

Section I - ECB Responsibilities

TRACE LEVEL Sulfur Dioxide Standard Operating Procedure Revision 2

Approval Sign Off-Sheet

I certify that I have read and approve of the contents of the Trace Level SO₂ ECB Standard Operating Procedure with an effective date of February 15, 2016.

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2.34.1 Trace – Level SO₂ Standard Operating Procedure (SOP): ECB Responsibilities

2.34.1.1 Equipment Selection and Procurement

The State of North Carolina Division of Air Quality (NC DAQ) operates sulfur dioxide monitors across the state for the purpose of monitoring the potential exposure of the general population to ambient levels of sulfur dioxide (SO₂). The standard ambient level SO₂ monitors currently being used within the state monitoring network, have historically been operated at the very low end of their detection range. Higher sensitivity (“trace level”) SO₂ monitors are now being required for the developing network of United States Environmental Protection Agency (U.S. E.P.A.) National Core (NCore) monitoring sites. The NCore initiative is the debut of an EPA shift towards new data quality objectives that emphasize a performance-based quality system that shows a tight control of precision and bias. The “Trace Level Enhanced” monitor(s) supports these initiatives.

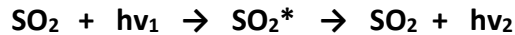
The Electronics and Calibration Branch (ECB) shall procure air monitoring equipment and supplies for the Division of Air Quality in support of the NCore Program. EPA’s Reference or Equivalent Methods list was reviewed to determine the makes and models acceptable for monitoring sulfur dioxide at the levels dictated by the NCore monitoring initiative.

All sulfur dioxide monitors used for “trace-level” applications must have an acceptable output for the data logging system deployed with the instrument (digital output or analog output of 0 to 10 volt DC). All monitors and calibrators must operate on 115 volt AC 60Hz line current. All analog data acquisition systems must be calibrated to accept a 0 to 10 volt DC signal, have an accuracy of ± 0.1 ppb on the 100 ppb scale, and must meet other specifications as necessary. All digital data acquisition systems must be at least 10-bit and have RS232 and/or Ethernet connections.

The following sections discuss the principle of operation of the analyzer and major support equipment, the set-up and initial, pre-deployment evaluation of the 43C-TLE or 43i-TLE. Post-evaluation activities, such as on-site installation, routine maintenance, and accuracy auditing, are also discussed.

2.34.1.2 Description / Principle of Operation of the Thermo-Environmental Inc. Model 43C-TLE Sulfur Dioxide Analyzer

The Model 43C-TLE and 43i-TLE are based on the same principles as the 43C and 43i instruments. Sulfur dioxide 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,



The trace-level instrument adds a longer optic flow path, and employs a more selective/sensitive detector to lower the limit of detection. Sample is drawn into the analyzer through the **SAMPLE** bulkhead, as shown in Figure 1: Principles of Operation for the Thermo Model 43C-TLE Analyzer and Figure 2: Principles of Operation for the Thermo Model 43i-TLE Analyzer. The sample flows through a hydrocarbon “kicker”, which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO₂ molecules pass through the hydrocarbon kicker unaffected. The sample flows into the fluorescence chamber, where pulsating UV light excites the SO₂ molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective mirrors that reflect only the wavelengths that excite SO₂ molecules. As the excited SO₂ molecules decay to lower energy states, they emit UV light that is proportional to the SO₂ concentration. The bandpass filter allows only the wavelengths emitted by the excited SO₂ molecules to reach the photo multiplier tube (PMT). The PMT detects the UV light emission from the decaying SO₂ 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 analyzer outputs the SO₂ concentration to the front panel display and the analog/digital outputs. The instrument is best described in detail, by separating it into three sections: the analyzer, optics, and electronics.

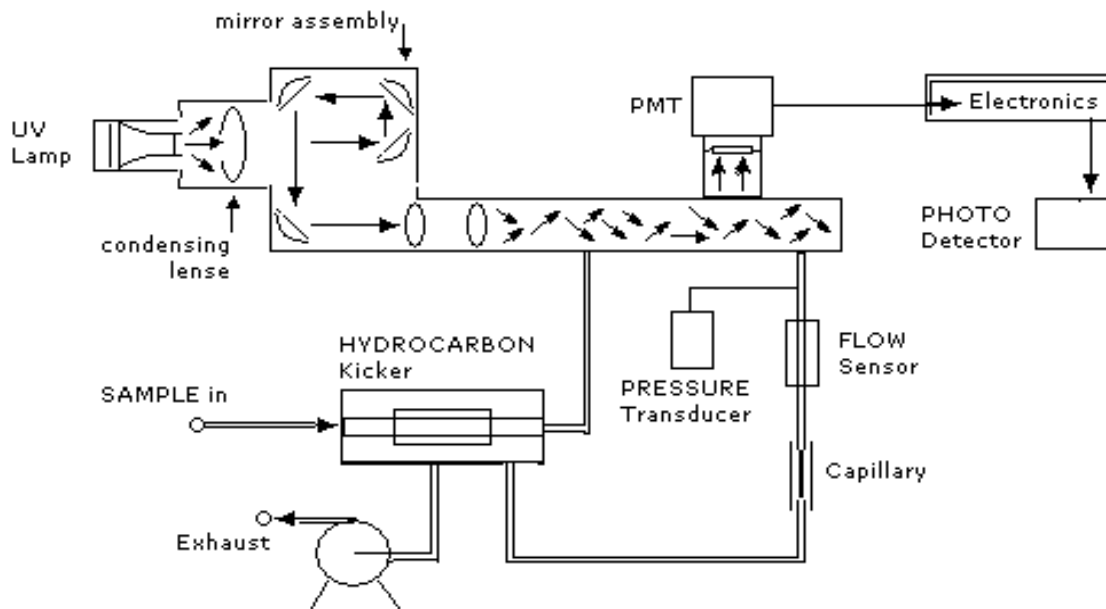


Figure 1: Principles of Operation for the Thermo Model 43C-TLE Analyzer

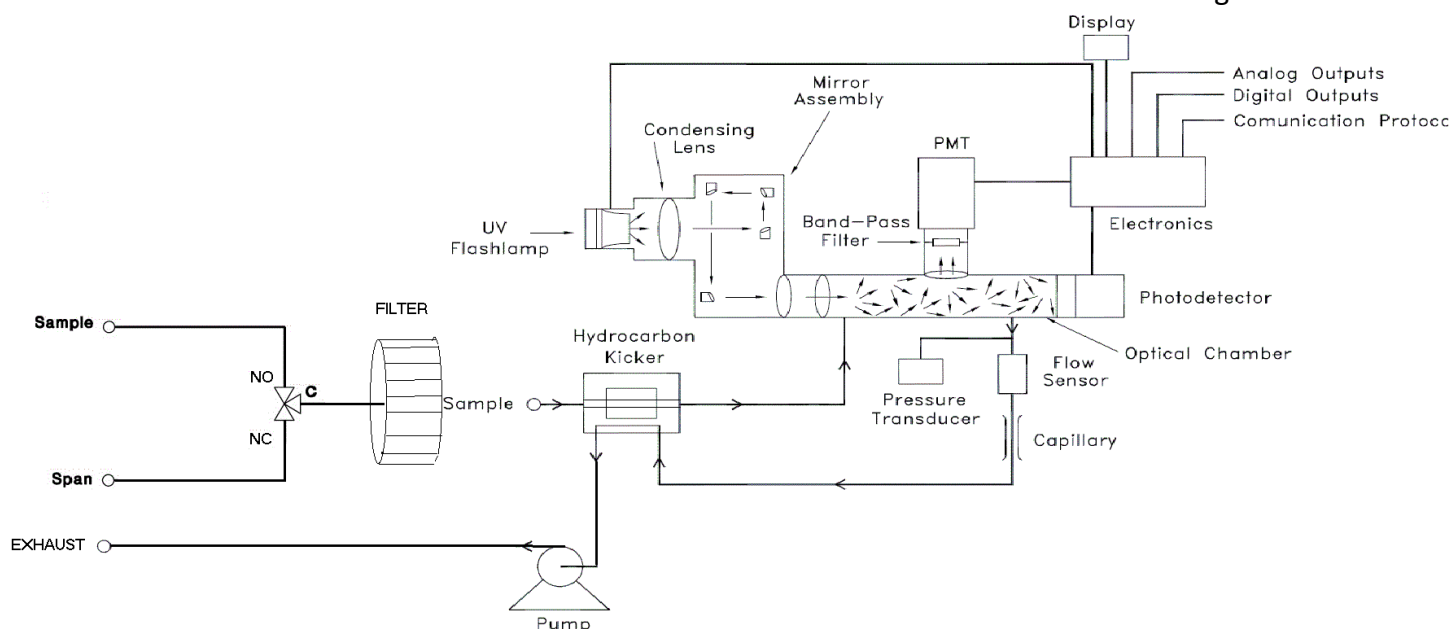


Figure 2: Principles of Operation for the Thermo Model 43i-TLE Analyzer

Model 43C-TLE and 43i-TLE Monitor Description (Specifications)

