly by chemiluminescence technology. However, NO₂ concentrations are determined indirectly by subtracting NO concentrations from NO_x concentrations.

3.2 Existing Monitoring Methods

Five NO₂ monitoring technologies are listed in the current United States Environmental Protection Agency (U.S. EPA) "List of Designated Reference and Equivalent Methods":

Sodium Arsenite Method for NO₂, Manual Equivalent Methods.

TGS-ANSA Method for NO₂ (triethanolamine, guaiacol, and sodium metabisulfate [TGS]; sulfanilamide; and 8-amino-1-naphthalene-sulfonic acid ammonium salt [ANSA]), Manual Reference Method.

Optical Long Path Automated Reference Method.

Optical Open Path Automated Equivalence Method.

Chemiluminescence Automated Reference Methods.

A Federal Reference Method (FRM) is defined in Title 40 of the Federal Code of Regulations (40 CFR), Section 53.1, as a method that samples and analyzes the ambient air for an air pollutant that is specified as a reference method in 40 CFR, Parts 50 and 53. 40 CFR, Part 50, Appendix F lists gas phase chemiluminescence as the reference method for determining NO₂. Furthermore, 40 CFR, Part 53, Section 53.2 (b), states that an automated NO₂ reference method must utilize the measurement principle and calibration procedure as specified in Appendix F in 40 CFR, Part 50 and meet the requirements specified in Part 53, Subpart B.

Accuracy and precision of the NO₂ measurements are reflected in the field audit data. (ARB, 2004; ARB, 2006). Accuracy is represented as an average percent difference of measurements of a NIST standard introduced through the probe used for NO₂ sampling. The average percent difference is the combined differences from the certified value of all the individual audit points. For 2002, 2003, 2004, and 2005, the percent differences were: 1.1, 0.9, -0.7, and -2.1, respectively, representing 96, 77, 78, and 79 analyzers, respectively. These are operating within the ARB's control limits (+/-15%) (ARB, 2004, 2006). The standard deviation (statistical variability) of these measurements reflect the precision of the method. For 2002, 2003, 2004, and 2005 the standard deviation of the method as evaluated by audit was 5, 5.3, 4.5, and 4.5 percent, respectively (ARB, 2004, 2006).

A Federal Equivalent Method (FEM) is defined (40 CFR, Part 50, Section 50.1) as a method for measuring the concentration of an air pollutant in ambient air that has been designated as an equivalent method (to the FRM) in accordance with 40 CFR, Part 53.

The California ambient air standard for NO₂ (California Code of Regulations, Title 17, Section 70200) stipulates that gas phase chemiluminescence is the method to be used to measure NO₂. The standard also allows an equivalent method to be used as described in the first footnote to the "Table of Standards" in Section 70200:

"Any equivalent procedure which can be shown to the satisfaction of the Air Resources Board to give equivalent results at or near the level of the air quality standard may be used."

Manual Equivalent Methods present in the U.S. EPA "List of Designated Reference and Equivalent Methods" are not recommended for use in California's ambient monitoring network. Manual gaseous

methods possess significant limitations due to the level of labor, analysis time, potential interferences, and operational costs. The ARB has not utilized manual Equivalent Methods for more than 25 years, therefore these manual methods have not been included in the list of recommended NO₂ methods.

Long path and open path methods are also not currently used in California's ambient air monitoring network. For these methods, ARB staff do not know the quality of the analytical data, reliability of the instruments, or the overall value to California's current monitoring network. Therefore, open path and long path methods are not included in the list of recommended NO₂ methods.

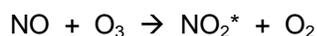
Since January 1980, chemiluminescence methods have proven robust while producing data with acceptable precision and accuracy. With the additional benefit of method continuity among air monitoring agencies throughout California, staff recommends only "federal designated automated chemiluminescence methods" as the approved method for determining compliance with California's NO₂ Ambient Air Quality Standard.

The U.S. EPA-designated NO₂ chemiluminescence automated reference methods are in accordance with 40 CFR, Part 53. Each method is currently acceptable for use in state or local air quality surveillance systems under 40 CFR, Part 58. Each method must be operated according to manufacturer's manual procedures along with CFR quality assurance procedures. Manufacturer or user modifications to a U.S. EPA designated "reference" method may invalidate its designative status (refer to 40 CFR, Part 58, Appendix C, Section 2.8, for user modification approval).

