

**Section I - Electronics and Calibration Branch (ECB)**  
**Responsibilities**

**TRACE LEVEL Sulfur Dioxide QA Plan for Thermo**  
**Environmental 43C-TLE**  
**Revision 1**

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### **2.34.1 Equipment Selection and Procurement, Description of the Thermo-Environmental Inc (TEI) Model 43C-Trace Level Enhanced (TLE) Sulfur Dioxide Analyzer**

The State of North Carolina 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 (SO<sub>2</sub>). The standard ambient level SO<sub>2</sub> monitors (TEI 43C), 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”) SO<sub>2</sub> monitors are now being required for the developing network of 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. One such monitor is the Thermo-Environmental Model 43C-Trace Level Enhanced (TLE) SO<sub>2</sub> monitor which was granted the status of “Approved Equivalent Method” on July 22, 2005.

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  $\pm 0.1$  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. Post-evaluation activities, such as on-site installation, routine maintenance, and accuracy auditing, are also discussed.

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

The Model 43C-TLE is based on the same principles as the 43C instrument. 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 Model 43C-TLE through the **SAMPLE** bulkhead, as shown in 'Figure 2.34.1-1 Principles of Operation'. 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 SO<sub>2</sub> molecules pass through the hydrocarbon kicker unaffected. The sample flows into the fluorescence chamber, where pulsating UV light excites the SO<sub>2</sub> 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 SO<sub>2</sub> molecules. As the excited SO<sub>2</sub> molecules decay to lower energy states, they emit UV light that is proportional to the SO<sub>2</sub> concentration. The bandpass filter allows only the wavelengths emitted by the excited SO<sub>2</sub> molecules to reach the photo multiplier tube (PMT). The PMT detects the UV light emission from the decaying SO<sub>2</sub> 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 43C-TLE outputs the SO<sub>2</sub> 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.