| | |
|----------------------------|---|
| Preset ranges | 0-10, -20, -50, -100, -200, -500, and -1000 ppb |
| Zero noise | 0.05 ppb RMS (60 sec. avg. time) |
| Lower detectable limit | 1.0 ppb (60 sec. avg. time) |
| Zero Drift (24 hour) | Less than 0.2 ppb |
| Span Drift (24 hour) | ±1% per week |
| Response time | 110 sec. (60 sec. avg. time) |
| Precision | 1% of reading or 1 ppb (whichever is greater) |
| Linearity | ±1% of full-scale |
| Sample flow rate | 0.5 liters/min (standard) |
| Interferences (EPA levels) | Less than the lower detectable limit except for the following: NO < 1ppb; m-Xylene < 1ppb; H ₂ O < 3% of reading |
| Operating temperature | 20 °C – 30 °C (may be safely operated over the range of 5 °C – 40 °C) |
| Power requirements | 105 – 125 VAC at 50/60 Hz 100 Watts |
| Physical dimensions | 16.75" (W) X 8.62" (H) X 23" (D) |
| Outputs | Selectable voltage 4 – 20 mA; RS-232/485 Interface |
| Precision Specified | Calculated for each instrument deployed as by US EPA. Must have a 95 percent probability limit for precision of ± 10% as described by US EPA calculation for coefficient of variance (CV) at the precision point measurement. See Precursor Gas Technical Assistance Document, version 4, section 3-SO ₂ , September 2005) |

2.34.1.3 Description of and Operation of Thermo 146C or 146i, Zero Air Generator, and Gas Cylinder

A) TEI Model 146C or 146i Calibrator

The calibrator supplies the required levels of SO₂ to perform zero, precision, span checks and multipoint calibrations. The 146C or 146i calibrator is operated remotely from the data logger to perform zero, precision, and span checks. It is an accurate mass flow controlled gas dilution system that meets the 40 CFR 50 requirements of $\pm 2\%$ accuracy. SO₂ gas (usually in an inert gas such as nitrogen) from a NIST traceable Protocol certified cylinder (of $\pm 2\%$ accuracy or less) (connected to Port C) is blended with "zero-air" to provide a desired concentration. From the known calibration of the two mass flow controllers, the exact concentration can be calculated. A typical dilution ratio of nominally 100:1 to 1000:1 is used to generate the appropriate concentrations.

B) Model 701 Zero-Air Generator System

The purpose of the Model 701 is to supply pollutant-free air ("zero air") for proper instrument zeroing and to provide clean diluent air for use with the 146C calibrators. Ambient air is drawn into the system which removes water vapor, SO₂, NO, NO₂, O₃, CO and hydrocarbons. In order to achieve the enhanced lower level of detection, consistently clean, zero air is essential to the operation of the trace level SO₂ instrument. Because the goal of the instrument is to detect/characterize SO₂ concentrations at levels very close to zero, determining the response to clean air (and hence the baseline of the instrument) is vital for collecting defensible data.

C) Zero Air Generator Certification

Please reference Section 2.3.5: Zero Air Pack Certification and Auditing for instruction on the certification of the Zero Air Generators.

D) Gas Cylinders

All gas cylinders must be traceable to a National Institute of Standards and Testing – Standard Reference Material (NIST-SRM) and must be used prior to the expiration date (i.e., 2 years). These are termed "Protocol" gas.

The Major Components of a Typical Trace-level SO₂ Monitoring System Include:

- Thermo 43C-TLE or 43i-TLE SO₂ Analyzer
- Thermo 146C or 146i Dynamic Gas Calibrator
- Zero Air Generator and Certified Protocol SO₂ cylinder
- ESC/AGILAIRE Model 8816 or 8832 Data Logger
- A dedicated Site PC and modem

2.34.1.4 Initial Laboratory Startup of the Analyzer Model 43C-TLE or 43i-TLE

The ECB shall conduct and document, initial operational tests before deploying an instrument. Refer to the Thermo 43C-TLE or 43i-TLE Instruction Manual (Model 43C: P/N 13399, 2004 and Model 43i-TLE: Part Number 102780-00, 2007). Items to be completed include:

- Inspection
- Assembly (Modification, Range Setting, Flow Verification, and Lamp Verification)
- Leak Check and Calibration

All original records (records documenting observations, initial pre-installation testing such as MDL, bias and linearity determinations, site installation and removal logbook, 109 Forms, maintenance log, and site logbook) must be legible, complete, dated, and signed by the electronic technician and retained at the ECB as part of the permanent equipment record (site log book remains at the site). The electronic technician's signature on the logbooks and forms certifies that the work has been performed in accordance with this SOP and that the information recorded is accurate and complete. All records will be reviewed and verified by the Electronics and Calibration Supervisor and audited by Raleigh Central Office on an annual basis.

A) Inspection

Visually inspect the exterior of all items for damage. Remove the cover and inspect the electronics assembly and circuit boards for loose connections, broken components, or other damage. Reconnect any loose components and if necessary, contact the manufacturer.

B) Assembly, Modification and Initial Verification

Prior to deployment in the field, each instrument will undergo basic operational tests in the ECB lab. Results will be recorded in the instrument's maintenance logbook, which is kept on file at the ECB laboratory.

The instrument should be set up in the lab with accompanying, calibrator, zero air system, cylinder, and data logging system.

These initial operational tests at ECB will include:

- Calibration at 3 levels plus zero on a range of 0-100 ppb (see Table 1 below);
- Verification, over a 4-5 day period, that the 24 hour zero and span drift do not exceed the specified 0.20 ppb and $\pm 1\%$ full scale limits, respectively;
- Installation of a Teflon particulate filter on the instrument at the sample inlet; and
- Verification that the output signal received by the data logger agrees with the instrument reading.

Table 1: Instrument Calibration Values for Instrument Range of 0-100 ppb

| | Concentration Range (ppb) | Nominal Concentration (ppb) |
|---------------|---------------------------|-----------------------------|
| Span 1 | 50 – 99.9 | 85 |
| Span 2 | 20 – 49.9 | 45 |
| Span 3 | 3 – 4.9 | 4 |
| Zero | 0.0 | 0.0 |

C) Initial Laboratory Setup

Attach a Teflon tube (FEP Teflon type only) from the fitting labeled "output" on the rear panel of the calibrator to the "span" input of the monitor. Connect a source of zero-air to the inlet port labeled zero-air. Connect the standard SO₂ gas cylinder to the port labeled C. Refer to Figure 3: Thermo Model 43C-TLE Flowchart or Figure 4: Thermo Model 43i-TLE Flowchart for a description of the instrument menu.

