Standard Operating Procedure for the Analysis of True Nitrogen Dioxide (NO2) in Ambient Air for the Photochemical Assessment Monitoring Stations (PAMS) Network

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**A. Scope and Applicability**

The purpose of this standard operating procedure (SOP) is to describe the measurement of “true” nitrogen dioxide (NO2) by chemiluminescent absorbance with photolytic conversion of NO2 to nitric oxide (NO) or cavity attenuated phase shift (CAPS) spectroscopy instruments for the Environmental Protection Agency (EPA) Photochemical Assessment Monitoring Stations (PAMS) network. This SOP describes the real-time, continuous measurement of “true NO2” by sampling ambient air with instruments approved as EPA Federal Equivalent Methods (FEMs) EQNA-0514-212 (Teledyne API T500U) and EQNA-0512-200 (Teledyne API T200UP). Procedures for the setup, calibration, and operation of the NO2 analyzer are described herein. This SOP is intended to provide instruction for properly trained instrument operators.

Monitoring requirements, training requirements, operation of specific models of dilution calibrators and gas generation/purification equipment, and handling of data through data acquisition systems (DAS)/dataloggers, reporting of measurement data to EPA’s Air Quality System (AQS), and independent assessments are outside the scope of this SOP and can be found elsewhere.1,2 This SOP does not describe or address indirect measurement of NO2 with molybdenum conversion chemiluminescent detection instruments, whose measurements of NO2 can be subject to positive bias when sampled air masses contain additional reactive nitrogen oxides (NOy). This SOP also does not include comprehensive information on method measurement principle background, as these details can be found elsewhere (in instrument manuals and manufacturer literature) and are not critical to operation of the instruments and support equipment.

*Disclaimer Notice: Mention of trade names, products, or services does not convey official EPA approval, endorsement, or recommendation.*

1. **Summary of Method**

Continuous monitoring of true NO2 can be achieved by use of either CAPS or photolytic conversion with chemiluminescent detection as described in Sections B.1 and B.2, respectively. For both measurement methods, ambient air is drawn in from an inlet probe, filtered of particulate matter, and introduced to the analyzer where the sampled atmosphere is interrogated for NO2 based on the instrument detector response standardized against a user-defined and verified calibration.

The true NO2 analyzer standard response is calibrated at a zero point with nominally NO2-free “zero” air and an upscale span NO2 concentration representative of approximately 80% of the expected measurement range. This measurement range is defined by the expected ambient measurements at the site, which will not exceed 200 parts per billion (ppb) for most sites. The standard NO2 gas employed to generate calibration standard gases may be sourced from a high pressure cylinder with a traceably certified concentration of NO2; gas phase titration (GPT) of nitric oxide (NO) with ozone (O3); or from a permeation tube of NO2 (which is not described or addressed within this SOP). Following establishment of the instrument response at the zero and span concentration, the calibration is verified by performing a multipoint verification (MPV), after which ambient air NO2 concentrations are to be measured continuously (i.e., continuous instrument output averaged each minute) and reported as the average for a given hour. Ambient air measurements for the PAMS Required Site Network should occur per the monitoring agency’s governing Quality Assurance Program Plan (QAPP), typically through the entirety of the PAMS season which begins June 1 and concludes August 31 annually. Completeness, as defined in the governing QAPP, requires that minimally 45 minutes (75%) of each collected sample hour include valid measurements and that 18 of the 24 daily hours consist of valid hours of data to fulfil the completeness data quality objective (DQO).3

For both CAPS and photolytic conversion chemiluminescent instruments, ambient air is drawn into the true NO2 analyzer inlet with a vacuum pump and particulates are filtered (removed) from the ambient air stream to prevent deposition of particulate matter (PM) on the analyzer optics.

1. Cavity Attenuated Phase Shift Spectroscopy (CAPS)

Particulate-scrubbed air enters the sample cell, which includes highly reflective mirrors to produce the optical path within the cell. NO2 in the sampled atmosphere absorbs light at 450 nm. Rather than a traditional absorbance method, where a reduction in intensity of light at a wavelength of 450 nm experienced at the detector is proportional to concentration of NO2, a CAPS monitor employs the average time spent in the cell by the 450-nm light to quantify the NO2 concentration in the cell. The presence of NO2 in the cell causes the average time to decrease as the NO2 concentration increases (due to absorption by the NO2 molecules). This reduction in time spent in the cell by the 450 nm light absorbed is proportional to the concentration of NO2 in the sampled atmosphere.

As of the release of this SOP, the following five EPA-approved FEM CAPS instruments are commercially available:

* Teledyne Advanced Pollution Instruments (API) Model T500U CAPS NO2 Analyzer (FEM EQNA-0514-212)
* Environnement S.A. AS32M CAPS NO2 Analyzer (FEM EQNA-1013-210)
* Ecotech Serinus 60 CAPS NO2 Analyzer (FEM EQNA-0217-242)
* Aerodyne Research, Inc. CAPS NO2 Monitor (FEM designation available from supplier)
* Teledyne API Model N500 CAPS NO2/NOx/NO Analyzer (FEM EQNA-0320-256)
1. Photolytic Conversion with Chemiluminescent Detection

Sample gas passes through the ultraviolet (UV)-based photolytic converter chamber and is exposed to blue light in the wavelength range of 350 to 420 nm from an array of light-emitting diodes (LEDs). This selectively converts NO2 to NO with negligible radiant heating or interference from other gases. Detection of NO is then achieved by chemiluminescence from the reaction of NO with O3 (Reactions 1 and 2):

 NO + O3 → NO2\* + O2 Reaction 1

 NO2\* → NO2 + hν Reaction 2

where NO2\* is an electronically excited NO2 molecule that emits light (hν) with intensity proportional to the NO2 concentration. The Teledyne API Model T200UP Photolytic Conversion NO2 Analyzer (FEM EQNA-0512-200) includes a pre-reactor to account for interferences from radical formation due to hydrocarbons in the sampled air stream.