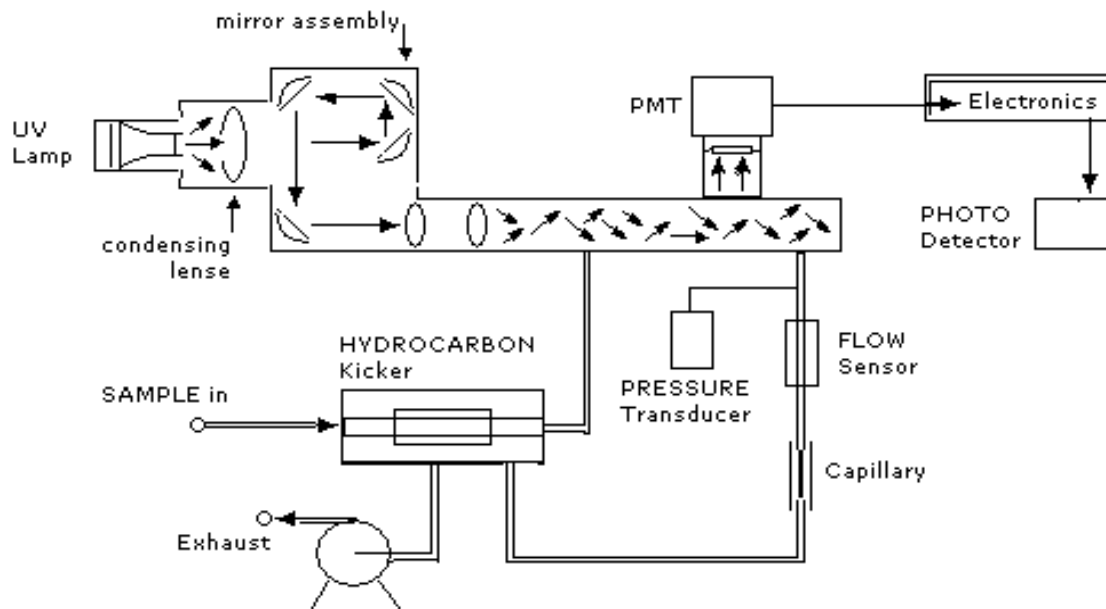


Figure 2.34.1-1 ; Principles of Operation

**Model 43C-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	0.10 ppb (60 sec. avg. time) (to be determined experimentally for each unit)
Zero Drift (24 hour)	Less than 0.2 ppb
Span Drift	± 1% per week
Response Time	110 sec. (60 sec. avg. time)
Linearity	± 1% of full-scale
Sample flow rate	0.5 liters/min. (standard)
Interferences (EPA levels)	less than lower detectable limit except for the following: NO < 1ppb; m-Xylene < 1ppb; H <sub>2</sub> O < 3% of reading
Operating temperature	20°-30°C (may be safely operated over the range of 0°-45°C)
Power requirements	105-125 VAC @ 50/60 Hz 100 Watts
Physical dimensions	16.75" (W) X 8.62" (H) X 23" (D)
Outputs	Selectable voltage 4-20 mA isolated, 4-20 mA non-isolated RS-232/485 Interface
Precision	calculated for each instrument deployed as specified by US EPA. Must have a 95 percent probability limit for precision of ± 15% 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 <sub>2</sub> , September 2005)

**2.34.1.2 Description of TEI Model 146C and Zero Air Supply**

• **TEI Model 146C Calibrator**

The Model 146C Calibrator supplies the required levels of SO<sub>2</sub> to perform zero, precision, span checks and multipoint calibrations. The Model 146C is operated remotely from the data logger to perform zero, precision, and span checks. The Model 146C is an accurate mass flow controlled gas dilution system that meets the 40 CFR 50 requirements of ± 2 % accuracy. SO<sub>2</sub> gas (usually in an inert gas such as nitrogen) from a NIST traceable Protocol certified cylinder (of ± 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.

- **Model 111 Zero-Air Supply System**

The purpose of the Model 111 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, SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>3</sub>, 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 SO<sub>2</sub> instrument. Because the goal of the instrument is to detect/characterize SO<sub>2</sub> 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.

### **Zero Air Pack Certification**

The generation of purified ("clean") air is critical to the operation of the trace analyzers that are to be used with the NCore program. The information provided by the EPA at the Precursor Gas Work Shop on 6/5/07, states that "zero air" should contain a concentration of SO<sub>2</sub> that is less than the lower detectable level (LDL) for the instrument or approximately 0.1 ppb. TEI Model 111 "Zero Air Packs" are currently being used as a constant supply of clean air. CO, SO<sub>2</sub> and NO<sub>y</sub> are scrubbed from ambient air using Purafil (oxidizes NO to NO<sub>2</sub>), charcoal (removes NO<sub>2</sub> and SO<sub>2</sub>) and Hopcolite (removes CO). Additionally, water vapor is removed using silica gel. The silica gel is changed as needed (indicated by color change) while the other materials are changed annually. The delivery pressure should be set to between 30 and 40 psig. A capillary "bleed" is installed to allow a constant low flow of air through the system when not requiring air for calibration. Each unit installed at a site will be certified (audited) annually on site to show that the zero air being generated meets the specifications given above. Two issues need to be addressed: 1) how to generate zero air to meet these criteria; and 2) how to verify that the levels meet the criteria. This will be accomplished as follows:

- a) Set up a Model 111 with new chemicals. Prepare a second set of chemicals (connected in series, Purafil, then Charcoal and then Hopcolite) and attach to the outlet of the Model 111. Then connect the outlet of the second set of chemicals to the inlet of a 146C calibrator as per standard operation. Let this configuration generate zero air (air flowing) for 24 hours to condition the system.
- b) Remove the second set of chemicals and connect the Model 111 to the 146C and introduce zero air to the trace level instrument. The instrument should be allowed to warm up for 24 hours. Introduce the zero air to the analyzer through the sample inlet port for a time sufficient to allow the readings to stabilize, set the instrument zero, and record the next 30 one-minute averages. This test is typically performed at a low flow rate (nominally 0.5 LPM) coming from the 146C calibrator. Calculate the average and standard deviation of the 30 values.
- c) Repeat b) after adjusting the flow rate from the 146C to be nominally 15 LPM (high flow rate). Review the data looking for any difference between instrument readings collected at the low flow and the high flow.

