Standard Operation Procedures for NO-NO_2-NO_X

In Use By

Polk County Air Quality
Ambient Air Monitoring Personnel

For Calendar Year 2018

Revised: January 26, 2018

Section: 2
Revision: 17

PREPARED BY

Jessica Moeller — 3-7-18

Polk County Air Quality Air Pollution Monitoring Specialist — *Date*

SIGNATURES/APPROVALS

Brent Blanchard — 3/7/2018

Polk County Air Quality Assurance Officer — *Date*

POLK COUNTY AIR QUALITY DIVISION
STANDARD OPERATING PROCEDURE MANUAL FOR THERMO SCIENTIFIC $NO-NO_2-NO_x$ MONITORING

Table of Contents

2 .0 STANDARD OPERATING PROCEDURE FOR $NO\text{-}NO_2\text{-}NO_X$

2.1 Purpose

To establish a standard operating procedure (SOP) manual for the Polk County Air Quality Division personnel concerning the setup, operation, bi-weekly zero/precision/span checks, calibrations, audits and maintenance of $NO\text{-}NO_2\text{-}NO_X$ monitors maintained and operated by Polk County staff. This SOP is intended for individuals responsible for collecting ambient air monitoring data supported by the Polk County Air Quality Division.

2.2 Scope

These procedures are to be used by Polk County Air Quality Division personnel. The objective of this SOP is to familiarize the station operator with procedures used in the collection of air monitoring data. The accuracy of the data obtained from any instrument depends upon the instrument's performance and the operator's skill. It is important that the station operator become familiar with both this SOP as well as the manufacturer's instruction manual in order to achieve a high level of data quality. This SOP is to be used as an outline and is not intended to replace the equipment manufacturer's manual or procedures. This SOP describes the proper procedures for the setup, operation, bi-weekly zero/precision/span checks, calibrations, audits and maintenance of Thermo Fisher Scientific's Trace Level 42*i* analyzers equipment operated by Polk County Air Quality personnel.

2.3 References

2.3.1 Thermo Scientific, Model 42*i* Trace Level, Chemiluminescence $NO\text{-}NO_2\text{-}NO_x$ Analyzer, Instruction Manual. Part Number 102855-00, December 20, 2007.

2.3.2 Thermo Electron Corporation, Model 146*i*, Dynamic Gas Calibrator, Instruction Manual. Part Number 102482-00, January 22, 2006.

2.3.3 EPA Quality Assurance Guidance Document 2.3, Reference Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescence), February, 2002, Draft.

2.3.4 EPA-600/4-75-003 December 1975, Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide.

2.3.5 EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards EPA-600/R-12/531, May 2012.

2.3.6 EPA-454/B-17-001, January, 2017. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program.

2.3.7 Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program, Appendix D. Revision 1, March, 2017.

2.3.8 40 Code of Federal Regulations (CFR) Part 50, Appendix F, Measurement Principle and Calibration Procedure for the Measurement of NOx in the Atmosphere.

2.3.9 40 Code of Federal Regulations (CFR) Part 58, Appendix A, Quality Assurance Requirements for State and Local Air Monitoring Stations (Slams).

2.3.10 40 Code of Federal Regulations (CFR) Part 58, Appendix D, Network Design for State and Local Air Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), and Photochemical Assessement Monitoring Stations (PAMS).

2.3.11 40 Code of Federal Regulations (CFR) Part 58, Appendix E, Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring.

2.4 Introduction

The U.S. Environmental Protection Agency (EPA) has determined nitrogen dioxide (NO_2) is a health and environmental concern. For this reason, National Ambient Air Quality Standards (NAAQS) have been

established for NO_2. As a result, an air monitoring network to monitor for NO_2 was established in the Des Moines Metropolitan Statistical Area (MSA) and is maintained by Polk County Air Quality Division, Iowa.