3.3 Chemiluminescence Methodology Principle

Chemiluminescence results from a chemical reaction in which light is emitted from a species or compound that is in an excited state. Chemiluminescent NO-NO₂-NO_x monitors directly measure the concentrations of NO and NO_x. The concentration of NO₂ is calculated by subtracting the measured NO concentration from the measured NO_x concentration.

NO is measured by mixing ozone into the NO sample flow path. In the mixing chamber, all NO is oxidized to NO₂, resulting in temporarily excited NO₂ molecules. As the excited NO₂ molecules release photons of energy, a photomultiplier tube measures the emitted light.



* = excited state of species

hν = light

[h] = Planck's constant (6.62 x 10⁻²⁷ erg sec)

[ν] = light frequency (sec⁻¹)

NO_x is measured by diverting a separate sample flow through a thermal converter prior to the addition of ozone, as mentioned above. In the thermal converter, NO₂ is reduced to NO. Analysis is performed using the same photomultiplier tube with the aid of a sample flow splitter.

Procedures for testing performance characteristics of automated NO₂ methods are located in 40 CFR, Part 53, Subpart B. In Section 53.20 of Subpart B, Table B-1 displays the automated method performance specifications and the corresponding testing procedure. In Section 53.23, analyzer interference is defined as a positive or negative response caused by a substance other than the one being measured. Table B-3 in Section 53.23(d) lists the interferences and test concentrations for each automated method. The compounds and concentrations listed to test NO₂ chemiluminescence analyzer interferences are:

0.1 ppm ammonia

0.5 ppm sulfur dioxide

0.5 ppm nitric oxide

20,000 ppm water vapor

3.4 Recommendation

Staff recommends that the Board continue to endorse the chemiluminescence method as the approved method in California for determining compliance with California's Ambient Air Quality Standard for NO₂. By reference, therefore, staff recommends all federally approved chemiluminescence methods be incorporated as "California Approved Samplers" for NO₂. This will result in no change in air monitoring practices, but will align state monitoring requirements with federal requirements. Specifically, we recommend that a new part be added to the California Administrative Code 70100.1 to read in part:

"NO₂ Monitoring Methods. The method for determining compliance with the NO₂ ambient air quality standard shall be the chemiluminescence Federal Reference Method for the determination of NO₂ in the atmosphere (40 CFR, Part 50, Appendix F). California Approved Samplers for NO₂ are set forth in the Air Monitoring Quality Assurance Manual, Volume IV, Part D: Monitoring Methods for NO₂."

The current U.S. EPA "List of Designated Reference and Equivalent Methods" may be obtained through the U.S. EPA Technology Transfer Network Ambient Monitoring Technology Information Center web site at <http://www.epa.gov/ttn/amtic/criteria.html>.

The following method constitutes "California Approved Samplers" for NO₂ for the purposes of determining compliance with California's ambient air quality standard: Gas phase chemiluminescence method for the determination of NO₂ in the atmosphere (40 CFR, Part 50, Appendix F). The specific instruments approved are:

Advanced Pollution Instrumentation, Inc. Model 200 NO₂ Analyzer - *Automated Reference Method*: RFNA-0691-082 "Advanced Pollution Instrumentation, Inc. Model 200 Nitrogen Oxides Analyzer". [Federal Register: Vol. 56, page 27014, 06/12/91]

Beckman Model 952-A NO/NO₂/NO_x Analyzer - *Automated Reference Method*: RFNA-0179-034 "Beckman Model 952-A NO/NO₂/NO_x Analyzer". [Federal Register: Vol. 44, page 7806, 02/07/79]

Bendix Model 8101-B Oxides of Nitrogen Analyzer - *Automated Reference Method*: RFNA-0479-038 "Bendix Model 8101-B Oxides of Nitrogen Analyzer". [Federal Register: Vol. 44, page 26792, 05/07/79]