- d) To the outlet of the Model 111, connect the second set of chemicals and connect the outlet of this second set to the 146C. Introduce zero air to the trace level instrument. Repeat b) and c) essentially looking for differences between low and high flow rates with dual scrubbers in place. Also look for differences between the values obtained with single scrubbing and with dual scrubbing.
- e) Determine if there is a significant difference between the two averaged values for single scrubbing/two flow rates, the two averaged values for dual scrubbing/two flow rates and the two averaged values for single scrubbing vs. dual scrubbing. The data will be reviewed to determine if dual scrubbing produces “cleaner” air than single scrubbing.
- f) The next task is to compare the Model 111 (with either single or dual scrubbing) zero air to an independent source. This independent source will be a cylinder of commercially available “Ultra Pure Zero Air. If the analyzer responds differently to the two sources, then the one with the lowest response will be designated as the system to be used to “audit” other “zero air” systems.

The ECB will audit the “zero air” systems of each NCore site on an annual basis, using the device (Model 111 or compressed gas cylinder) selected based on the procedures given above. The selected device will be temporarily substituted for the one in service. The zero air system being audited should produce SO<sub>2</sub> concentrations within  $\pm 0.5$  ppb of the concentration generated by the audit device. If the audited zero air system produces a concentration of 0.5 ppb or greater than that of the audit device, the source of contamination should be identified and/or the chemicals changed out.

### • **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., 6 months for standards at concentrations less than 40 ppm). These are termed “Protocol” gas.

The Major Components of a Typical Trace-level SO<sub>2</sub> Monitoring System Include:

- Thermo Environmental 43C TLE SO<sub>2</sub> Analyzer;
- Thermo Environmental 146C Dynamic Gas Calibrator;
- Zero Air Pack and Certified Protocol SO<sub>2</sub> cylinder;
- ESC/AGILAIRE Model 8816 or 8832 Data Logger (primary and/or secondary depending on location); and
- A dedicated site PC and Modem.

### **2.34.1.3 Initial Laboratory Startup of the Model 43C TLE**

The ECB shall conduct and document, initial operational tests before deploying an instrument. Refer to the TEI 43C TLE Instruction Manual. 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 QA/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 Headquarters on an annual basis.