Measurements of nitrogen dioxide (NO_2) in ambient air are based on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO_2 molecules decay to lower energy states:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

Ambient air is drawn into the NO-NO_2-NO_x sample inlet. The sample flows into a solenoid valve which splits the flow between the NO and NO_x mode. NO_x mode converts NO_2 to NO (measuring total NO_x) while the NO mode makes no changes to the air stream and measures NO only. Samples from both modes flow to a reaction chamber where they are alternately introduced to react with dry air passed through an ozonator to provide a source of O_3. The O_3 reacts with the NO present in each sample producing electronically excited NO_2 molecules. A photomultiplier tube housed in a thermoelectric cooler detects the NO_2 luminescence and converts it to an electrical signal, which is then sent to the analyzer's front panel display and analog outputs. The concentration of NO and NO_x are both measured with NO_2 concentration calculated by difference. (NO_x – NO = NO_2).

The dynamic parameter requirement ensures that the NO-O_3 reaction has been completed. The dynamic parameter conditions are met for any reasonable NO flow (12.5–100 sccm) and [NO]STD (40-60 ppm). If the NO concentration of the stock gas cylinder, or flow through the NO MFC in the calibrator falls outside of these ranges, a calculation will be done to ensure that the residence time is $\leq$ 2 minutes and the dynamic parameter is $\geq$ 2.75 ppm-min, in accordance with formulas given to the analyzer operator's manual. Section 8-4, Thermo Scientific 146*i* Instruction Manual.

2.5 Health and Safety Warning/Precautions

Only properly trained personnel should perform TL-42*i* testing, installation, operation, maintenance and calibration procedures. As with all monitoring equipment, precautions should be taken when working around electricity, power tools and above ground elevations.

Cylinder gases are used in tandem with Mass Flow Control (MFC) calibrators for the TL-42*i*. Gas cylinders can sometimes contain pressures as high as 2000 pounds per square inch (psi). Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and valve breaks off, the cylinder can become explosive or a projectile.

Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders. It is possible to blend other compounds with CO cylinder gas. In this case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders or permeation tubes.

2.6 Sampler Setup

2.6.1 Site Selection

In selecting a location to measure for NO_2, it is important to understand that the reactive oxides of nitrogen in the atmosphere are primarily nitric oxide (NO) and nitrogen dioxide (NO_2), known together

as NO_x. During the daytime, there is a rapid interconversion of NO and NO_2. NO emitted into the air is converted to NO_2 by photochemical reactions promoted by sunlight eventually creating ozone downwind of the sources. The main sources of NO_x are motor vehicles, power plants, industry, and outdoor burning. It is recommended that the station be located downwind of the expected point of maximum NO_x to allow more time for the formation of NO_2.

For more detailed information concerning site selection for NO-NO_2-NO_x monitoring, refer to the 40 Code of Federal Regulations (CFR), Part 58, Appendix D, or the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Section 6.2, entitled "Monitoring Site Location."

2.6.1.1 The Monitoring Station

The structure housing the monitoring equipment may consist of a trailer, a room in a building, or a shelter designed specifically for air monitoring purposes. A clean, dry, secure and temperature controlled space is required so that the sampling equipment can operate properly.

Careful thought and planning is required in locating a monitoring station. The individual responsible for the installation must consider:

- Proximity to the nearest power source. A 120 VAC source is required for the operation of the NO-NO_2-NO_x monitoring equipment.
- The space where the equipment is housed must maintain a temperature range of 20-30 degrees Celsius. This usually requires the need for an air conditioner and a heater controlled by a thermostat.
- The accessibility of the equipment to the operator. The operator must be able to safely access the equipment during regular business hours.
- The security of the equipment. Monitoring instruments are expensive. They must be placed in a location where security can be assured.
- Contracts for rental of space or power. Contracts need to be signed with the owner of the property where the instruments are located.
- Local building codes. In most cases, the contractor installing the power, structure, concrete, etc. know the local building codes.
- Dirty, dusty areas must be avoided.