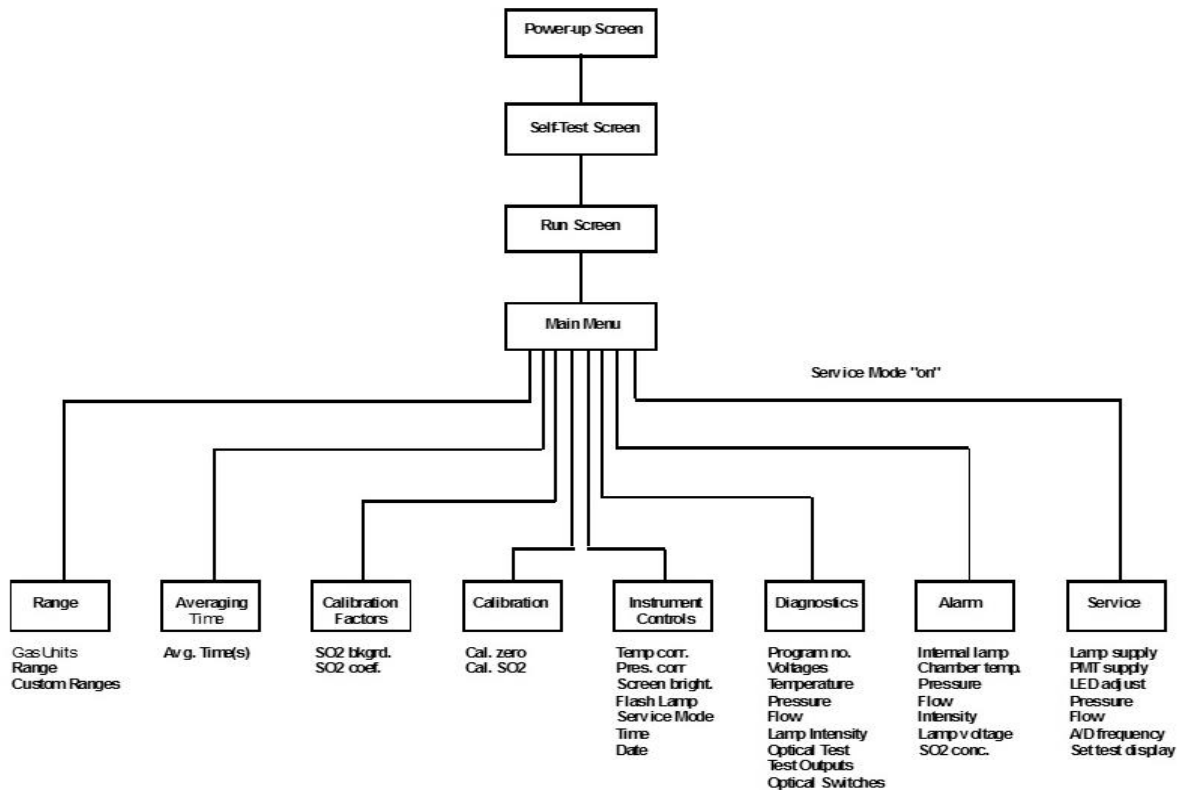


Figure 3: Thermo Model 43C-TLE Analyzer Flowchart

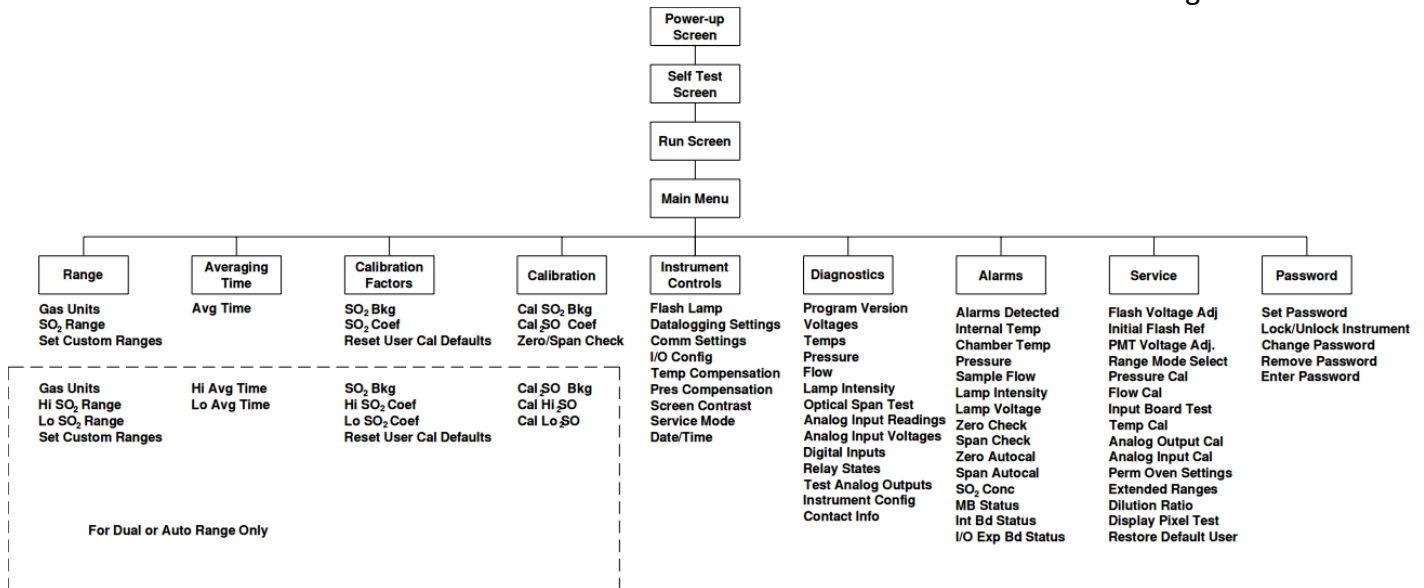


Figure 4: Thermo Model 43i-TLE Analyzer Flowchart

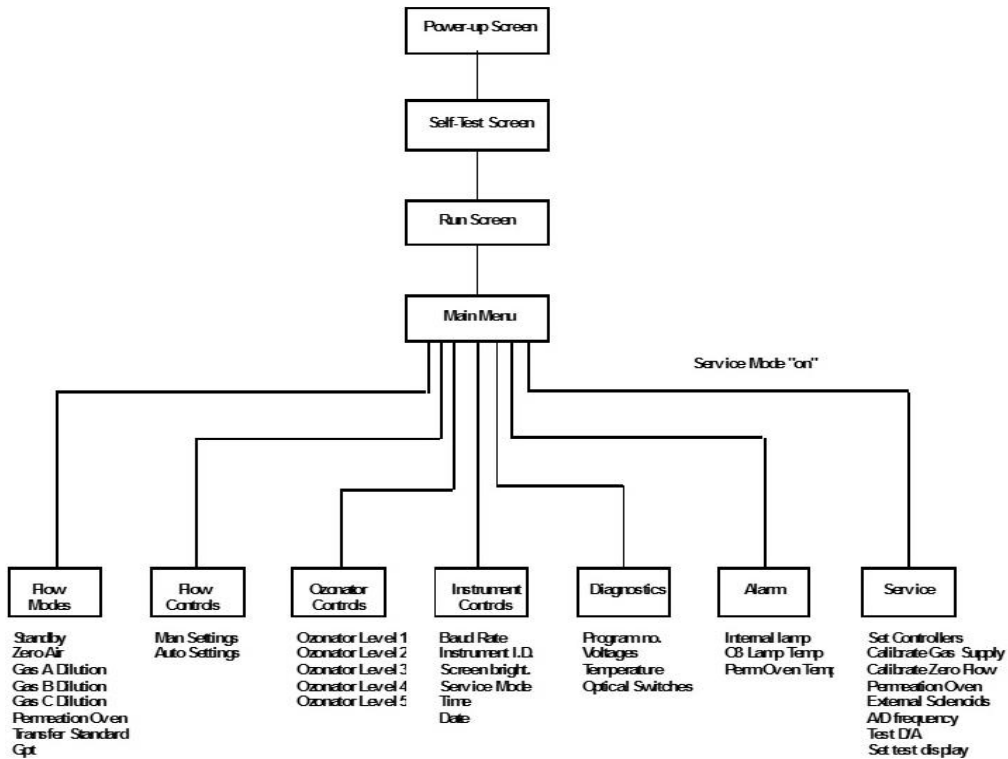


Figure 5: Thermo 146C Calibrator Flowchart

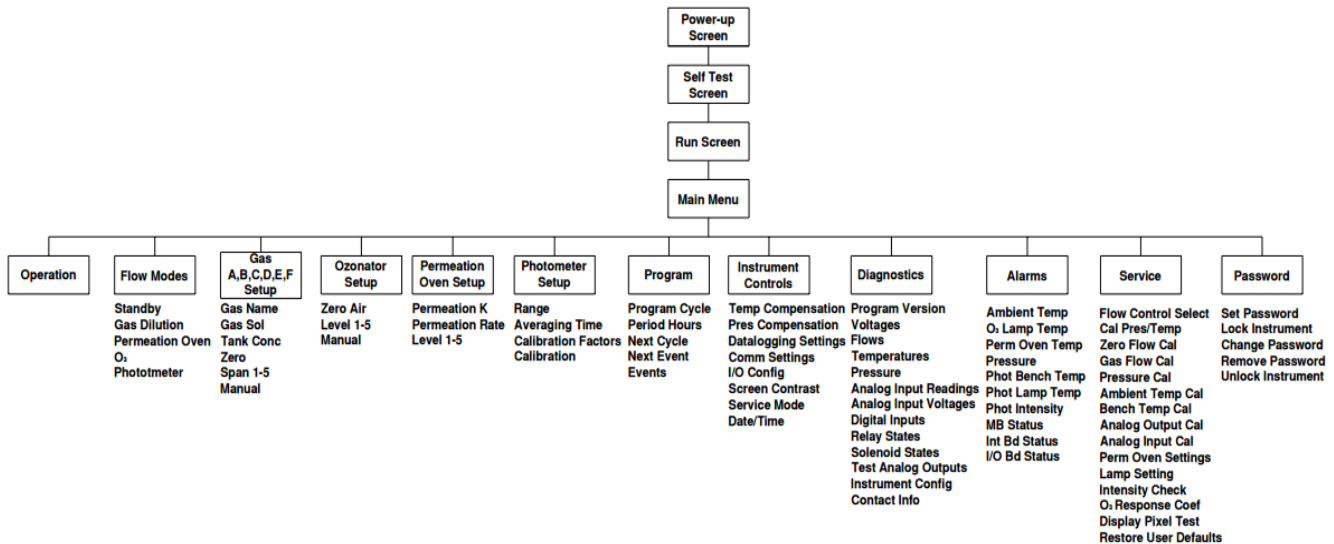


Figure 6: Thermo 146i Calibrator Flowchart

D) Remote, Local, and Service Modes

1. Thermo Model 43C-TLE

There are three modes on the 43C-TLE analyzer. While in the field, the SO₂ analyzer should always be on **Remote** mode. When performing a calibration, the analyzer will need to be switched to **Local** mode. When performing maintenance, the analyzer will need to be switched to **Service** mode.

To switch between **Local** and **Remote** modes, simply press the **Enter** key on the front panel keypad while on the main screen.