### **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.

### **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:

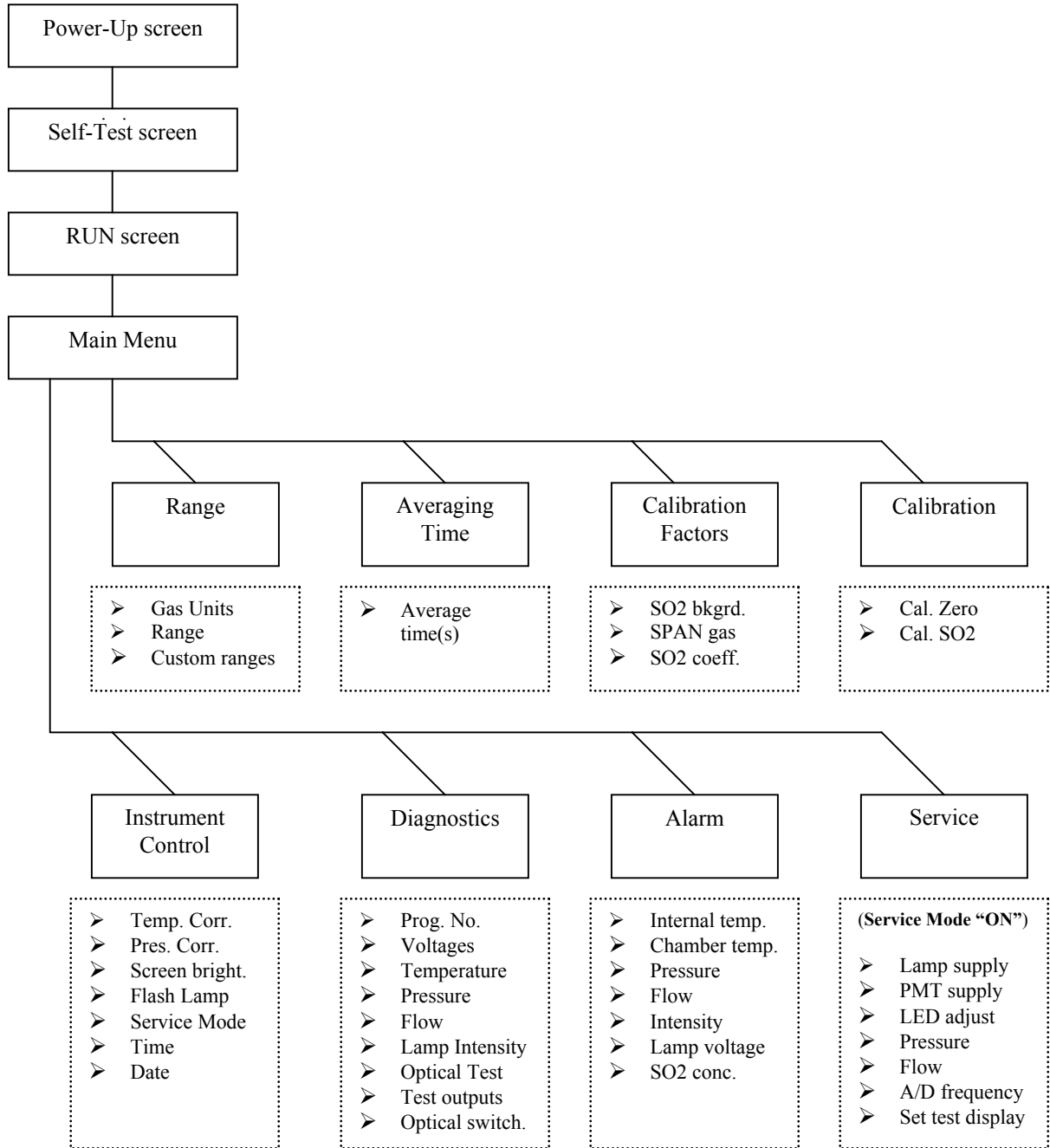
- Calibration at 3 levels plus zero on a range of 0-100 ppb (see Table 1 below);
- Verification, over a 4-5 day period, that the 24 hour zero and span drift do not exceed the specified 0.20 ppb and  $\pm 1\%$  full scale limits, respectively;
- Installation of a Teflon particulate filter on the instrument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