**Table 1. Specifications4,5 for Example True NO2 Instruments**

|  |  |  |
| --- | --- | --- |
| **Make & Model** | **Teledyne API T500U** | **Teledyne API T200UP** |
| **Method** | CAPS | Photolytic Conversion with Chemiluminescent Detection |
| **NO2 Measurement Range** | Minimum 0 - 5 ppb Maximum 0 - 1 ppm  | Minimum 0 - 5 ppb Maximum 0 - 2,000 ppb |
| **Detection Limit** | < 0.040 ppb | < 0.050 ppb |
| **Inlet Flowrate** | 900 ± 90 cm3/minute | 1100 ± 110 cm3/minute |
| **Inlet filter** | Yes | Yes |
| **Sample dryer** | none | Nafion® |
| **Dimensions****(L** × **W** × **H)** | 597 × 432 × 178 mm | 597 × 432 × 178 mm |
| **Weight (kg)** | 15 | 18 (Analyzer)9.5 External pump  |
| **Operating Temperature** | 5 to 40°C  | 5 to 40°C |

1. **Definitions and Abbreviations**
	1. ADQ: audit of data quality
	2. BOA: back of the analyzer
	3. °C: degree Celsius
	4. CAPS: cavity attenuated phase shift spectroscopy
	5. CFR: Code of Federal Regulations
	6. cm3: cubic centimeter
	7. COA: certificate of analysis
	8. DAS: data acquisition system
	9. DDC: dynamic dilution calibrator – gas flow selection and control device that employs mass flow controllers (MFCs) to precisely and accurately meter the amount of one or more standard gases and mix the standard gas with a diluent gas to prepare an accurate dilution of the standard gas. Some DDCs also include onboard ozone generators that can be calibrated to provide a standard ozone concentration.
	10. EPA: Environmental Protection Agency
	11. FEP: fluorinated ethylene propylene
	12. ID: inner diameter
	13. L: liter
	14. LED: light emitting diode
	15. MDL: method detection limit
	16. MFC: mass flow controller
	17. MPV: multi-point verification
	18. NCore: National Core Monitoring Network
	19. NIST: National Institute of Standards and Technology
	20. NO: nitric oxide
	21. NO2: nitrogen dioxide
	22. NOx: combination of chemical species NO and NO2
	23. NOy: total reactive nitrogen – all oxides of nitrogen in which the oxidation state of the nitrogen atom is 2+ or greater. This is the sum of all reactive nitrogen species, including NOx and other oxides of nitrogen designated as NOz.
	24. NOz: total reactive nitrogen oxides excluding NO and NO2. The main constituents of NOz include: nitrous acids (nitric acid [HNO3] and nitrous acid [HONO]), organic nitrates (peroxyl acetyl nitrate [PAN], methyl peroxyl acetyl nitrate [MPAN], and peroxyl propionyl nitrate [PPN]), and particulate nitrates.
	25. OD: outer diameter
	26. PAMS: Photochemical Assessment Monitoring Stations
	27. ppb: part per billion – concentration unit of measurement equivalent to a mixing ratio of 10-9 L (or moles) of a trace gas in 1 L (or mole) of diluent. One ppb is equivalent to 2.46 × 1010 molecules cm-3 at 760 mm Hg pressure and 25°C.
	28. PE: performance evaluation – test of the measurement system performed by providing a known standard concentration of NO2 gas to the monitoring station analyzer and evaluating the bias of the measurements at each provided concentration. PEs are required annually.
	29. PFA: perfluoroalkoxy
	30. PTFE: polytetrafluoroethylene
	31. QAPP: quality assurance project plan
	32. SOP: standard operating procedure
	33. True NO2: “True” nitrogen dioxide – a method-based definition of NO2 that includes direct detection of NO2 by various spectroscopic approaches such as CAPS or photolytic conversion of NO2 to NO followed by chemiluminescence absorption.
	34. TSA: technical systems audit
	35. UV: ultraviolet (light)
	36. ZAG: zero air generator
	37. Zero Air: Air or synthetic air matrix (containing bulk gases N2, O2, CO2, and Ar) that is free of water vapor, particulate matter, volatile organic compounds (VOCs), and other impurities which would impact measurement of NO2.
2. **Interferences**
	* + 1. Temperature Effects

The true NO2 instrument must be operated in an environment controlled to a temperature between 5 to 40°C to comply with the EPA FEM designation specifications and to between 20 to 30°C to comply with the environmental conditions for NCore stations. Note also that the maximum deviation in hourly temperature over a 24-hour period cannot exceed ±5°C. The following temperature effects resulting in measurement interference are typically obviated by operating within this defined temperature range and reducing temperature fluctuation as practical:

* + 1. Because detection of NO2­ involves use of optics and mirrors, temperature should be maintained to mitigate the formation of moisture condensation on internal surfaces.
		2. Temperature fluctuations should be minimized to minimize the effect of NO2 adsorption coefficient changes.
		3. For photolytic instruments only: The stability of the chemiluminescence reaction between NO and O3 can be affected by changes in the temperature and pressure of the O3 and sample gases in the reaction cell. To reduce temperature effects, the reaction cell is maintained at a constant 50°C, just above the high end of the instrument’s operation temperature range.

2. Dirty Mirrors and Optics

Contamination of mirrors and optics on CAPS analyzers can occur because of pressure changes, inline particulate matter filter failure, or other events, causing loss of signal and a decrease in sensitivity. The internal oven temperature of the T500U increases the incoming gas temperature to approximately 45°C to minimize the formation of condensation on the mirrors.

3. High Particle Loadings

High particle loadings on inlet particulate matter filters can result in a pressure drop and reduced flow through the system and degradation of sampling pump performance due to the extra load on the pump. Replace inline filters at appropriate frequencies (annually or more often) to minimize flow restrictions.

4. Lamp Degradation

Lamp intensity declines over time with use, resulting in lower overall intensity and a corresponding loss of sensitivity. Replace lamps per the recommended instrument manufacturer frequency.

5. Dirty Reaction Chamber

A dirty reaction chamber on the T200UP will result in increased signal noise, calibration drift (zero and/or span), and/or decreased response (calibration slope).

6. Generation of Excess Ozone (specific to use of GPT for standards preparation)

Excessive ozone in the DDC and/or analyzer can result in formation of higher order nitrogen compounds which can consume NO2, resulting in negatively-biased instrument response as well as deposits of PAN, MPAN, and other similar species on the instrument flow path and measurement surfaces, resulting in corrosion of analyzer components.

7. When employing GPT, proper hygiene and purging of NO standard high pressure regulators must be practiced to minimize the introduction of ambient air into the cylinder. The reaction of O2 from ambient air with NO will result in the formation of NO2 in the gas cylinder and degrade the NO. Additionally, humidity and other oxidative substances in ambient air can result in irreversible contamination in the standard cylinder.

8. For the CAPS NO2 analyzers, there are few other substances that absorb light at 450 nm, and those that do are not expected to be present at sufficient concentrations to interfere with ambient air measurements of NO2.

9. Use of an accessory strip chart recorder or data acquisition system (DAS) requires proper configuration to ensure NO2 analyzer outputs are properly transmitted and recorded. While outside the scope of this SOP, operators must ensure that these components are properly configured to accurately record NO2 analyzer signals.