2.6.1.2 Probe Placement

Once the location of the station has been identified, the individual responsible for the installation must be familiar with the criteria for locating the probe. The location of the sample probe is critical and individuals performing the installation must follow these specific guidelines:

- The inlet probe must be located between 3-15 meters about ground level.
- The inlet probe must be at least 1 meter vertically or horizontally away from any supporting structures.
- To avoid interference from obstructions, air flow must be unrestricted in an arc of at least 270 ° around the inlet probe, or 180° if the probe is on the side of a building.
- Trees can provide surfaces for NO_2 adsorption or reactions and obstruct wind flow. To reduce this possible interference, the inlet probe must be at least 10 meters from the drip line of the trees.
- When siting NO_2 analyzers for neighborhood and urban scale monitoring, it is important to minimize interferences from automotive sources. Minimum

separation distance between roadways and probes depends on the roadway's average daily traffic.

For more detailed information concerning site selection for $NO\text{-}NO_2\text{-}NO_x$ monitoring, refer to the 40 Code of Federal Regulations (CFR), Part 58, Appendix E, or the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II.

2.6.2 Inspecting New Equipment

When shipment of the monitor is received, verify that the package contents are complete as ordered. Inspect the instrument for external physical damage due to shipping, such as scratched or dented panel surfaces and broken knobs or connectors.

Remove the instrument cover and all interior foam packing and save (in case future shipments of the instrumentation are needed). Make note of how the foam packing was installed.

Inspect the interior of the instrument for damage, such as broken components or loose circuit boards. Make sure that all of the circuit boards are completely secured. Loose boards could short out the motherboard. If no damage is evident, the monitor is ready for calibration, installation and operation. If any damage due to shipping is observed contact Thermo Scientific at 1-866-282-0430 for instructions on how to proceed.

If you discover that the instrument was damaged during shipping and it becomes necessary to return it to the manufacturer, repack it in the same way it was delivered.

2.6.3 Equipment Installation

Polk County Air Quality Division will use the Thermo Scientific Model 42*i* Trace Level (TL-42*i*) Chemiluminescence $NO\text{-}NO_2\text{-}NO_x$ Analyzer displayed in Figure 2-1 for sampling nitrogen dioxide. Installation of the TL-42*i* consists of connecting the sample tubing to the sample gas inlet fitting and connecting the primary power and the data logger device. An external pump must also be plumbed to the instrument. The sampler inlet line connection should be made with ¼ -inch outer diameter Teflon tubing.

Figure 2-1: Thermo Scientific TL-42*i* $NO\text{-}NO_2\text{-}NO_x$ Analyzer

The Thermo TL-42*i* runs on an external twin-head vacuum pump. Connect the pump vacuum port (inlet) to the Exhaust bulkhead. Connect the pump exhaust to a suitable vent or charcoal scrubber.

Because the analyzer is an optical instrument, it is possible that particulate in the gas sample could interfere with the NO-NO_2-NO_X readings, even though the sampling/referencing cyclic operation of the instrument is designed to eliminate such interference. In order to avoid frequent cleaning of the optics and flow handling components, a Teflon filter must be installed between the ambient sample line and the sample port of the analyzer prior to operation. A 0.5-micron Teflon filter will not degrade the NO_2 concentration. However, if particulate matter builds up on the filter, the particulate matter will destroy some of the NO_2 in the sample.

Since the instrument's exhaust consists of ambient air with some NO_2 removed, ensure that the exhaust cannot re-enter the sample system.

Install the monitor's electrical connections as indicated in the manual.

The power backup, data acquisition equipment, and any monitoring equipment, calibration equipment, or other ancillary equipment should be installed according to information supplied in the appropriate manuals.