To switch between **Local/Remote** and **Service** modes:

- Press the **Menu** button to go to the **Main Menu**.
- Use the arrow buttons to toggle to **Instrument Controls**, and then press **Enter**. Then toggle to **Service Mode**.
- When on the **Service Mode** screen, press **Enter** to switch between **Local** and **Service** modes.

Always return the analyzer back to **Remote** mode after completing any tasks that require **Service** or **Local** mode. Refer to Figure 5: Thermo Model 146C Flowchart for a description of the instrument menu.

2. Thermo Model 43i-TLE

There are two modes on the 43i-TLE analyzer. While sampling in the field, the SO₂ analyzer should always be in its **Standard**, operating mode. When performing any

maintenance, the analyzer will need to be switched to **Service** mode.

To switch between the **Standard** and **Service** modes:

- Press the **Menu** button to go to the **Main Menu**.
- Use the arrow buttons to toggle to **Instrument Controls**, and then press **Enter**. Then toggle to **Service Mode**.
- When on the **Service Mode** screen, press **Enter** to switch between **Standard** and **Service** modes.

Always return the analyzer back to **Standard** mode after completing any tasks that require **Service** mode. Refer to Figure 6: Thermo Model 146i Flowchart for a description of the instrument menu.

E) Range Setting

Set the "range" setting on the analyzer to the **Single** range mode of 100 ppb. (This range is subject to change after the collection of sufficient historical data.) In the "Single" range mode, there is one range, one averaging time, and one span coefficient. To use the single range mode, **set option switches 4 and 5 off** (on Model 43C-TLE only).

Using the 43C-TLE front panel, Choose **Range** from the Main Menu choices.

1. Use the arrow buttons to move the cursor to each choice on the Range Menu.
2. Press **Enter** to select a choice.
3. Press **Menu** to return to the Main Menu.
4. Press **Run** to return to the Run screen.

Using the 43i-TLE analyzer front panel, Choose **Range** from the Main Menu choices.

1. Use the arrow buttons to move the cursor to each choice on the Range Menu.
2. Press **Enter** to select a choice.
3. Press **Menu** to return to the Main Menu.
4. Press **Run** to return to the Run screen.

F) Verify the Lamp Voltage

The analyzer is equipped with a lamp voltage control circuit, which automatically corrects for the degradation of the flash lamp with age.

To display the lamp voltage on the 43C-TLE:

1. From the Diagnostics Menu, use the ↓ push-button to move the cursor to **Voltage**.
2. Press **ENTER** to display the Lamp voltage screen.
3. If this voltage is at 1200 V, it is necessary to either replace the lamp or adjust the lamp voltage control circuit.

4. Log the lamp voltage in the instrument logbook.
5. Press **Menu**, and then press **Run**.

To display the lamp voltage on the 43i-TLE:

1. From the Diagnostics Menu, move the cursor to Voltage, and press **ENTER**.
2. Cursor down to **Interface Board** and press **ENTER**.
3. The Lamp voltage is displayed as Flash Supply.
4. If this voltage is at 1200 V, it is necessary to either replace the lamp or adjust the lamp voltage control circuit.
5. Log the lamp voltage in the instrument logbook.
6. Press **Menu**, and then press **Run**.

G) Flow Measurement on Monitor

Choose **Diagnostics** from the Main Menu. Choose **Flow** from the Diagnostics menu, verify the current sample flow rate and record in logbook. The flow is measured by an internal flow sensor. A flow rate of about 0.5 LPM should be observed, if a flow rate of less than 0.35 LPM is observed a leak may be present.

H) Concentration Units

Set the instrument to read in parts per billion (PPB).

I) Averaging Time

The longer the averaging time, the smoother the data will be. Initially North Carolina will use 60 seconds as the averaging time.

J) Calibration Factors

Leave SO₂ background at zero and coefficient at one initially. They will automatically be corrected after zero/span points are run. Discussion of these factors is covered in later sections (Operator, calibration).

K) Diagnostic Checks / Settings

The following diagnostic menu settings for the Trace Level Analyzer:

| Parameter | Minimum | Maximum |
|----------------------|-----------|------------|
| PMT Voltage | -400 V | -1200 V |
| Lamp Voltage | 950 V | 1200 V |
| +5 Supply | (±1 volt) | |
| +15 Supply | (±1 volt) | |
| -15 Supply | (±1 volt) | |
| Battery | 2.8 V | 3.2 V |
| Internal Temperature | 15 °C | 48 °C |
| Chamber Temperature | 43 °C | 47 °C |
| Pressure | 400 mm Hg | 1000 mm Hg |
| Flow | 0.350 LPM | 0.750 LPM |
| Lamp Intensity | 10,000 Hz | 20,000 Hz |

L) Alarm Settings

The following Alarm Limits are used in Trace Level Analyzers:

| Parameter | Minimum | Maximum |
|--------------------------|-----------|------------|
| Internal temperature | 15 °C | 45 °C |
| Chamber Temperature | 43 °C | 47 °C |
| Pressure | 400 mm Hg | 1000 mm Hg |
| Flow | 0.350 LPM | 0.750 LPM |
| Lamp Intensity (43C-TLE) | 10,000 Hz | 20,000 Hz |
| Lamp Intensity (43i-TLE) | 40% | 100% |
| Lamp Voltage | 750 V | 1200 V |

M) Leak Check and Calibration

Two leak tests are performed (SAMPLE and SPAN)

Leak test the Monitor **SAMPLE** port. A leak test should be performed before deployment to the field, and also whenever the flow is observed to be less than 0.35 LPM:

1. Disconnect the sample line from the analyzer up-stream of the filter inlet (i.e., bulkhead fitting on rear of instrument) and block the opening with a leak-tight cap.
2. Press **Menu** and use the arrow buttons to move the cursor to **Diagnostics**. Select **Pressure** and press **Enter**. The pressure reading should be dropping. Wait until pressure drops below 180 mm Hg (flow should also go to zero). **NOTE:** If the pressure has not dropped below 180 mm Hg within three minutes, immediately remove the cap. Check that all fittings are tight and input lines are not cracked or broken. Do not cap off the line for more than three minutes or the system may pressurize.

3. Remove the cap and leak test the monitor SPAN port. Document in the logbook.

Leak test the Monitor **SPAN** port. Begin a “zero” event using the AV-Trend data logging system. Perform the following steps:

1. Disconnect the calibrator line from the analyzer and block off the opening with the leak-tight cap.
2. Press **Menu** and use the arrow buttons to move to **Diagnostic**. Select **Pressure** and press **Enter**. The pressure reading should be dropping. Wait until pressure drops below 180 mm Hg (flow should also be at zero). **NOTE:** If the pressure has not dropped below 180 mm Hg within three minutes, immediately remove the cap. Check that all fittings are tight and input lines are not cracked or broken and retest. **Do not cap off the line for more than three minutes or the system may pressurize.**
3. If leak check passes, remove the cap, reconnect the calibrator line to the span port and the sample line to the sample inlet. Clear the zero mode by aborting the zero cal. Document in the logbook. If leak check fails, troubleshoot the instrument and conduct any necessary repairs and repeat the leak check. Proceed to “multi-point calibration”.

N) Multi-Point Calibration

To perform a multi-point calibration:

1. Place the analyzer into **Service** mode.
2. Activate the zero. Run the zero until the reading has stabilized. A good baseline for a stable reading is ten consecutive minutes where the concentration values are within ± 2 ppb of each other.
3. From the **Main Menu**, use the arrows to toggle to **Service**, and then to **Flash Voltage Adjustment**.
4. Adjust the voltage until it is 800V for the 43C or 43i, or until it is 1000V for the 43C-TLE or the 43i-TLE.
5. Go back to the **Main Menu**. Again, use the buttons to move to **Service**, and then to **Initial Flash Reference**. The voltage should be between 2.8V – 4.5V for the 43C or 43i, or between 1.0V – 2.0V for the 43C-TLE or the 43i-TLE.
6. Activate Span 1. Run Span 1 until there are ten consecutive readings that are stable (within ± 2 ppb of each other).
7. After the reading has stabilized, from the **Main Menu**, use the arrows to toggle to **Service**, and then to **PMT Supply Settings**.
8. Use the arrows to adjust the voltage so that the monitor concentration matches that on the calibrator. Hit **Enter** to save the span concentration.
9. Activate the zero air again. Let the zero run long enough to provide a stable reading

(at least 10 consecutive minutes where the measured concentration values are within ± 2 ppb of each other).

10. After the zero readings has stabilized, from the **Main Menu**, use the arrow buttons to toggle to **Calibration**, and then **Calibration SO₂ Background**.
11. Hit **Enter** to set the SO₂ background to zero.
12. Activate the Span 1, and let the span gas flow long enough to provide a stable reading (at least 10 consecutive minutes where the measured concentration values are within ± 2 ppb of each other).
13. After the reading has stabilized, from the Main Menu, **Main Menu**, use the arrow buttons to toggle to **Calibration**, and then **Calibration SO₂ Coefficient**. Ensure that the SO₂ coefficient is set to the Span value.
14. Verify that the SO₂ background value and SO₂ coefficient value are correct by going to the **Main Menu**, and then using the arrows to toggle to **Calibration Factors**. The background and coefficient should be what you just inputted.
15. When you are sure that the correct values are used, place the instrument back into **Local** mode.