1. **Safety**

1. Refer to the instrument manuals for safety information specific to the NO2 instrument and DDC manufacturer and model and support equipment.

2. The zero air generation (ZAG) system consists of an air compressor and high pressure storage tank. Rupture of the storage tank or compressor connection lines can result in injury to persons in close proximity. The zero air generation system is heavy and requires caution when moving.

3. Standard gases and support gases are contained within high pressure cylinders. Staff working with high pressure cylinders must be trained on their proper handling and use. Steel-toed shoes and leather gloves are recommended personal protective equipment (PPE) when handling and moving high pressure cylinders.

4. Do not vent gases into enclosed areas such as within a monitoring shelter. Vent lines for excess gas flow and instrument exhausts should terminate outside the monitoring shelter. Note that exhausts should be routed sufficiently far from sampling inlet probes to prevent entrainment of exhaust gases into the sampling inlet.

5. Follow precautions for electrical safety, including use of properly grounded power connections. Turn off the analyzer power before disconnecting or connecting electrical subassemblies. Do not operate the analyzer with the cover removed. Disconnect the power source before working inside the analyzer housing.

6. Instrument operators should don standard eye protection when working with equipment and compressed gases.

1. **Apparatus and Materials**
2. Dynamic Dilution Calibrator (DDC)

A DDC is needed to provide standard NO2 gas to the true NO2 analyzer. DDCs typically consist of several mass flow controllers (MFCs) to meter standard gas containing either NO or NO2 and zero air diluent gas. Metered gases are mixed in a mixing chamber/space to ensure thorough mixing of the combined gas streams. If employing GPT of NO gas with ozone to produce NO2 standard gas, the DDC will also comprise a calibrated onboard ozone generator. If standard gas provided to the NO2 analyzer is sourced from a high pressure cylinder of NO2 standard gas, the DDC need not comprise an ozone generator.

* 1. Mass Flow Controllers

DDCs employ a combination of MFCs to control flows of compressed diluent and standard gas(es) to generate calibration standards for calibration and ongoing quality control (QC) checks of the NO2 analyzer. MFCs must have been calibrated at their range of use within the previous 12 months and the flow calibration verified quarterly (this frequency will be prescribed in the governing program QAPP). The DDC is employed to provide calibration standard gases at desired user-defined concentrations by either dilution of a standard NO2 gas or by GPT. Specific flow rate criteria for diluent and standard gas channels are dependent on the concentration of the standard gases desired, the stock standard gas concentrations, and dilution factors required to obtain the desired concentrations. DDCs typically include an MFC for the diluent channel capable of operating at 1 to 10 L/minute or 2 to 20 L/minute and one or more MFCs for delivering standard gases at ranges of 2 to 20 mL/minute, 5 to 50 mL/minute, and/or 10 to 100 mL/minute. The DDC must be equipped with an ozone generator for accurate and precise delivery of ozone as well as a reaction/mixing chamber for the GPT of ozone with excess NO to produce NO2. Several commercially-available DDCs incorporate such an ozone generator for this application, some of which include ozone photometers for measuring the ozone output and employ feedback loops to adjust ozone lamp output, resulting in improved ozone production accuracy. Such models with ozone photometers are typically marketed as “trace level” calibrators capable of stable ozone generation to approximately 3 ppb. Note that “regular range” calibrators typically cannot reliably generate ozone at concentrations below approximately 10 ppb. The instrument manual will provide information on the minimum level at which ozone can be reliably generated and quarterly calibration verification will verify the ozone generator performance. DDCs with onboard ozone generator capability include the following (list not exhaustive):

* Environics Series 6100, 6103, and 9100
* Teledyne API Models T700 and T700U
* Thermo ScientificTM Model 146i
* Ecotech Serinus Cal Models 2000 and 3000
* Envea Model MGC101
* Sabio Model 4010M
1. Flow Transfer Standard

To measure and verify flow rates of the DDC MFCs, a National Institute of Standards and Technology (NIST)-certifiably traceable flow transfer standard meter or combination of meters with calibrated flow rate range covering the flow range of the DDC flows with accuracy of ±1% is required.

1. High purity, high pressure gas cylinder regulators
	1. For NO2 or NO, regulator constructed of 316 stainless steel with 316 stainless steel diaphragm, CGA660 cylinder fitting, and polytetrafluoroethylene (PTFE) Teflon® seals (or equivalent)
	2. For zero air high pressure cylinders, regulator of stainless steel (preferred) or brass construction with 316 stainless steel diaphragm, CGA590 cylinder fitting, and PTFE Teflon® seals (or equivalent)
2. Zero Air Source

Zero air meeting the specifications in Section G.1 can be supplied from a compressed gas cylinder (typically synthetic air matrix composed of 78 to 82% nitrogen and 18 to 22% oxygen) or a ZAG (ambient air scrubbed of contaminants and water). The zero air source should be capable of providing zero air at a flow rate and pressure sufficient to supply the DDC such that it is able to achieve the desired dilution factor of calibration standards and to meet the flow demand of the associated analyzers.

* 1. Compressed gas cylinder(s): If zero air is sourced from compressed gas cylinders, it should be procured from a reputable supplier and will include a certificate of analysis (COA) indicating the composition and specifications for levels of impurities (NO, NO2, hydrocarbons, and water).
	2. ZAG: Gas generation component employing various scrubbers (e.g., graphitized carbon, Purafil SPTM, and/or catalytic oxidation) to remove particulates and impurities (e.g., hydrocarbons, oxides of nitrogen [NO, NO2, etc.], H2S, CO2, and water) from ambient air to provide a continual supply of clean, dry air. Appropriate ZAGs are commercially available from several providers and include the following (list not exhaustive):
* Environics Series 7000
* Teledyne API Models T701 and T701H
* Thermo ScientificTM Models 111 and 111iQ
* Ecotech Series 8301
* Envea Model ZAG7001
* Sabio Models 1001 and 2020
1. Data Acquisition System (DAS)

The NO2 analyzer will have an internal onboard DAS for storing multiple calibration routines and collected measurement data. The monitoring site should also employ a standalone DAS unit for acquiring, storing, and handling data. Modern DAS units connect to analyzers via Cat5 ethernet cables, USB cables, or RS232 serial cables.

1. True NO2 Analyzer

Suitable NO2 analyzers will have been designated as an FEM and include those listed in Section B.2.