2.6.4 Programming the TL-42*i*

When the instrument is first turned on, the exhaust fan will start and the Power-Up and Self-Test screens will be displayed. These screens will be displayed until the instrument has completed its warm up and self-checks. Allow 30 minutes for the instrument to stabilize.

After the warm-up period the Run Screen, or Normal Operating Screen, is displayed. The Run Screen displays the NO-NO_2-NO_X concentrations. Press the MENU button to access the Main Menu, which contains a list of submenus. Instrument parameters and features are divided into the submenus according to their function. Use the ↑ **or** ↓ buttons to move the cursor to each submenu.

2.6.4.1 Range and Units

The Range menu defines the concentration range of the analog outputs. Polk County Air Quality will use the "Single Range" option with the selected range of 0 – 250 ppb for the analyzer. To set the range for the instrument, press the **MENU** button to access the Main Menu. Press the ↓ button until the cursor is on "NO Range", and press **ENTER**. Press the ↓ button until the cursor is on **SET CUSTOM RANGES,** and press **ENTER**. Press the ↓ button to scroll to **CUSTOM RANGE 1** and press **ENTER**. Use the ← and → buttons to move the cursor left or right. Use the ↑ **or** ↓ buttons to increment or decrement the numeric value to set the range to "250" and press **ENTER**. Press **MENU** to return to the Range Menu. Repeat procedures to set NO_2 Range and NO_X Range.

The Gas Units Screen defines how the NO-NO_2-NO_X concentration reading is expressed. From the Range Menu, select **GAS UNITS** to display the Gas Units screen. Use the ↓ button to select "PPB" and press **ENTER**. Press **MENU** twice to return to the Run Screen.

2.6.4.2 Averaging Time

The averaging time defines a time period (1 to 300 seconds) during which $NO\text{-}NO_2\text{-}NO_X$ measurements are taken. The average concentration of the readings is calculated for that time period. Polk County Air Quality will use 60 seconds as the averaging time for data collection and during calibrations, audits, and zero/precision/span checks.

From the Main Menu, use the ↓ button to scroll to **AVERAGING TIME** and press **ENTER**. From the Averaging Time Screen, use the ↑ **or** ↓ buttons to scroll through the preset ranges. Press **ENTER** to select the desired averaging time. Press **RUN** to return to the Run Screen.

2.6.4.3 Temperature Compensation

Temperature compensation corrects for any changes to the instrument's output signal due to variations in internal instrument temperature. When the temperature compensation is off, the first line of the display shows the factory standard temperature of 30°C. Polk County Air Quality will run the $NO\text{-}NO_2\text{-}NO_X$ analyzer with the temperature compensation set to **ON**.

From the Main Menu, use the ↓ button to scroll to **INSTRUMENT CONTROLS** and press **ENTER**. From the Instrument Controls Screen, use the ↓ button to scroll to **TEMPERATURE COMPENSATION**, and press **ENTER**. Press **ENTER** to toggle the temperature compensation on or off. Press **RUN** to return to the Run Screen.

2.6.4.4 Pressure Compensation

Pressure compensation corrects for any changes to the instrument's output signal due to variation in the reaction chamber pressure. When the pressure compensation is off, the first line display shows the factory standard pressure of 150 mmHg. Polk County Air Quality Department will run the $NO\text{-}NO_2\text{-}NO_X$ analyzer with the pressure compensation set to **ON**.

From the Main Menu, use the ↓ button to scroll to **INSTRUMENT CONTROLS** and press **ENTER**. From the Instrument Controls Screen, use the ↓ button to scroll to **PRESSURE COMPENSATION**, and press **ENTER**. Press **ENTER** to toggle the pressure compensation on or off. Press **RUN** to return to the Run Screen.

2.6.4.5 Baud Rate

The Baud Rate Screen is used to set the RS-232 interface baud rate. The Polk County Air Quality Department will use a baud rate of 9600.

