# Standard Operation Procedures for Trace Level $SO_2$

In Use By

## Polk County Air Quality
## Ambient Air Monitoring Personnel

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**POLK COUNTY AIR QUALITY DIVISION**

**STANDARD OPERATING PROCEDURE MANUAL FOR THE THERMO SCIENTIFIC 43*i* TRACE LEVEL $SO_2$**

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# 24.0 STANDARD OPERATING PROCEDURE FOR $SO_2$ MONITORING USING THE THERMO SCIETIFIC 43*i* TRACE LEVEL MONITOR

## 24.1 Purpose

To establish a standard operating procedure (SOP) manual for the Polk County Air Quality Division personnel concerning the setup, operation, zero/precision/span checks, calibrations, audits and maintenance of trace level sulfur dioxide (TL-$SO_2$) 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.

## 24.2 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 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, zero/precision/span checks, calibrations, audits and maintenance of trace level sulfur dioxide equipment operated by Polk County Air Quality personnel.

## 24.3 References

**24.3.1 40 Code of Federal Regulations (CFR) Part 53.23c. Test Procedures.**

**24.3.2 40 Code of Federal Regulations (CFR) Part 58, Appendix A. Quality Assurance Requirements for State and Local Air Monitoring Stations (Slams).**

**24.3.3 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 Assessment Monitoring Stations (PAMS).**

**24.3.4 40 Code of Federal Regulations (CFR) Part 136, Appendix B.**

**24.3.5 The National Air Monitoring Strategy, Final Draft, 4/29/04. http://www.epa.gov/ttn/amtic/monstratdoc.html.**

**24.3.6 Model 43*i* Trace Level-Enhanced Pulsed Fluoresence $SO_2$ Analyzer Instruction Manual. Thermo Scientific. Part Number 102780-00. January 14, 2008.**

**24.3.7 Model 146*i* Dynamic Gas Calibrator. Thermo Scientific. Part Number 102482-00, January 30, 2008.**

**24.3.8 Trace $SO_2$ Monitoring Guidance for the MANE-VU Regional Aerosol Intensive Network (RAIN) program, Draft (dated March 7, 2005).**

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

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

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

## 24.4 Introduction

Sulfur dioxide ($SO_2$) has been identified as a key precursor of fine particulate matter (PM2.5) and, thus, plays an important role in PM-related health effects. Sulfur Dioxide ($SO_2$) is a colorless, nonflammable gas that has a strong suffocating odor. $SO_2$ originates from fuel containing sulfur (mainly coal and oil) burned at power plants and during metal smelting and other industrial processes. High levels of $SO_2$ can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. Long-term exposure to high levels of $SO_2$, in the presence of high levels of particulate matter, may aggravate existing cardiovascular disease and respiratory illness.

Polk County Air Quality Division uses the Thermo Scientific Model 43*i*-TLE pulsed fluorescence $SO_2$ analyzer to measure Trace Level $SO_2$. The 43*i*-TLE is based on the principle that $SO_2$ molecules absorb ultraviolet (UV) light and become excited at one wavelength, then decay to a lower energy state emitting UV light at a different wavelength. Specifically,

$$SO_2 + h\nu_1 \rightarrow SO_2^* \rightarrow SO_2 + h\nu_2$$

where: $h\nu_1$ = incidence light,
$h\nu_2$ = fluoresced light, and
$SO_2^*$ = $SO_2$ in its excited state

In sample mode, the sample is drawn into the analyzer through the SAMPLE bulkhead, as shown in Figure 24-1. The sample flows through a hydrocarbon "kicker," which operates on a selective permeation principle, allowing only hydrocarbon molecules to pass through the tube wall. The driving force for the hydrocarbon removal is the differential partial pressure across the wall. This differential pressure is produced within the instrument by passing the sample gas through a capillary tube to reduce its pressure and feeding it into the shell side of the hydrocarbon kicker. The $SO_2$ molecules pass through the hydrocarbon "kicker" unaffected.

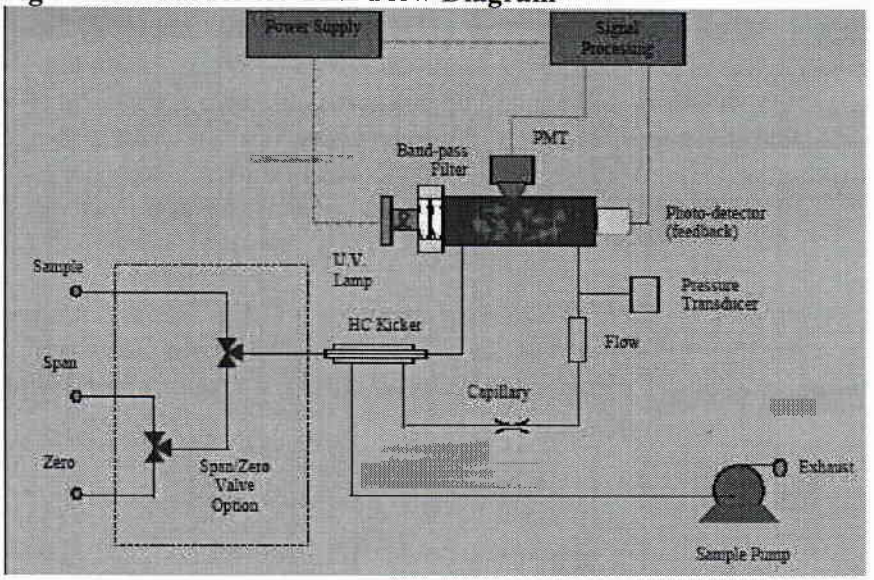
The sample flows into the fluorescence chamber, where pulsating UV light excites the $SO_2$ molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains eight selective mirrors that reflect only the wavelengths, which excite $SO_2$ molecules.