1. Gas connection tubing: PTFE Teflon® tubing – ¼-inch outer diameter (OD)
2. Ferrules and other plumbing connection hardware to connect gas cylinder regulators and ZAG to the DDC, DDC output to the NO2 analyzer, and venting of these components. Refer to equipment manuals for specific connection, composition, and fitting torque requirements.
3. Uninterrupted power supply (UPS), optional.
4. **Reagents and Chemicals**
	* + 1. Zero Air

Zero air consists of a dry (< ~7 ppm H2O), clean air matrix of nitrogen and approximately 18 to 22% oxygen without significant impurities (e.g., PM or oxides of nitrogen), having < 1 part per million (ppm) of total hydrocarbons (HC). The zero air should not have contaminants that are detectable on the NO2 analyzer or that interfere (by reaction) with dilution of NO2 standard gases or the preparation of NO2 by GPT (i.e., contaminants that may react with NO, O3, and/or NO2). Zero air for use in true NO2 monitoring should contain ≤ 1.0 ppb NO2 when employed as a diluent gas for compressed NO2 standards, and ≤ 1.0 ppb of NO and/or ozone for use in GPT standard generation. Zero air must be provided at a sufficient flow rate to achieve the desired dilution of calibrated gas and to satisfy the DDC and NO2 analyzer flow demand.

* + - 1. Standard Gases – NO2, NO, and Ozone

Standard gases used to generate calibration standards and standard (span) gases for routine QC checks may be provided by several sources including compressed gas standard cylinders and/or dynamic dilution calibrator equipped with an ozone generator. Compressed gas standard cylinders should be procured from reputable suppliers, and the sourced standards will indicate acceptably low levels of contaminants or interferences. Gas standards should comply with the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards.6

* + - * 1. Nitrogen dioxide (NO2)

When opting to perform standard gas generation using dilution of NO2 standard gas, the operator must procure the cylinder from a reputable supplier and certified concentrations must be traceable to a reference material, such as those prepared by the NIST or the Van Swinden Laboratorium (VSL). Although the EPA has not designated gas vendor approval to prepare Protocol Gas Verification Program (PGVP) compliant high-pressure cylinders of NO2, several gas vendors providing NO PGVP-compliant gases offer a high-quality NO2 gas standard product. Such NO2 standard gases will be accompanied by a certificate of analysis (COA) indicating the levels of impurities, and will contain less than 1 ppm of residual NO. The NO2 standard will typically have been prepared in a specially-prepared cylinder, that is, the internal cylinder surfaces coated with an inert substance to reduce degradation of NO2.

The concentration of NO2 in the certified standard gas should be selected such that the desired diluted concentrations can be prepared by operating the DDC MFCs within the approximate middle of their flow range. In this way, the accuracy and stability of the concentration of the diluted gas is maximized. For example, if a span concentration of 80 ppb is desired and the DDC comprises a 2 to 20 L/minute diluent channel and a 10 to 100 mL/minute standard channel, a 200-fold dilution factor is achievable (10 L/minute diluent flow and 50 ml/minute standard flow). Thus, a 16,000 ppb (16 ppm) standard cylinder of NO2 would be appropriate.

* 1. Nitric Oxide (NO)

When opting to provide calibration gases to the NO2 analyzer by performing GPT of ozone and NO to generate NO2 calibration gas, the NO standard gas concentration will exceed the ozone concentration (ozone will be the limiting reagent and the process will assume 100% of the ozone reacted with the NO to generate NO2 with a slight excess of NO remaining). NO standard gas must be of Standard Reference Material (SRM) or Certified Reference Material (CRM) quality and compliant with Protocol 2 of the PGVP requirements listed above in Section G.2.

The concentration of NO should be greater than ozone, minimally by 20%. Similar to the discussion above in Section G.2.a, the concentration of NO in the standard gas should be selected to provide the desired diluted concentration at flow rates in the approximate mid-range of the diluent and standard MFC channels. The COA must indicate the concentration of residual NO2 in the NO standard cylinder which should not exceed 1% of the NO concentration.

* 1. Ozone (O3)

Ozone is supplied as the limiting reagent during reaction with NO to yield NO2 by GPT. Users of this SOP will not require ozone if they are not generating NO2 standard gases by GPT. Ozone will be generated at the time of use with the onboard ozone generator in the DDC employing the ozone lamp and zero air source. The ozone generator in the DDC will be calibrated annually (settings adjusted) and the calibration verified quarterly against a Level 1 or Level 2 ozone standard.7 Note that agencies employing the DDC to calibrate ozone analyzers will already be performing these calibrations and calibration verifications.

1. **Installation**

Per manufacturer instructions, unpack the instrument and inspect the analyzer to ascertain that is in good physical condition and that there are no missing components or loose fasteners. Ensure proper installation and electrical connections per the manufacturer instrument manual. Prior to use, the analyzer should be powered on and allowed to warm up for approximately 60 minutes before commencing monitoring and/or calibration.

1. **Sample Collection and Handling**
	* + 1. Probe Construction

All components comprising the inlet flow path from the inlet probe through to the back of the analyzer (BOA) must be constructed of borosilicate glass, fluorinated ethylene propylene (FEP) Teflon®, or equivalent (PTFE or PFA Teflon®). Note that other commonly available materials such as rubber, brass, aluminum, and copper are not suitable and must not be in the sampling flow path.

The sampling inlet line can consist of a standalone line that extends to the exterior of the monitoring shelter or can be connected to a laminar flow inlet manifold to which other instrument inlets are connected. Consideration must be given to the volume (length and internal diameter [ID]) of the sampling inlet pathway to ensure that the sample residence time to the BOA is kept to 20 seconds or less. Note that sample ingestion rates of laminar flow manifolds assume that air within the manifold is equivalent to the ambient outside atmosphere, therefore the residence time calculation should begin from the NO2 analyzer port on the manifold. Consideration should also be given to minimize intrusion of water into the sampling line which can effectively be reduced by inverting the inlet and installing a rain shield (such as inverted funnel) on the inlet probe. For connections to an inlet manifold, the analyzer can be connected to any port.

Though many of the FEM NO2 analyzers incorporate an integrated particulate matter (PM) filter on the sample inlet, installation of a PTFE particulate filter in the analyzer inlet line is strongly recommended for reducing PM to the analyzer, and the monitoring agency should prescribe a frequency for inspecting and changing the filter(s) to avoid filter clogging and reduced sample flows. Additionally, the monitoring agency will prescribe frequencies for visually inspecting and cleaning or replacing inlet line tubing to the NO2 analyzer. Particulate residue buildup in inlet pathways can scrub NO2 from the sampled air and result in a negative bias for associated measurements. Inlet manifolds are particularly susceptible to PM buildup due to the high flow rate and large volume of air ingested; therefore, the monitoring agency will prescribe an inspection (visual) and cleaning schedule for employed inlet manifolds.