Bendix/Combustion Engineering Model 8101-C Oxides of Nitrogen Analyzer - *Automated Reference Method*: RFNA-0777-022 "Bendix or Combustion Engineering Model 8101-C Oxides of Nitrogen Analyzer". [Federal Register: Vol. 42, page 37435, 07/21/77]

Columbia Scientific Industries Models 1600 and 5600 Analyzers - *Automated Reference Method*: RFNA-0977-025 "CSI Model 1600 Oxides of Nitrogen Analyzer". [Federal Register: Vol. 42, page 46574, 09/16/77]

Dasibi Model 2108 Oxides of Nitrogen Analyzer - *Automated Reference Method*: RFNA-1192-089 "Dasibi Model 2108 Oxides of Nitrogen Analyzer". [Federal Register: Vol. 57, page 55530, 11/25/92]

DKK-TOA Corporation Model GLN-114E Nitrogen Oxides Analyzer - *Automated Reference Method*: RFNA-0798-121 "DKK-TOA Corporation Models GLN-114E and GLN-114E-1 Nitrogen Oxides Analyzer". [Federal Register: Vol. 63, page 41253, 08/03/98]

Environnement S. A. Model AC31M NO₂ Analyzer - *Automated Reference Method*: RFNA-0795-104 "Environnement S. A. Model AC31M Chemiluminescent Nitrogen Oxide Analyzer". [Federal Register: Vol. 60, page 38326, 07/26/95]

Environnement S. A. Model AC32M NO₂ Analyzer - *Automated Reference Method*: RFNA-0202-146 "Environnement S. A. Model AC32M Chemiluminescent Nitrogen Oxides Analyzer". [Federal Register: Vol. 67, page 15567, 04/02/02]

Horiba Instruments Models APNA-360 or APNA-360-CE NO-NO₂-NO_x Monitor - *Automated Reference Method*: RFNA-0196-111 "Horiba Instruments, Inc. Models APNA-360 or APNA-360-CE Ambient NO-NO₂-NO_x Monitor". [Federal Register: Vol. 61, page 11404, 03/20/96]

Horiba Instruments Model APNA-370 NO₂ Monitor *Automated Reference Method*: RFNA-0506-157 “Horiba Instruments Incorporated Model APNA-370 Ambient NO_x Monitor,” standard specification, operated with a full scale fixed measurement range of 0 - 0.50 ppm with the automatic range switching off, at any ambient temperature in the range of 20 °C to 30 °C, and with a 0.3 micrometer sample particulate filter installed. [Federal Register: Vol. 71, page 25587, 05/01/06]

Meloy Model NA530R Nitrogen Oxides Analyzer - *Automated Reference Method*: RFNA-1078-031 “Meloy Model NA530R Nitrogen Oxides Analyzer”. [Federal Register: Vol. 43, page 50733, 10/31/78 and Vol. 44, page 8327, 02/09/79]

Monitor Labs Model 8440E Nitrogen Oxides Analyzer - *Automated Reference Method*: RFNA-0677-021 “Monitor Labs Model 8440E Nitrogen Oxides Analyzer”. [Federal Register: Vol. 42, page 37434, 07/21/77; Vol. 42, page 46575, 09/16/77; Vol. 46, page 29986, 06/04/81]

Monitor Labs/Lear Siegler Model 8840 Nitrogen Oxides Analyzer - *Automated Reference Method*: RFNA-0280-042 “Monitor Labs or Lear Siegler Model 8840 Nitrogen Oxides Analyzer”. [Federal Register: Vol. 45, page 9100, 02/11/80 and Vol. 46, page 29986, 06/04/81]

Monitor Labs/Lear Siegler Model 8841 Nitrogen Oxides Analyzer - *Automated Reference Method*: RFNA-0991-083 “Monitor Labs or Lear Siegler Model 8841 Nitrogen Oxides Analyzer”. [Federal Register: Vol. 56, page 47473, 9/19/91]

Philips Model PW9762/02 NO/NO₂/NO_x Analyzer - *Automated Reference Method*: RFNA-0879-040 “Philips Model PW9762/02 NO/NO₂/NO_x Analyzer”. [Federal Register: Vol. 44, page 51683, 09/04/79]