From the Main Menu, use the ↓ button to scroll to **INSTRUMENT CONTROLS** and press **ENTER**. From the Instrument Controls Screen, use the ↓ button to scroll to **COMMUNICATION SETTINGS** and press **ENTER**. From the Communication Settings Screen, use the ↓ button to scroll to **BAUD RATE**, and press **ENTER**. Use the ↑ **or** ↓ buttons to scroll through the preset rates. Press **ENTER** to select the desired baud rate. Press **RUN** to return to the Run Screen.

2.6.4.6 Clock Set

To set the correct time and date on the instrument, press **MENU** to return to the Main Menu. Use the ↓ button to scroll to **INSTRUMENT CONTROLS** and press **ENTER.** Use the ↓ buttons to scroll to **DATE/TIME** and press **ENTER**. The date and time should be set to the data logger time. Use the → button to select: year, month, day, hour, minutes, or seconds. Use the ↑

or ↓ buttons to increase/decrease the desired value. Set the appropriate date and time and press **ENTER**. Press **RUN** to return to the Run Screen. The instrument is now set with the appropriate time, date, full scale range and units.

NOTE: The clock should be checked at each site visit and adjusted if off from the data logger by more than 2 minutes.

3.6.4.7 Auto Mode

The Auto/Manual Mode screen allows selection of the automatic mode (NO/NO_X), NO Mode (manual NO), or NO_X mode (manual NO_X). **Polk County Air Quality will always run the TL-42*i* in Auto Mode.** The auto cycle mode switches the mode solenoid valves automatically on a 10 second cycle so that NO, NO_2, and NO_X concentrations are determined.

To set the TL-42*i* to Auto Mode, press **MENU** to return to the Main Menu. Use the ↓ button to scroll to **INSTRUMENT CONTROLS** and press **ENTER.** Use the ↓ buttons to scroll to **AUTO/MANUAL MODE** and press **ENTER**. Use the ↓ buttons to scroll to **NO/NO_X MODE** and press **ENTER**.

NOTE: It is recommended that you allow the TL-42*i* to warm up for 24-hours before you attempt checks or calibration.

2.7 Standards

A cylinder containing 9 to 20 ppm NO in N_2 with less than 1.0 ppm NO_2 is used as the concentration standard for verifications, calibrations and audits. The cylinder must be certified to EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards as stated in EPA Publication NO. EPA-600/R-12-531. Procedures for certifying the NO cylinder (working standard) against a NIST traceable NO or NO_2 standard and for determining the amount of NO_2 impurity are given in EPA Publication NO. EPA-006/4-75-003, "Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide." The cylinder should be recertified on a regular basis as determined by the local quality control program.

The gas certification process is quite rigorous. However, it is still possible to receive a cylinder gas out of specification. Polk County Air Quality will verify that a new cylinder gas is within specification before it is put into use. Immediately prior to removing an old cylinder, perform a zero/precision/span check, making sure that relevant criteria are met. Change to the new cylinder, and update the Thermo 146*i* with the new stock gas concentration. Adjust the 146*i* to produce a target concentration equivalent to the precision level last used with the old cylinder. If the instrument reading is within 4% of the expected value, proceed to calibrate the analyzer with the new stock cylinder. If it is not within 4%, investigate and resolve the disparity prior to using the new cylinder. Record all information on the Gas Comparison Spreadsheet, Form 1, Appendix A.

Operators will be required to replace the NO cylinder when the cylinder pressure drops below 200 PSI. This will involve removing the regulator on the depleted cylinder and installing the regulator on a replacement cylinder.

Precautions must be taken to remove "dead" pockets of contaminants which are created within the regulator whenever it is removed from the cylinder. This problem can be minimized by carefully evacuating the regulator (also known as purging) after it is connected to the cylinder. Air trapped in the regulator can result in the NO converting to NO_2 within the regulator resulting in errors during calibration. Better results will be achieved by alternately pressurizing and depressurizing the regulator once it has been attached to the cylinder.