* + - 1. Inlet Probe Siting

Siting of the inlet probe will comply with the requirements in 40 Code of Federal Regulations (CFR) Part 58 Appendix E. These requirements are summarized below.

The inlet probe will be 2 to 15 m above ground level (AGL) and at least 1 m horizontally and vertically from any supporting structures. The inlet must also be more than 10 m (preferably 20 m) from the dripline of the nearest tree to avoid impacts from adsorption and surface reactions. The inlet probe will be minimally 10 meters from the nearest roadway traffic lane – greater distances are required for roadways with average daily traffic (ADT) counts greater than 15,000 as defined by the monitoring site measurement scale and the ADT of the surrounding roadways. Lastly, inlet probes will be positioned such that any object that could obstruct the flow of air to the probe is minimally twice as far horizontally from the inlet probe as the obstruction extends vertically above the inlet probe.

* + - 1. Sampling and Measurement Frequency

The true NO2 analyzer will run continuously measuring ambient air except when performing routine quality checks. Instruments should be configured to report one-minute data and the hourly average for each sampling hour is to be reported to EPA AQS. A valid sampling hour will minimally include 45 valid minutes of data and a valid sampling day will include minimally 18 valid hourly averages.3

1. **Quality Assurance**

Independent assessments, whether by quality assurance (QA) staff internal to the monitoring organization or external from the EPA or associated contractor, will be performed according to the frequency prescribed in the governing monitoring agency QAPP. A detailed description of these QA assessments is outside the scope of this SOP. Typical QA assessments include the following:

* + - 1. Annual Performance Evaluation (PE): The monitoring agency is required to annually conduct the PE per 40 CFR Part 58 Section 3.1.2.
			2. National Performance Audit Program (NPAP) Evaluations: Each monitoring site must be subjected to an external performance audit every 6 years per 40 CFR Part 58 Section 3.1.3.
			3. Audit of Data Quality (ADQ): The monitoring agency is encouraged to have a member of the QA office perform an ADQ annually whereby the QA staff member reviews/verifies all portions of the measurement system, starting with calibrations of the DDC and NO2 analyzer and flowing through calculations and data transformations to final reported measurements.
			4. Technical Systems Audit (TSA): The monitoring agency is encouraged to have a member of the QA office perform a TSA annually whereby the QA staff member observes the instrument operator performing calibration, MPV, and/or routine QC checks to ensure the operator follows the prescribed procedures according to this SOP.
1. **Stability of Measurements**

NO2 measurements for QC purposes (calibration, MPV, span, precision, MDL, and zero) employing true NO2 analyzers will require the instrument readings to be stable – that an introduced test gas of known concentration shows a consistent measurement reading. Such measurement stability will be defined in the monitoring agency governing QAPP or within an appropriate SOP.

In lieu of a specific stability definition, general guidance is that the instrument reading is considered to be stable if there is no general increasing or decreasing trend and the measurements indicate that the 10 most recent one-minute averages are within 1 ppb of the average of the five most recent 1-minute data points. Once stable, the operator may record the next one-minute datapoint or may begin the averaging period (e.g., the average over the next 10 minutes), as defined in the monitoring agency governing QAPP.

1. **Method Detection Limit**

Limitations for determining the MDL for true NO2 analyzers depend on the ability of monitoring agencies to provide low concentration (e.g., ~ 1 ppb or less) NO2 gas to the analyzer in order to gauge the measurement precision for low concentration standards approaching, but above, the detection limit. Due to these limitations, experimental determination of the MDL is recommended for agencies with suitable capability, but is not required. Analyzer manufacturers typically report a minimum detection level or similar metric in their instrument literature; however, these concentration values are typically not representative of the real-world instrument operation and often underestimate concentrations that can be reliably measured in ambient air. Providing suitably low concentration standards when employing GPT is not practical, as the ozone generator in most DDCs is unable to reliably or accurately produce an NO2 concentration below approximately 5 or 10 ppb (note that some DDCs with onboard ozone photometers and ozone measurement feedback loops may be able to reliably generate ozone, and therefore NO2, down to approximately 3 ppb). Such concentrations are not sufficiently low to properly gauge the variability of the NO2 analyzer measurements near the MDL and generate meaningful MDL data. Low concentration standards in the appropriate concentration range are more reliably generated by dilution of gaseous NO2 standards, as they are not subject to the limitations of onboard ozone generators. Monitoring agencies would ideally experimentally determine the NO2 analyzer MDL for each deployed NO2 analyzer; however, agencies employing GPT for standards preparation may not be able to successfully conduct an MDL determination study. Furthermore, monitoring agencies employing dilution of compressed NO2 gas standards may not possess a DDC with the proper dilution factor range to generate NO2 gas with concentrations in the sub-1 ppb range. It is for these reasons that EPA has not required monitoring agencies to determine the MDL for the NO2 analyzers as of the publication of this SOP; therefore, the reader is referred elsewhere 1 for the MDL procedure.

Monitoring agencies that are able to produce acceptably low concentration standards should determine the MDL for their true NO2 analyzers annually, preferably prior to PAMS season. The MDL should be re-determined when changes to the instrument would reasonably expect to affect the sensitivity (such may include replacing a detector lamp, detector, and/or flow cell mirrors, for example). Typically, such changes would require recalibration of the analyzer.

A brief summary of the MDL process follows:

The MDL for true NO2 analyzers is determined according to the Method Update Rule (MUR) as described in Section 3.3.5.1 of the PAMS Technical Assistance Document1, where users (1) measure zero air to estimate the MDL attributable to background (whether chemical, instrument electronic noise, or instrument drift) in the absence of NO2 and (2) measure a low concentration NO2 standard to characterize instrument variability in the presence of a low concentration of NO2. Neither the zero drift nor span are adjusted during the MDL procedure.

The monitoring agency will generate low concentration NO2 standards in the 0.3 to 1.0 ppb range and make discrete measurements covering a stable period of instrument operation, over minimally 5 to 20 minutes of measurement (typically the standard is provided for 5 to 10 minutes to allow the analyzer reading to stabilize, then measurements are made for approximately 10 minutes). A minimum of seven such measurements is required and should be performed over the course of 3 preferably non-consecutive days. Likewise, for the zeroes/blanks, zero gas is introduced to the NO2 analyzer and once stable readings are attained, the measurements are recorded for approximately 10 minutes. The average concentration over the measurement period is assigned as the measurement for that “sample.”