Verify that the instrument passed all tests and document in the logbook. Fill out Form 109 and forward it to the Branch Supervisor.

O) Additional Practices and Considerations

Although the trace level sulfur dioxide monitoring system is very similar to the standard compliance-type systems, there are several additional practices and concerns that must be addressed including:

Method Detection Limit (MDL): The MDL is the lowest concentration of a substance that can be reliably determined (99% confidence) by a given procedure. Any measurement falling at or above the MDL reflects a concentration that is significantly different from zero at a 1% percent false positive rate. The MDL should be 0.30 ppb or lower (for an averaging time of no more than 5 minutes per EPA Precursor Gas TAD, ver-4). The operational MDL *is not* given by manufacturing. The vendors' advertised lower detection limit (LDL), which is defined as the minimum concentration that produces a signal that is twice the noise level, is determined under ideal conditions and is sufficient for making purchasing decisions but cannot be substituted for the experimentally determined MDL. The ECB will estimate and document the LDL by sampling zero air and estimating the noise level according to 40 CFR 53.23 (b). The LDL must be 0.2 ppb or lower over an averaging time of no more than five minutes.

The EPA specifies that the MDL must be established (initially at the ECB or on-site) at the time the instrument is being brought on-line for data collection. Generally, this is accomplished by supplying the analyzer at least seven times with a test atmosphere of

SO₂ at 2.5 to 5.0 times the instrument noise level as provided by the manufacturer and performing a statistical calculation on the results. During initial ECB bench testing of a trace level, a test atmosphere of 0.25 ppb was supplied to the analyzer over the course of seven days. Using the results of 32 data points, an MDL of 0.027 ppb was calculated, demonstrating that the 0.30 ppb MDL is achievable. The details of this procedure are given in the Precursor TAD (Ver. 4) and below with an example provided in Appendix A:

Method Detection Limit Procedure

1. Each trace level SO₂ monitor that is placed in service at an NCore site will have an initial MDL determined and subsequent MDL determinations performed annually thereafter.
2. If time permits, the initial MDL can be performed at the ECB and then placed in service. If time does not permit, a new or reconditioned instrument can be placed in service per standard procedures (i.e., leak check, full calibration etc., see Operator's QA for details) followed by a MDL determination within the first month of being placed in service.
3. The MDL determination will be performed as follows:
 - a) Determine the concentration of the challenge gas to be introduced to the analyzer. This is defined as a value that is 2.5 to 5 times the noise as provided by the manufacturer (see instrument manual). Since this is a **Method** Detection Limit, the gases should be introduced at the sample inlet.
 - b) Establish and set the instrument "zero" using a source of pollutant free air (see Zero Air Supply discussion in Section 2.34.1.2). This is performed immediately prior to performing the MDL and can be associated with an instrument "Adjusted Calibration". Performing an "Adjusted Calibration" is not required. However, no adjustments to the instrument are allowed during the MDL study. If adjustments or maintenance is required for routine data collected, the MDL determination must be restarted.
 - c) Introduce the challenge gas to the analyzer through the sample inlet port for a time sufficient to allow the readings to stabilize plus at least 25 additional minutes. Total time required is approximately 45 minutes.
 - d) Collect, record and calculate the average of the last 20 sixty-second averages using a spread sheet such as Excel. This will be data point number one. The spread sheet should have data entry areas allocated for up to 10 sets (two per each 24-hour period) of data (a minimum of seven data sets is required).
 - e) Repeat item "d" above once every 12 hours for 5 days. This will result in ten data points. If the instrument is in service for ambient data collection, these events should be scheduled such that they do not interfere with other calibration check activities. The routine daily calibration checks can be suspended during this study since a separate, low concentration gas cylinder (nominally 1 ppm, non-protocol) will be required.

- f) The performance of the MDL study is the primary responsibility of the ECB. However, the regional office will provide on-site assistance at the beginning of the MDL study. The data logger and calibrator will be programmed by the ECB as required to perform the MDL determination. At the completion of the MDL test, the ECB will return to the site to verify that the necessary data has been collected and return the data logger and calibrator to normal operation. After all 10 sets of data have been entered into the spread sheet and the average value for each data set has been calculated, calculate the MDL following the example provided in Appendix A of this document.
- g) Save the raw data and completed Excel file and provide to the PPB for review and inclusion into AQS.

Precision: Precision is a measure of agreement among individual measurements taken under the same conditions. Precision shall be determined from checks performed every two weeks or less, and will be used to assess precision on a quarterly basis. For the trace level SO₂ the precision is required to be $\pm 10\%$ at the 90 percent probability level. The calculation for precision uses the percent difference (d_i) for each precision point to estimate a coefficient of variance (CV) upper bound.

$$CV = \sqrt{\frac{n \times \sum_{i=1}^n d_i^2 - (\sum_{i=1}^n d_i)^2}{n(n-1)}} \times \sqrt{\frac{n-1}{\chi_{0.1, n-1}^2}}$$

$\chi_{0.1, n-1}$ is the 10th percentile of a chi-squared distribution with n-1 degrees of freedom. The initial ECB bench tests of the trace level analyzer resulted in precisions of less than 5% at all three calibration levels.

Bias: Sulfur dioxide monitors can have positive interferences from volatilized aromatic hydrocarbons (such as xylenes), nitric oxide or stray light entering the optical chamber. Negative interferences can come from SO₂ molecules colliding with N₂, O₂ or water vapor. Bias is defined as a systematic or persistent distortion of a measurement process that causes errors in one direction. The bias of a process is assessed from the degree of agreement (disagreement) between a measured value and the true or expected value. The same points used to assess precision should be used to assess bias.

$$|bias| = AB + t_{0.95, n-1} \times \left[\frac{AS}{\sqrt{n}} \right]$$

The term AB is the mean of the absolute values of the individual d_i 's. The number of comparisons is n . The value $t_{0.95, n-1}$ is the 95th quantile of a t-distribution with n-1

degrees of freedom. The quantity *AS* is the standard deviation of the absolute values of *d*'s bias.

EPA requires that the instrument perform with an average bias of no greater than ±15 percent. The “direction” of the bias is determined by rank ordering the individual percent differences of the QC checks and taking the 25th and 75th percentiles. If the signs of the 25th and 75th percentiles match, then the sign of the bias is defined as that sign (if both +, the bias is flagged as “positive”; if both –, the bias is flagged “negative”). If the signs do not match (one +, one –) the bias is not flagged. The initial ECB bench tests of the analyzer resulted in bias calculations of less than 5% at all levels. If the bias is greater than ± 10% at the 95 percent probability level, then trouble-shoot the instrument and/or return it the manufacturer.

$$AS = \sqrt{\frac{n \times \sum_{i=1}^n |d_i|^2 - (\sum_{i=1}^n |d_i|)^2}{n(n-1)}}$$

$$AB = \frac{1}{n} \times \sum_{i=1}^n |d_i|$$

Linearity: The EPA recommends that the trace level SO₂ instrument be linear over the range of 0.2 ppb to 100 ppb.

Drift: Drift, the change in response to a known quantity (zero or span) over time, is measured over a 24-hour period of operation without adjustment. The trace level SO₂ instrument guidance from US EPA does not require a documented drift test. However, zero drift should be less than 0.20 ppb per 24-hour period. Span drift should be less than ±1% full scale. This test should be documented, if performed, by ECB staff in the instrument logbook.

NO Rejection Ratio: The EPA recommends that the NO rejection ratio be at least 100:1, i.e., 100 ppb of NO must produce a response equivalent to no more than 1 ppb of SO₂.

2.34.1.5 On-site Installation

The ECB will install the monitor and its support equipment. Acquiring access to a site, and approval of the site is the responsibility of the DAQ regional office and the Projects and Procedures Branch. Internet/wireless service and electrical power should be secured, along with any needed permits, new wiring, etc., prior to installation of the monitoring equipment. The site location must meet the applicable site requirements and be approved by the Projects and Procedures Branch Supervisor and the EPA. Refer to Figure 7: Plumbing and Wiring Diagram for Monitoring Setup for general schematic of the set-up.