As the excited $SO_2$ molecules decay to lower energy states they emit UV light that is proportional to the $SO_2$ concentration. The band pass filter allows only the wavelengths emitted by the excited $SO_2$ molecules to reach the photomultiplier tube (PMT). The PMT detects the UV light emission from the decaying $SO_2$ molecules. The photo detector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light.

The sample then flows through a flow sensor, a capillary, and the shell side of the hydrocarbon "kicker." The Model 43*i*-TLE trace level outputs the $SO_2$ concentration to the front panel display and the analog or digital outputs

The Detection Limit (DL) for a non-trace level $SO_2$ analyzer is 10 parts per billion (ppb) (40 CFR 53.23c). However, the 43*i*-TLE has an estimated DL of 100 parts per trillion (ppt), which is accomplished by an increased detector sensitivity, as well as increasing the length of the standard instrument's optics bench. This document will discuss the Trace Level (TL) operating procedures in detail. The goal of this method is a "true" 1-hour average limit of detection (LOD) of less than 0.3 ppb, for determining ambient air concentrations of $SO_2$.

**Figure 24-1 Model 43*i*-TLE Flow Diagram**




## 24.5 Health and Safety Warning/Precautions

Only properly trained personnel should perform 43*i*-TLE 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 43*i*-TLE. 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 $SO_2$ 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.

## 24.6 Sampler Setup

### 24.6.1 Site Selection

For detailed information concerning site selection for trace level $SO_2$ monitoring, refer to Table 24-3 of this SOP or the 40 Code of Federal Regulations (CFR), Part 58, Appendix E, or the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Section 6.2, entitled "Monitoring Site Location."

#### 24.6.1.1 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 operation of the $SO_2$ monitoring instruments.
- The space where the equipment is housed must maintain a temperature range of 20-30°C. 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 to be located.
- Local building codes. In most cases, the contractor installing the power, structure, concrete, etc. know the local building codes.

#### 24.6.1.2 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 sample inlet should be located between 3-15 meters above ground level
- The distance of the probe inlet must be at least 20 meters from nearby obstructions (buildings and trees)
- The vertical and horizontal distance of the probe inlet must be at least one meter from the ground and support structure
- The probe should be positioned with at least 270 degrees of unrestricted airflow

For more detailed information concerning site selection for sulfur dioxide monitoring, refer to Table 24-3 of this SOP or the 40 CFR 58, Appendix E or the Quality Assurance Handbook for Air Pollution Measurement Systems , Volume II, Section 7.2, entitled "Sampling Probes and Manifolds."

### 24.6.2 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.

### 24.6.3 Equipment Installation

Installation of a 43*i*-TLE (Figure 24-2) monitor consists of connecting the sample tubing to the sample gas inlet fitting and connecting the primary power and the data logger device. The sampler inlet line connection should be made with ¼ -inch outer diameter Teflon tubing.

The entrance of the sampling system must ensure that rain cannot enter the system. An inverted funnel and sample line must be placed outside the trailer or enclosure to prevent water from entering the sample line.

Because the analyzer is an optical instrument, it is possible that particulate in the gas sample could interfere with the TL-$SO_2$ readings. Although, 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, installation of a 0.5-micron Teflon filter between the ambient sample line and the sample port of the analyzer must be done before the operation of the analyzer. A Teflon filter will not degrade the TL-$SO_2$ concentration. However, if particulate matter builds up on the filter, the particulate matter will destroy some of the TL-$SO_2$ in the sample.

Since the instrument's exhaust consists of ambient air with some TL-$SO_2$ removed, ensure that the exhaust cannot re-enter the sample system.

Install the monitor's electrical connections as indicated in the operating 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 operating manuals.

**Figure 24-2: Thermo Scientific Model 43*i*-TLE $SO_2$ Analyzer**


### 24.6.4 Programming Equipment

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 TL-$SO_2$ concentration. 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.

#### 24.6.4.1 Range and Units

The Range Screen defines the concentration range of the analog outputs. Polk County Air Quality will use the "Single Range" option with the selected range of 0 – 100 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 "Range." Press **ENTER** to display the $SO_2$ Range Menu, and select **RANGE**. Use the ↑ or ↓ buttons to scroll through the preset ranges. Select "100.0" and press **ENTER**. Press **MENU** to return to the Range Menu.

The Gas Units Screen defines how the $SO_2$ concentration reading is expressed. From the Range Menu, select **GAS UNITS** to display the Gas Units screen. Use the ↑ or ↓ button to select "PPB" and press **ENTER**. Press **RUN** to return to the Run Screen.

#### 24.6.4.2 Averaging Time

The averaging time defines a time period (1 to 300 seconds) during which $SO_2$ measurements are taken. The average concentration of the readings is calculated for that time period. Polk County Air Quality will use the setting of 60 seconds as the averaging time for the collection of data. An averaging time of 60 seconds will also be used 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.

#### 24.6.4.3 Temperature Compensation

Temperature Compensation provides compensation for any changes to the instrument's output signal due to variations in internal instrument temperature. When the temperature correction is off, the first line of the display shows the factory standard temperature of 30°C. Polk County Air Quality will run the TL-$SO_2$ analyzer with the temperature correction 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.

#### 24.6.4.4 Pressure Compensation

Pressure Compensation provides compensation for any changes to the instrument's output signal due to variation of fluorescence chamber pressure. When the pressure correction is off, the first line display shows the factory standard pressure of 750 mmHg. Polk County Air Quality will run the TL- $SO_2$ analyzer with the pressure correction 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**