These averaged measured concentrations for the zeroes and low level standards are input into the defined calculations in the PAMS TAD to establish the lowest concentration that is distinguishable from background with 99% confidence.

1. **Calibration and Calibration Verification**

The NO2 analyzer must be calibrated (the instrument response adjusted for zero and span):

* Initially when placed into service
* Minimally every 365 days
* Following failure of span check, i.e. where the percent difference in the observed concentration is > ±10% from theoretical
* Following zero drift > ± 0.5 ppb
* Following operations interruptions ≥ several days (e.g., 48 hours)
* Following maintenance of the instrument that would be expected to change the instrument response.

*Note: Instrument operators should carefully consider timing of calibration and QC check routines so they are not performed during peak NO2 measurement hours, e.g., during morning or evening commuting periods when NO2 concentrations are expected to be elevated.*

* + - 1. Pre-calibration Activities

Prior to performing calibration of the NO2 analyzer, it should be powered on and operating for a minimum of several hours and preferably overnight. Operators should also verify that the NO2 analyzer does not show alarms or error messages that would impact the calibration process. If the NO2 analyzer has more than one measurement range (e.g., single [0 to 500 ppb] versus dual [0 to 1000 ppb] range as is the case for the T500U) the operator must specify the instrument settings for the measurement range and this setting be maintained throughout calibration and routine operation.

When performing calibration routines and multipoint verification (MPV) routines on the NO2 analyzer, the instrument should be taken “offline” on the DAS or the associated measurement data marked as null to ensure the instrument output is not inadvertently reported to AQS as ambient measurement data.

Prior to performing a calibration on the NO2 analyzer when the instrument is in routine operation, the instrument should be subjected to an instrument performance audit (equivalent to the PE described above in Section J where zero and upscale NO2 concentration points are introduced to the analyzer) to verify NO2 analyzer performance. Such an independent check should be performed prior to making adjustment to the NO2 analyzer and is useful in downstream data handling and validation procedures as it brackets measurement data to demonstrate that the NO2 analyzer calibration and background were within control prior to the adjustment.

* + - 1. DDC Setup and Operation

Configuration, calibration, and operation of the DDC will comply with the monitoring agency SOP for DDC operation. MFCs in the DDC will have been flow calibrated within the previous year and flow calibrations will have been verified within the previous three months (calendar quarter) against a NIST-traceable flow transfer standard. Flow rates in the DDC must be shown to be within ±2% of the flow transfer standard. MFCs in the DDC should be operated within 10 to 90% of the full-scale flow range to ensure stable and consistent gas metering. Instrument operators should ensure that at all times the NO2 analyzer flow demand is exceeded and the excess flow vented to atmosphere to ensure the NO2 analyzer experiences the test gases at ambient pressure and do not experience an over pressure or vacuum condition (refer to instrument manual for vent requirements).

The DDC should be connected to the NO2 analyzer through the same inlet as the ambient (sample) air and should also be routed through the particulate filter(s) to account for any scrubbing or bias imparted by the filter. Ideally, the DDC output would be plumbed into the inlet probe to calibrate and verify calibration of the NO2 analyzer by introducing gas through the entire sampling flow path (this is also referred to as sample introduction through the probe [TTP]).

The following are general instructions for instrument operator consideration.

1. Regulator Connection and Purging

Regulators installed on the NO or NO2 standard cylinder must be purged prior to connection to the DDC inlet to remove ambient air entrained in the regulator and inlet lines. Proper purging and cylinder hygiene are critical in preventing backflow of ambient air and other contaminants into the standard cylinder. The following steps will ensure proper regulator purging (refer to Figure 1):



**Figure 1. Cylinder and Regulator Components**

1. Connect a vent line to the regulator outlet connection to ensure the vented gas is exhausted outside the monitoring shelter.
2. Ensure the regulator outlet valve and cylinder valve are closed.
3. Attach the regulator to the cylinder valve and hand tighten the regulator inlet fitting.
4. Securely tighten the regulator inlet fitting connection with a wrench.
5. Turn the pressure adjusting knob (typically counterclockwise) to minimize output pressure until the knob turns freely.
6. Fully open the regulator outlet valve.
7. Slowly open the cylinder valve (gas will rush from the regulator) and quickly close the cylinder valve.
8. Close the regulator outlet valve.
9. Wait 1 minute to allow cylinder gas to passivate the interior wetted surfaces of the regulator.
10. Repeat Steps 6 through 9 two more times.
11. Gas Connections to DDC

Consult the DDC operation manual for the correct inlet pressure range for the standard and diluent gases (DDCs typically require inlet gas pressures of approximately 25 to 35 pounds per square inch [psi]).

1. Standard gas cylinder: After the regulator and transfer lines have been purged, connect the standard gas line (either NO or NO2) to the appropriate standard gas inlet on the DDC. Connection of the standard gas to the DDC should be with appropriately pressure-rated PTFE, PFA, or FEP Teflon® tubing of appropriate OD. Use of other materials such as copper, rubber, brass, etc. is not acceptable.
2. Zero air supply: Connect the zero air supply to the diluent gas inlet on the DDC using appropriately pressure-rated tubing. Tubing can consist of chromatographic grade stainless steel or PTFE, PFA, or FEP Teflon®.
	* + 1. Generation of NO2 Standard Gas

Calibration of the NO2 analyzer involves standardizing the response of the analyzer by introduction of a known concentration of NO2 and a zero air point. As discussed previously in Section B, standard gases can be generated either by dilution of an NO2 standard gas supplied in a high-pressure cylinder or by generation of standards by GPT of ozone with NO.

While both methods to generate NO2 calibration standards are acceptable, dilution of NO2 from a cylinder requires specific equipment configurations and procedures to ensure quantitative transfer of NO2 to the NO2 analyzer, generally requiring longer passivation and equilibration times. GPT, by contrast, is more complicated from a procedural standpoint, requiring gas metering, gas generation (production of ozone), and gas mixing; however, it does not typically exhibit extended passivation times observed when diluting NO2 gases from high pressure cylinders.

A detailed overview of each option is described below.

* 1. Dilution of an NO2 Standard Gas Cylinder

Passivation time for diluting NO2 standard gas from a high-pressure cylinder tends to be longer than when generating standards by GPT. Minimizing passivation time can be achieved by ensuring the connecting tubing from the standard cylinder to the DDC is as short as possible and of small internal diameter (1/4-inch OD PTFE tubing is commonly available with IDs from 3/16 inch down to 1/8 inch).