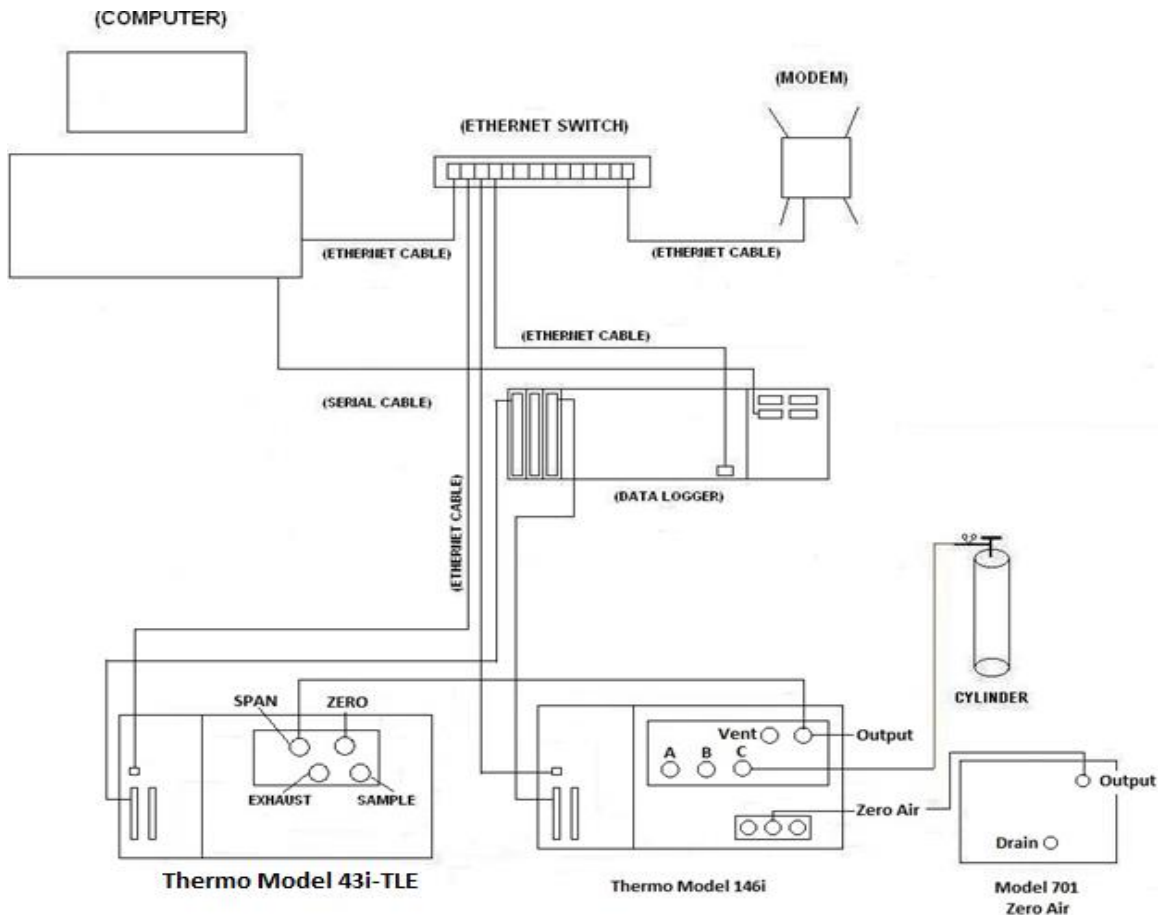


Figure 7: Plumbing and Wiring Diagram for Monitoring Setup

A) Installation

1. Verify that the building/shelter is sound and that the heating/cooling system is working and can control the temperature at a preset level within the range of 20-30 °C. The sampling probe and lines must be FEP Teflon, or of an equivalent material. Lines must be clean, and have a sample residence time of less than 20 seconds. The inlet line should be wrapped with removable polyurethane foam in order to prevent condensation. In extreme cases, heat tape may be used. For continuous, year-round sites, the probe and funnel will be changed at least every two years during the audit (even calendar years).
2. Install one end of a short piece of vent line (any type of ¼" tubing) to the analyzer monitor exhaust fitting and place the other end through an opening to the outside of the shelter to vent the instrument (do not obstruct).

WARNING: Do not plug in the monitor, calibrator, modem, data logger, and interface box until all cables are connected. ELECTRICAL SHOCK AND/OR EQUIPMENT DAMAGE MAY OCCUR OTHERWISE.

3. Connect the monitor, modem, data logger, and computer as shown in Figure 7: Plumbing and Wiring Diagram for Monitoring Setup. Observe polarity markings. Connect all instruments and support equipment power cords to a grounded surge suppressor, connected to a 115v AC, 60 Hz grounded receptacle.
4. Configure the data logger and PC software, including the scheduler, to run auto poll/cal. Data loggers can be ESC Model 8816's or 8832's. The ECB verifies that the system can be accessed remotely by computer from the ECB lab. (It is the responsibility of the region to program AV-Trend for the polling of information that is specific to the needs of the region.)
5. Verify that all operational events, such as solenoid on/off are working. Bleed the calibration cylinder regulators and lines to purge the calibration system. It is *imperative* that precautions be taken when putting low concentration SO₂ cylinders into service. The *regulator* must be *fully purge* to avoid any chance of moisture affecting the delivery of SO₂ from the cylinder. Check the analog outputs on the instrument after performing the operational checks.

B) **Check and Set Computer Time and Date**

The times for the data logger, AV-Trend, and computer must be EASTERN STANDARD TIME. Additionally, they must have the same time and be synched to the NIST time provider in Colorado (± 1 minute). A task can be set up in AV-Trend to ensure that the times are synchronized.

1. Click on the date and time in the lower right corner of the computer screen.
2. Select **Change Date and Time** settings.
3. Select the **Internet Time** tab, and then press the **Change Settings** button.
4. Check the box that states **Synchronize with an Internet Server**. From the server drop down menu, select time.nist.gov.
5. Press **Update Now**.
6. Select **OK** to exit. The created task scheduler named "**Clock Sync**" in AV-Trend will sync the data logger and computer times.

If the data logger time is not within 1 minute of NIST time but it matches the computer time, then there is a problem with the computer time. Either the computer is not synchronizing properly with the NIST time or the clock is drifting too much and needs to be synchronized more often or the computer needs to be replaced. Call the ECB and they will help identify the issue and tell you what to do to correct it.

If the data logger time is not within 1 minute of NIST time and it does not match the computer time and the computer matches NIST time, then there is a problem with the synchronization of the data logger time with the computer. Call the ECB and they will give you instructions on how to synchronize the data logger to the computer.

Sources for getting the correct time:

1. Call the ECB and ask for the NIST time
2. Call the NIST Colorado time at (303) 499-7111
3. Correct time loaded into cell phone
4. Correct time website, <http://nist.time.gov>

C) Leak Check the System

Before running an installation zero or span, leak check the SO₂ sampling system.

For the Monitor SAMPLE port:

1. Disconnect the sample line from the analyzer and block the opening with a leak-tight cap.
2. Press **"Menu"** and use the arrow buttons to go to **Diagnostics**. Select **"Pressure"** and press **"Enter"**. The pressure reading should be dropping. Wait until pressure drops below 180 mm Hg. The flow should also be at zero.

NOTE: If the pressure has not dropped below 180 mm Hg within three minutes, immediately remove the cap. Check to see that all fittings are tight and input lines are not cracked or broken. Do not cap off the line for more than three minutes or the system may pressurize.

For the Monitor SPAN port:

1. Disconnect the calibrator line from the analyzer above the filter and block the opening with a leak-tight cap.
2. Press **Menu** and use the arrow buttons to go to **Pressure** and press **"Enter"**. The pressure reading should be dropping (flow should also go to zero). Wait until pressure drops below 180 mm Hg.

NOTE: If the pressure has not dropped below 180 mm Hg within three minutes, the leak check has failed. Immediately remove the cap. Check to see that all fittings (leak-tight cap, filter housing, and filter inlet/outlet fittings) are tight and input lines are not cracked or broken and re-test. **Do not cap off the line for more than three minutes or the system may pressurize.** If the leak check passes, remove the cap, reconnect the calibrator line to the span port and the sample line to the sample inlet. Clear the zero mode by aborting the zero cal.

D) Running an Installation Zero-Span-QC Check

In order to ensure the monitoring equipment was not damaged in transit or during installation, run a three point check of the instrument to include; the zero point (**z**), the span point relative to the instruments expected operating range (**s**) and the QC calibration check point (**p**) (usually identified as span 3, see Section 2.34.1.4). This procedure **IS NOT** a substitute for the initial calibration to be performed by the region. The ***“installation Z-S-P” is intended as a field check*** to verify the instrument (and its associated components) has not suffered a catastrophic mishap from lab bench to field shelter. The sampling system should introduce, and the instrument should successfully recognize, SO₂ concentrations at expected ambient levels. If a problem is found with any component of the sampling system, the installers will contact the region and the ECB office with the details to initiate a resolution.

The Zero point will include checking the analog output (Z1) to the data logger The Span point check will include checking the analog output (SP1) to the data logger Whenever possible the data logger (Z1/SP1) should be adjusted as close to correct as possible.

In addition to new site installation, the “installation zero-span-precision” check ***will be performed*** any time a component potentially affecting calibration is replaced, modified, or repaired including:

1. Monitor replacement/repair
2. Calibrator replacement/repair
3. Zero air system replacement/repair
4. Cylinder swap-out
5. Lamp replacement

The installation z-s-p after any of these events **does not** replace the region’s responsibility to perform a full calibration (and hence “take ownership” of the monitor), but is intended to boost the overall confidence in the equipment at the transition point between the ECB and the Operator(s).

E) Communication Confirmation

Whenever possible, it is recommended that the ECB office be contacted at the conclusion of an installation, and asked to poll the site to insure that it is ‘reachable’. Before leaving the site, sign out and reset the scheduler for normal operation.