Seres Model NO_x 2000 G Nitrogen Dioxide Analyzer *Automated Reference Method*: RFNA-0706-163 “Seres Model NO_x 2000 G Nitrogen Dioxide Ambient Air Analyzer,” operated with a full scale measurement range of 1 - 0.50 ppm, at any ambient temperature in the range of 20°C to 30 °C. [*Federal Register*: Vol. 71, page 42089, 07/25/06]

SIR S.A. Model S-5012 Nitrogen Oxides Analyzer - *Automated Reference Method*: RFNA-0804-152. [Federal Register: Vol. 69, page 47924, 08/06/04]

Teledyne - Advanced Pollution Instrumentation, Inc. Models 200A, 200AU, 200E; Teledyne Analytical Instruments Model 9110A; or Teledyne Monitor Labs sensor-e™ Model TML-41 NO₂ Analyzers - *Automated Reference Method*: RFNA-1194-099 “Teledyne - Advanced Pollution Instrumentation, Inc. Models 200A, 200AU, 9110A, or 200E; Teledyne Analytical Instruments Model 9110A; or Teledyne Monitor Labs, Inc. sensor-e™ Model TML-41 Chemiluminescence Nitrogen Oxides Analyzer”. [Federal Register: Vol. 59, page 61892, 12/02/94]

Teledyne Monitor Labs/Casella/Ecotech Models ML9841, ML9841A/EC9841A, Teledyne Monitor Labs/Casella/Ecotech Model ML9841B/EC9841B, or Wedding & Associates Model 1030 NO₂ Analyzers - *Automated Reference Method*: RFNA-1292-090– “Teledyne Monitor Labs, Casella Monitor, or Ecotech Models ML9841, ML9841A/EC9841A, or ML9841B/EC9841B, or Wedding & Associates, Inc. Model 1030 Nitrogen Oxides Analyzers”. [Federal Register: Vol. 57, page 60198, 12/18/92]

Thermo Electron/Thermo Environmental Instruments Model 14 B/E – *Automated Reference Method*: RFNA-0179-035 “Thermo Electron or Thermo Environmental Instruments, Inc. Model 14 B/E Chemiluminescent NO/NO₂/NO_x Analyzer”. [Federal Register: Vol. 44, page 7805, 02/07/79 and Vol. 44, page 54545, 09/20/79]

Thermo Electron/Thermo Environmental Instruments Model 14 D/E – *Automated Reference Method*: RFNA-0279-037 “Thermo Electron or Thermo Environmental Instruments, Inc. Model 14 D/E Chemiluminescent NO/NO₂/NO_x Analyzer”. [Federal Register: Vol. 44, page 10429, 02/20/79]

Thermo Environmental Instruments Models 42, 42C, 42i NO/NO₂/NO_x Analyzer - *Automated Reference Method*: RFNA-1289-074 “Thermo Environmental Instruments Inc. Model 42, Model 42C, or Model 42i NO-NO₂-NO_x Analyzer”. [Federal Register: Vol. 54, page 50820, 12/11/89]

3.5 Estimated Costs and Impacts

Automated reference NO₂ chemiluminescence methods are currently utilized throughout California's Ambient Monitoring Network. Therefore, the recommendation to continue with existing NO₂ chemiluminescence methods should not impact routine NO₂ monitoring costs or resources.

3.6 References

ARB (2004). Annual Data Quality Report. For the Monitoring and Laboratory Division's and Local Districts' Air Monitoring Networks. Monitoring and Laboratory Division. Quality Assurance Section

ARB (2006) Performance audits. Gaseous Pollutants.

<http://www.arb.ca.gov/aaqm/qmosqual/sysaudit/audrslts/audrslts.htm>

Code of Federal Regulations, Title 40, Part 50, Appendix F – Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence).

Code of Federal Regulations, Title 40, Part 53, Subpart B – Procedures for Testing Performance Characteristics of Automated Methods for SO₂, CO, O₃ and NO₂.

Code of Federal Regulations, Title 40, Part 58 – Ambient Air Quality Surveillance.

United States Environmental Protection Agency, Office of Research and Development, "List of Designated Reference and Equivalent Methods", December 5, 2006:

<http://www.epa.gov/ttn/amtic/criteria.html>.