NO2 is a “sticky” gas that adsorbs to the interior walls of the gas delivery flow path, and this may result in a slow instrument response for each generated calibration, span, or MPV concentration point. The analyzer-measured concentration will typically initially be approximately 10 to 15% lower than for the same concentration generated by GPT of NO with ozone until given sufficient time to passivate the transfer tubing.

* 1. Gas Phase Titration of NO with Ozone:

Generation of NO2 concentrations by GPT is accomplished by providing a desired standard concentration of ozone and mixing excess NO.

*Note: GPT performed by providing excess ozone and employing NO as the limiting reagent is not recommended. EPA collaborated with several monitoring agencies in 2019 to investigate the feasibility of employing NO as the limiting reagent and providing excess ozone; however, this convention proved to be inconsistent at best and demonstrated poor correlation to the conventional method of GPT with ozone as the limiting reagent with excess NO. This poor correlation is presumed to be due to the further reaction/consumption of NO2 with excess ozone in or downstream of the reaction chamber to form higher order nitrogen oxides.*

Efficiency of the reaction between NO and O3 is such that one mole of NO2 is produced for every mole of the limiting reagent (O3) consumed per the following reaction:

 NO + O3 → NO2 + O2

When employing GPT, users should program the DDC to provide excess NO such that a minimum of 20% (and no more than 80 ppb) NO remains after the GPT. For example, when a 160 ppb NO2 standard is desired, the DDC should be programmed to provide 160 ppb of ozone and 190 to 200 ppb of NO. If a conventional (molybdenum conversion chemiluminescent) calibrated NOx analyzer with an NO measurement channel is available, it is prudent to verify the concentrations of NO and NO2 in the produced standard gas by measurement with the NOx analyzer. Measurement with a calibrated NOx analyzer will demonstrate that the amount of NOx measured should equal the amount of NO2 produced plus the amount of excess remaining NO after GPT. The amount of NO2 produced via GPT can be verified by subtraction of the NO channel measurement which should be equal to the expected excess remaining NO after GPT.

* + - 1. Establishing Calibration – Setting the Zero and Span

Calibration of the NO2 analyzer involves standardizing the NO2 analyzer response with a two-point response curve where the two points include a zero and a standard concentration of NO2 gas in the span range, at approximately 80% of the intended measurement scale range. For example, for NO2 analyzers intended to operate in the 0 to 200 ppb range, the calibration span point concentration should be 160 ppb. Once the calibration response has been set in the instrument, the operator will verify the calibration by performing the multi-point verification (MPV) as described below in Section M.5.

* + - * 1. Power on the DDC and allow 30 to 60 minutes for warmup.
				2. Provide zero air to the NO2 analyzer from the DDC and wait for the NO2 analyzer reading to stabilize.
				3. Once the reading is stable, reset the zero reading to show 0.000 ppb and wait several minutes to ensure the reading remains stable.
				4. Begin to generate the span concentration (e.g., 160 ppb) of NO2 with the DDC and allow the NO2 analyzer reading to stabilize (note this may take several minutes if employing dilution of an NO2 compressed gas standard).

Set flows on the diluent gas MFC and the standard gas MFC as appropriate, operating MFCs within their calibrated flow range and within the 10 to 90% full scale flow range.

* + - * 1. Once the NO2 analyzer reading is stable, input the theoretical concentration into the analyzer to set the span concentration and assign the analyzer response.
				2. The NO2 analyzer response is now set and the operator can begin the MPV to verify the calibration.
			1. Verifying Calibration - Multi-Point Verification (MPV)

The MPV follows the initial calibration to verify the NO2 analyzer response over the measurement range by analyzing gases absent of NO2 (zero) and with NO2 at four concentrations covering the desired measurement range. The NO2 concentrations chosen are to cover approximately 10 to 90% of the measurement range. A recommended suite of NO2 concentration levels for an NO2 analyzer measurement range of 0 to 200 ppb would include the following MPV sequence:

* 0 ppb – zero air
* 175 ppb (80 to 90% full scale)
* 125 ppb (60 to 70% full scale)
* 75 ppb (20 to 30% full scale), and
* 25 ppb (10 to 15% full scale)

The measured concentrations for the zero and each subsequent NO2 concentration level are then plotted against the theoretical concentration and the data points modeled by linear regression. Linear regression can be performed with commonly available spreadsheet programs (e.g., Microsoft® Excel) or other statistical software programs.

Conduct the MPV as follows:

1. Provide zero air to the NO2 analyzer from the DDC and allow the NO2 analyzer reading to stabilize. Record this value for input into the regression.
2. Starting with the highest (80 to 90% full measurement scale) concentration, program the DDC to provide the standard gas to the NO2 analyzer and allow the instrument reading to stabilize.

*Note: Stabilization may take several minutes for the internal flow path from the DDC to the NO2 analyzer to equilibrate and for the NO2 analyzer response to stabilize.*

1. Record the stable corresponding NO2 analyzer reading and the theoretical standard concentration for entry into the linear regression.
2. Follow Steps b and c above for the additional three NO2 standard concentrations.
3. Provide zero air to the NO2 analyzer and verify the instrument response returns to zero.
4. Plot the instrument readings for the zero and standards on the y-axis against the theoretical NO2 standard concentrations on the x-axis and perform a 2-parameter (intercept and slope) linear least-squares regression on the data points.
5. The results of the linear regression must show:

The correlation coefficient (r2) is ≥ 0.995

The percent difference for the instrument readings at each concentration level is within ±10% of the theoretical concentration

The x-intercept (which equals the y-intercept divided by the slope) of the linear regression is ≤ ±0.2 ppb

1. If any of these criteria are not met, the analyzer calibration must be re-established (follow the process in Section M.4).
2. **Quality Control Measurements**

40 CFR Part 58, Appendix A Section 3.1.1 prescribes that a one-point QC check be conducted every 14 days and strongly encourages more frequent checking. Details for the number of, frequency for, and acceptance criteria for true NO2 analyzer QC measurements are prescribed in the governing monitoring agency QAPP. These QC parameters are described below and are summarized with associated acceptance criteria in Table 2.

* + - 1. QC Measurement Timing

Performance of these QC checks should occur during overnight hours, typically between 2:00 and 4:00 a.m. local standard time (02:00 and 04:00 hours) to avoid missing ambient air sampling hours of particular interest to the PAMS program.