2.34.1.6 Routine Maintenance

A) Thermo 43C-TLE or 43i-TLE Analyzer

Periodic maintenance procedures should be performed when necessary to ensure proper operation of the trace level analyzer. Maintenance includes preventive, routine,

and corrective tasks. The ECB is expected to be entirely responsible for the corrective maintenance issues and to assist with preventative and routine maintenance that may fall outside the regions' comfort levels or capabilities. All maintenance activities must be documented by ECB personnel in the monitor's maintenance logbook.

Step-by-step procedures for all maintenance activities need to be followed as presented by the manufacturer in the instrument's operation manual ("Model 43C Trace Level Pulsed Fluorescence SO₂ Analyzer", P/N 13399, August 23, 2004).

Items requiring maintenance by ECB are:

1. Replacing the UV lamp (performed when lamp voltage approaches 1200 volts)
2. Replacing the printed circuit boards (performed when operational problem is traced to a particular component)
3. Leak Checks (performed after filter changes or when sample flow drops below 0.35 LPM as determined during bi-weekly QC checks)
4. Replacing the pump or pump diaphragm (performed when sample flow of 0.35 – 0.65 LPM or a vacuum of at least 180 mm Hg during a leak check cannot be achieved as determined during bi-weekly QC checks)
5. Clean Optic Bench as needed
6. Replace PMT as needed
7. Clean/Replace capillary (if sample flow falls below 0.35 LPM)

B) Thermo 146C or 146i Site Calibrator

Periodic maintenance and/or adjustment to the Model 146C or 146i is required to ensure proper operation. Refer to the "Thermo Model 146C or 146i Calibrator" SOP (as separate document, Section 2.3.4.1). Except for mass flow controller re-certification, which occurs every 12 months, the following maintenance activities are performed only when the calibrator malfunctions as determined by the site operator:

1. Leak Checking
2. Solenoid Replacement
3. Circuit Board Replacement
4. Mass Flow Controller Replacement
5. Replacement of DVM
6. Internal Adjustments
7. Certification of Mass Flow Controllers (reference the Calibrator SOP Section 2.3.4)

After conducting any maintenance, "up" the data logger channel (enable/mark channel online), document the work done in the site logbook (and instrument logbook if appropriate), and flag the data.

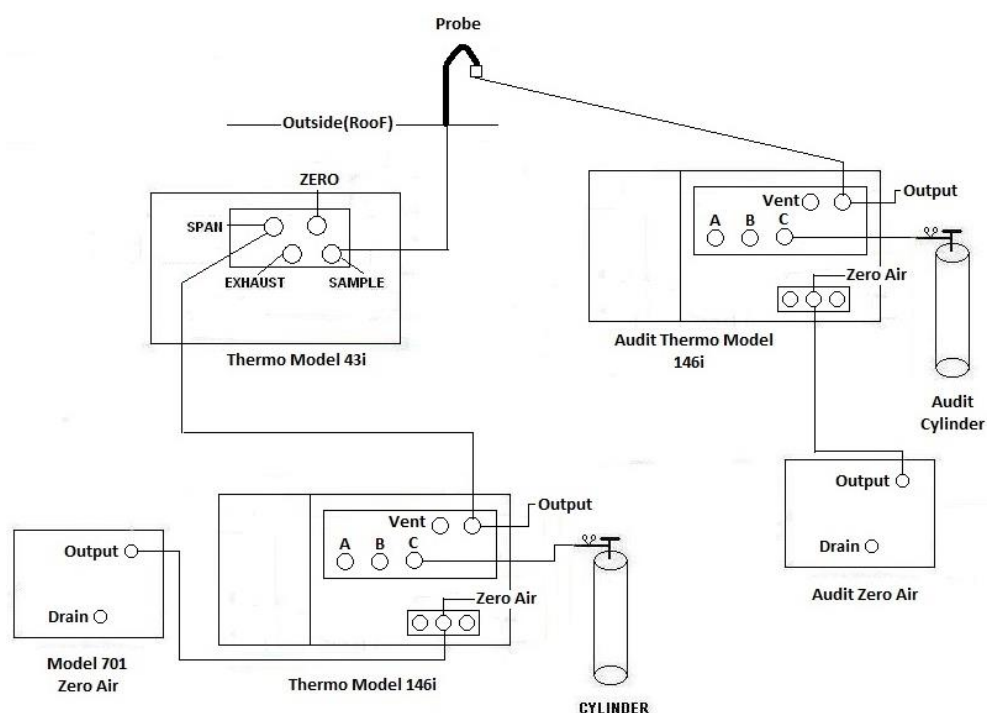


Figure 8: Audit Plumbing Diagram for Monitoring Setup

2.34.1.7 Accuracy Auditing

Each analyzer must be audited by the ECB at least once per year. At least one quarter of the state's monitors must be audited each calendar quarter. The audit must be performed using a calibrator and gas cylinder standard that is different from the calibrator and gas cylinder standard that is used for routine calibration and one point QC checks. The ECB accomplishes this task by performing a through-the-probe audit. Several routine items that shall be included in the audit are:

- Security of the Building
- Site/Building Temperature (document NIST temperature and data logger temperature on the audit form)
- Condition of the Sample Line, Probe, and Funnel (replace as required)
 - The sample line will be leak tested at least once a year, and when the monitor is installed or when the line is replaced
 - The concentration of sampled gas measured through the probe should be compared to the concentration when the line is run directly into the back of the instrument at least once per year
- Normal Operating Status of the Monitoring System

- A)** The auditor must not be the operator who conducts the routine monitoring, calibrations, and analysis. **Conduct the audit before making adjustments.** The monitor must operate in its normal sampling mode, and the audit gas must pass through the existing particulate filter. The difference between the actual concentration of the audit test gas and the concentration indicated by the analyzer is used to assess the accuracy of the monitoring data.
- B) The audit calibrator must be certified against a primary standard every nine months.** Allow audit calibrator to equilibrate at least one-half to one hour before challenging the monitor. Check and review the site temperature and the ambient SO₂ concentration for the day (never conduct an audit during an ambient SO₂ exceedance or a potential ambient SO₂ exceedance).
- C)** Down (disable) the SO₂ channel.
- D)** Connect output of audit calibrator to probe funnel on roof as shown in Figure 8: Audit Plumbing Diagram for Monitoring Setup. The probe funnel setup should be connected as shown in Figure 9: Funnel and Probe Audit Setup Diagram. Perform and record the following audit calibrator checks:
1. Verify the audit calibrator certification is current
 2. Power ON - Verify calibrator has power by observing the LED screen
 3. Perform Audit - At least four concentrations levels, plus zero, must be introduced to an analyzer being operated in the zero to 100 ppb range. Concentration ranges are given below:

| Analyzer Span, ppb | 100 |
|---------------------------------|------------|
| Audit Zero (ppb) | 0.00 |
| Audit Gas 1 concentration (ppb) | 50-99 |
| Audit Gas 2 concentration (ppb) | 20-49 |
| Audit Gas 3 concentration (ppb) | 3-4.9 |

Review and record, on an audit form, the current site temperature taken during audit.

4. For each audit setting, record on the audit form; the instrument concentration and five corresponding stable one-minute data logger averages
5. If the audit results are greater than $\pm 10\%$ of the expected value, contact the ECB supervisor and print out the last available auto calibration routine
6. Disconnect the audit calibrator line from the outside probe, up the data logger channel, and log out

- E)** If the audit results are suspicious or unacceptable, the ECB supervisor will initiate the investigation of the problem and will notifying the responsible regional chemist and the Projects and Procedures Branch Supervisor of the issue.
- F)** The Investigation can include, but is not limited to:
1. Examination of the audit equipment
 2. Review of the calibration records (both auto and manual)
 3. Confirming the audit results with a follow-up audit

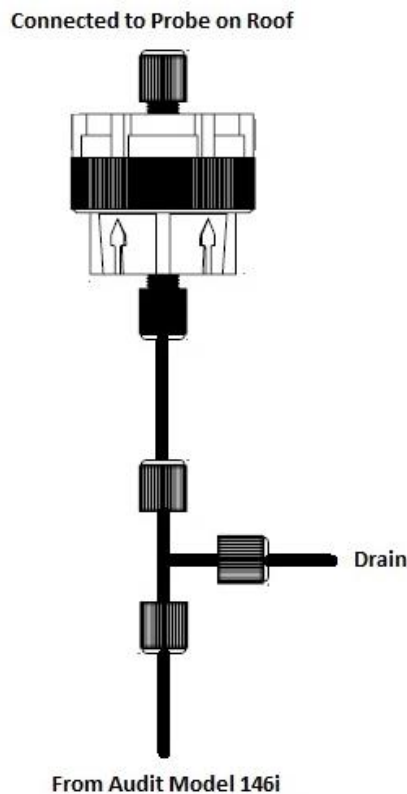


Figure 9: Funnel and Probe Audit Setup Diagram

2.34.1.8 Trouble Shooting

High sensitivity SO₂ analyzers are subject to many factors that can cause inaccurate measurements or down time. The following table summarizes common problems, their possible causes and their possible solutions.