* + - 1. Routine QC Checks

Routine QC checks for true NO2 analysis include: zero, span, and precision. These checks are performed sequentially (back-to-back) where the zero check is performed first followed by upscale calibration check points (span and precision). The NO2 analyzer is operated in the normal sampling mode for all QC checks, allowing the zero air or standard gas to pass through all filters, scrubbers, and other components employed during routine monitoring. QC checks must be performed on the NO2 analyzer in as-is condition; the operator must not adjust the NO2 analyzer zero or span settings prior to conducting QC checks.

Instrument operators will determine the time it takes for the NO2 analyzer reading to stabilize and this period will be programmed into automated QC check routines prior to measuring and subsequently measure the QC check for a minimum of 10 minutes. The average of this measurement period will be reported as the measured concentration of the given QC check.

A zero/span check must be performed minimally every 14 days. A zero/span/precision check is optional, but monitoring agencies are encouraged to perform these checks frequently (i.e., nightly or every other night) to reduce ambient data invalidation due to unacceptable zero and/or calibration drift.

* + - * 1. Zero Check

Zero checks assess the zero drift (instrument response in the absence of NO2) of the NO2 analyzer by analyzing zero air. A zero check is to be conducted before any calibration or adjustment is made to the analyzer. The instrument reading for the zero check should be ≤ ±0.3 ppb and must not exceed ±3 ppb over ≤ 24 hours or ±5 ppb over > 24 hours up to 14 days.

* 1. Span Check

Span checks assess the NO2 analyzer calibration at approximately 80 to 90% of the measurement scale of the analyzer. Span checks should immediately follow a zero check. The selected span check concentration should be above 99% of the routine ambient measurement data over the previous three-year period. The measured concentration of the span check percent difference must be within ±10% of the theoretical concentration or recalibration of the NO2 analyzer is required.

* 1. Precision Check

Precision checks assess the NO2 analyzer calibration at approximately the lower third of the measurement scale of the analyzer. Precision checks should immediately follow a span check. The measured concentration of the precision check percent difference must be within ±10% of the theoretical concentration or recalibration of the NO2 analyzer is required.

1. **Data Reporting and Calculations**
	* + 1. Data Reporting

Measured NO2 concentrations (AQS parameter code 42602) are to be reported in units of ppb (AQS unit code 8) or ppm (AQS unit code 7) as hourly averages (AQS duration code 1).

* + - 1. Calculations
				1. Standard dilution concentration using dynamic dilution:

$$C\_{d}= \frac{\left(F\_{s}∙C\_{s}\right)}{\left(F\_{s}+F\_{d}\right)}$$

where:

 Cd = diluted standard concentration (ppb)

 Cs = stock standard concentration (ppb)

 Fs = flow of stock standard gas (standard mL/minute)

 Fd = flow of diluent gas (standard mL/minute)

* 1. Percent difference (PD) is calculated as:

PD = (concentration measured – theoretical concentration) x 100

 theoretical concentration

1. **Troubleshooting**

For troubleshooting the NO2 analyzer, DDC, and/or ZAG, the operator should consult the manufacturer instrument manual for specific issues. General troubleshooting instructions are detailed below.

* + - 1. Displayed error, fault, or warning messages should prompt the operator to take corrective action to address the indicated condition. Refer to the relevant instrument manual for diagnosing and correcting error conditions. Note that warning messages are not uncommon during instrument warm-up periods.
			2. For failure to initiate automated QC checks or other remote-controlled functions, ensure proper communications status with DDC and/or DAS and verify cables are firmly connected. Power outages may reset custom configured settings to factory defaults.
			3. Lower than expected span recoveries or elevated zero drift values may be the result of a leak in the system, which can occur at many places in the system. To evaluate whether a leak is present, follow the leak checking procedures in the relevant instrument or support equipment manual (*note: these require support equipment not described in this SOP*). Some common locations for leaks to occur include:
				1. From the gas cylinder or zero air source to the DDC
				2. Within the DDC
				3. From the DDC to the NO2 analyzer
				4. Within the NO2 analyzer

Pump connections and gaskets

Failing pump and/or pump seals

Compromised internal tubing

**Table 2: Quality Control Parameter and Acceptance Criteria**

| **QC Parameter** | **Description** | **Required Frequency** | **Acceptance Criteria** | **Suggested Corrective Action** |
| --- | --- | --- | --- | --- |
| Calibration  | Setting zero and span levels on the true NO2 analyzer by introducing zero air and an NO2 standard at 80% of the desired measurement range covering the expected range of ambient measurements (e.g., 160 ppb NO2 for a measurement range of 0 to 200 ppb NO2) | Initially when deployed, minimally every 365 days, following maintenance to the instrument expected to alter the instrument response, following operation interruption of several days (e.g., 48 hours), and following failing span check or zero check | None. Verified by MPV. | Repeat calibration if indicated by MPV. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement (check filters, perform leak checks, clean mirrors, etc.) |
| Multipoint Verification (MPV) | Introduction of a zero and four upscale NO2 concentration points covering the measurement range. (e.g., 0, 175, 125, 75, and 25 ppb) | Immediately following establishing a new calibration. | Linear regression of the measurements plotted against the theoretical must show r2 of ≥ 0.995 and have an x-intercept within ± 0.2 ppb NO2 of the origin. Percent difference of each standard measurement must be within ±10% of the theoretical concentration. | Repeat verification. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement of analytes. Recalibration may be necessary. |
| Zero/Span Check | Analysis of zero air and span NO2 standard (~80% of measurement range) to monitor for drift in zero and span levels. Checks are performed on analyzer in as-is condition before modifying instrument settings. | Required every 14 days. More frequent checks are recommended. | Zero drift must be less than ± 0.3 ppb. Span level must be within ±10% of the theoretical concentration. | Repeat zero and span checks to confirm. Investigate system for contamination, leaks, or other causes of drift. Qualify or invalidate data since the last passing QC check. Perform calibration and MPV.  |

**Table 2 (continued): Quality Control Parameter and Acceptance Criteria**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **QC Parameter** | **Description** | **Required Frequency** | **Acceptance Criteria** | **Suggested Corrective Action** |
| Zero/Span/Precision Check | Verification performed by analyzing a zero and two standard NO2 concentration levels – span point at approximately 80% of the measurement range and a precision point in the lower 1/3 of the measurement range (e.g., 160 and 50 ppb, respectively for a measurement range of 0 to 200 ppb) | Optional – Recommended minimally every 14 days or more frequently. | Zero drift must be less than ± 0.3 ppb. Span and precision levels must be within ±10% of their theoretical concentration. | Repeat Zero/Span/Precision Verification to confirm. Investigate system for contamination, leaks, or other causes of drift. Qualify or invalidate data since the last passing QC check. Perform calibration and MPV. |

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