Table 2: Instrument Trouble Shooting for High sensitivity SO₂ Analyzers

| Problem | Possible Cause | Possible Solution |
|---------|----------------|-------------------|
|---------|----------------|-------------------|

| | | |
|-------------------------------|---------------------------|---------------------------|
| Noisy Output | Defective Power Supply | Replace Power Supply |
| | Dirty Optics | Clean Optical Bench |
| | PMT Failure | Replace PMT |
| High positive Zero Drift | Defective bandpass filter | Replace filter |
| | PMT failure | Replace PMT |
| No response to span gas | UV source defective | Replace UV lamp |
| | UV power supply defective | Replace power supply |
| | PMT failure | Replace PMT |
| Zero output at ambient levels | Pump failure | Check Pump |
| | UV lamp failure | Replace UV lamp |
| | UV power supply defective | Replace power supply |
| | PMT failure | Replace PMT |
| No flow through analyzer | Pump failure | Replace/rebuild pump head |

2.34.1.9 Revision History

- A) Added an Approval Sign-Off page.
- B) Added Section 2.8.1.8: Revision History to the document.
- C) Updated and unified outlining throughout document.
- D) Added clarification on common acronyms throughout document.
- E) Updated instrument models throughout document. Thermo 43C-TLE Sulfur Dioxide Analyzer is now Thermo 43C-TLE or 43i-TLE Sulfur Dioxide Analyzer. Thermo 146c Dynamic Gas Calibrator is now Thermo 146C or 146i Dynamic Gas Calibrator. Model 111 Zero Air Pack is now Teledyne API Model 701 Zero Air Generator.
- F) Removed back up data logger (BUDL) and changed primary data logger (PDL) to data logger throughout document.
- G) Changed name of polling software from EDAS to AV-Trend throughout document.
- H) Added Figure 2: Principles of Operation for the Thermo Model 43i-TLE Analyzer.
- I) Added reference to Section 2.3.5: Zero Air Pack Certification and Auditing to 2.34.1.3 Section C.
- J) Updated Table 1 to reflect current practices.
- K) Added Section D, Local, Remote, and Service Modes, to 2.34.1.4, with instruction on switching between modes on the analyzer.
- L) Added instruction to Section 2.34.1.4.E regarding monitor range setting for the 146i-TLE analyzer.

- M) Added instruction to Section 2.34.1.4.F regarding how to verify the lamp voltage for both the 146C-TLE and 146i-TLE monitors.
- N) Added Section 2.34.1.4.N, with performing a multi-point calibration at the ECB prior to putting monitor in the field.
- O) Revised Section 2.34.1.4.O with the correct Method Detection Limit procedure.
- P) Added Figure 4: Thermo Model 43i-TLE Flowchart.
- Q) Added Figure 6: Thermo Model 146i Flowchart.
- R) Updated the requirements for a site in Section 2.34.1.5.
- S) Updated Section 2.34.1.5.B with instruction on how to synchronize the computer clock with NIST time. Also added instruction to create a task in AV-Trend that will synchronize the computer clock, the data logger, and the analyzers. Removed the requirement that the site computer must be set 5 minutes slower than the data loggers.
- T) Added further instruction to Section 2.34.1.5.C with leak checking the sampling system.
- U) Combined Figures 4 and 5 into Figure 7: Audit Plumbing Diagram for Monitoring Setup.
- V) Added Figure 8: Audit Plumbing Diagram for Monitoring Setup
- W) Added information to Section 2.34.1.7 regarding replacement and care of sample line and probe.
- X) In Section 2.34.1.7.A, changed frequency of comparison between audit calibrator and primary standard to nine months from quarterly.
- Y) Added instruction to Section 2.34.1.7.D for setting up and conducting a through the probe audit and added a table with current audit gas concentrations.
- Z) Added Figure 9: Funnel and Probe Audit Setup Diagram.

Appendix A

EXAMPLE OF MDL CALCULATION PROCEDURE

| | Day 1 | Day 1 | Day 2 | Day 2 | Day 3 | Day 3 | Day 4 | Day 4 | Day 5 | Day 5 |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 | 0.2145 | 0.247 | 0.2143 | 0.287 | 0.2571 | 0.225 | 0.2344 | 0.2446 | 0.2153 | 0.2363 |
| 2 | 0.2612 | 0.2553 | 0.2532 | 0.2753 | 0.2934 | 0.2125 | 0.221 | 0.2182 | 0.2142 | 0.2056 |
| 3 | 0.2695 | 0.2303 | 0.2626 | 0.2573 | 0.272 | 0.2055 | 0.2374 | 0.2638 | 0.2417 | 0.2276 |
| 4 | 0.2391 | 0.2466 | 0.2339 | 0.2912 | 0.2009 | 0.2132 | 0.2839 | 0.2795 | 0.2594 | 0.2446 |
| 5 | 0.2704 | 0.2412 | 0.2141 | 0.2446 | 0.2381 | 0.3152 | 0.2318 | 0.1953 | 0.2726 | 0.2334 |
| 6 | 0.2188 | 0.2106 | 0.2625 | 0.2514 | 0.2579 | 0.2652 | 0.2282 | 0.2591 | 0.3068 | 0.1977 |
| 7 | 0.2324 | 0.2743 | 0.2543 | 0.226 | 0.2872 | 0.2332 | 0.2632 | 0.288 | 0.1736 | 0.2743 |
| 8 | 0.2766 | 0.2773 | 0.2482 | 0.2569 | 0.3174 | 0.2968 | 0.1748 | 0.2374 | 0.2183 | 0.2323 |
| 9 | 0.2395 | 0.2744 | 0.2709 | 0.2265 | 0.25 | 0.2397 | 0.1923 | 0.2226 | 0.2186 | 0.2607 |
| 10 | 0.2551 | 0.1866 | 0.2929 | 0.2277 | 0.2361 | 0.2173 | 0.2474 | 0.2632 | 0.2284 | 0.2174 |
| 11 | 0.1879 | 0.234 | 0.2064 | 0.2758 | 0.1907 | 0.1751 | 0.2188 | 0.2538 | 0.2225 | 0.1936 |
| 12 | 0.2693 | 0.2145 | 0.2513 | 0.2684 | 0.2249 | 0.216 | 0.2468 | 0.2534 | 0.2055 | 0.2478 |
| 13 | 0.2719 | 0.2008 | 0.2191 | 0.2199 | 0.2397 | 0.2552 | 0.258 | 0.2113 | 0.2613 | 0.2639 |
| 14 | 0.2264 | 0.2499 | 0.2679 | 0.1927 | 0.2426 | 0.2577 | 0.2812 | 0.226 | 0.2574 | 0.2456 |
| 15 | 0.2356 | 0.2662 | 0.2525 | 0.2425 | 0.2268 | 0.2516 | 0.2619 | 0.2605 | 0.2512 | 0.2572 |
| 16 | 0.261 | 0.2464 | 0.2085 | 0.2738 | 0.205 | 0.2206 | 0.2108 | 0.2648 | 0.2332 | 0.224 |
| 17 | 0.2405 | 0.2211 | 0.2323 | 0.2579 | 0.2678 | 0.2369 | 0.2469 | 0.2704 | 0.1986 | 0.1876 |
| 18 | 0.2149 | 0.197 | 0.2265 | 0.276 | 0.2594 | 0.2159 | 0.251 | 0.1838 | 0.2083 | 0.1965 |
| 19 | 0.2518 | 0.2033 | 0.2747 | 0.2638 | 0.2448 | 0.1972 | 0.2349 | 0.213 | 0.2345 | 0.2063 |
| 20 | 0.2434 | 0.2066 | 0.2723 | 0.2418 | 0.3207 | 0.2066 | 0.2535 | 0.2599 | 0.2824 | 0.1553 |
| Avg | 0.24 | 0.237 | 0.249 | 0.246 | 0.251 | 0.237 | 0.238 | 0.243 | 0.242 | 0.228 |

Average of averages = 0.241

Standard Deviation of Averages = 0.007

MDL = student t (n-1) x STDEV

Student t for n-1 readings = 2.821 MDL= 2.821 x 0.007

MDL= 0.0193

In the above example, the average of the last 20 sixty-second averaged concentration values for each of the ten data collection periods is calculated. The result will be a total of ten data points (point one being 0.240, point two being 0.237 and so forth). Next, calculate the average and standard deviation of the ten data points (average of ten data points is 0.241 and the standard deviation is 0.007). Finally, multiply the standard deviation by the “student’s *t*” value (2.821) for “n-1” data points (10-1=9). The standard deviation times the student’s *t* is the MDL value (0.0193 ppb). In probability and statistics, the t-distribution or Student’s *t* is a probability distribution that arises from trying to estimate the mean (or average) of a normally distributed population when the sample size is small such as in this case. The average and standard deviation can be automatically calculated by using the “functions” commands within a spread sheet such as Excel. Student’s *t* values can be obtained from most statistical handbooks or from the internet.