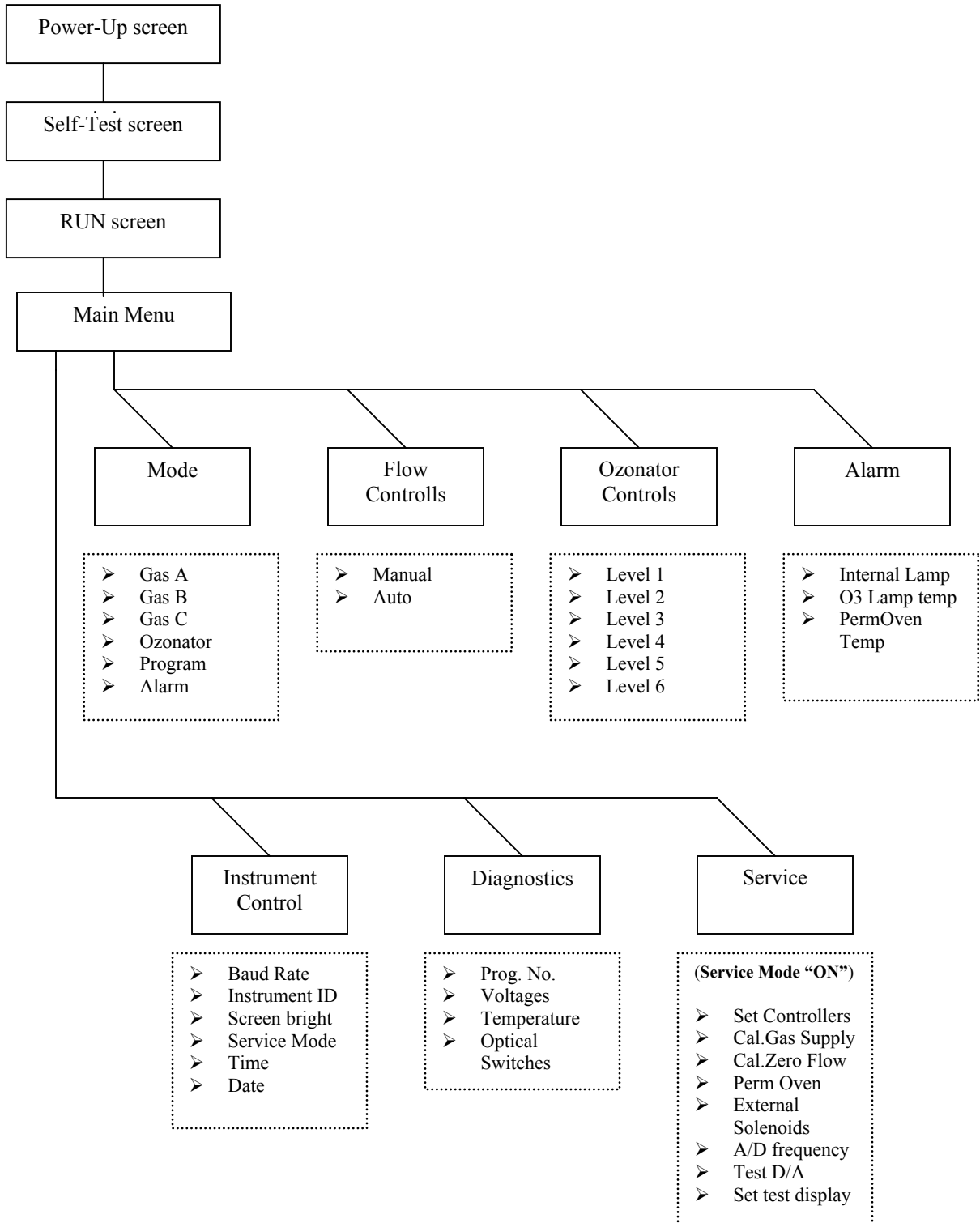
	<b>Range % full scale</b>	<b>Nominal Concentration, ppb</b>
<b>Span 1</b>	70-90	80
<b>Span 2</b>	40-60	50
<b>Span 3<sup>A</sup></b> (QC, precision point)	10-50 ppb	10
<b>Zero</b>	0.0	0.0

<sup>A</sup> The one point QC precision point must be between 10 and 50 ppb

**43C TL-E Menu Flow**  
**(Figure 2.34.1-2)**



**146C Calibrator Menu**  
**(Figure 2.34.1-3)**



### **Initial Laboratory Checkout**

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 SO<sub>2</sub> gas cylinder to the port labeled C. Refer to 'Figure 2.34.1-3; TEI Model 146C Flowchart' for a description of the instrument menu. Using the 146C front panel menu - Press **Enter** to go into "Local" mode. Activate the zero mode as follows:

1. Press the ↓ pushbutton to place \* / cursor, at 'gas offline'.
2. Using → , select **SO<sub>2</sub> C**, press **Enter**.
3. Press the ↓ pushbutton to move the \* / cursor, at **Span** line,
4. Using → , select **Span 0**, and press **Enter**.

#### **• Range Setting**

Set the "range" setting on the 43C-TLE 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**. Using the 43C-TLE front panel, Choose **Range** from the Main Menu choices and do the following:

1. Press the ↑ and ↓ pushbuttons 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.

#### **• 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.

#### **• Concentration Units**

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

#### **• Averaging Time**

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

#### **• Calibration Factors**

Leave SO<sub>2</sub> background and coefficient at zero initially. They will automatically be corrected after zero/span points are run. Discussion of these factors is covered in later sections (Operator, calibration).

• **Diagnostic Checks / Settings**

The following diagnostic menu settings for the TEI 43C TLE Analyzer:

<u>Parameter</u>	<u>Min.</u>	<u>Max.</u>
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	2.8V	3.2V
Internal Temperature	15 °C	35 °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

• **Alarm Settings**

The following Alarm Limits are used in TEI 43C TLE Analyzers:

<u>Parameter</u>	<u>Min.</u>	<u>Max.</u>
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
Lamp Voltage	950 V	1200 V
SO <sub>2</sub> Concentration	0 ppb	100 ppb

• **Leak Check and Calibration**

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 move ↑ and ↓ buttons and 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 and retest. 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 EDAS data logging system, or by activating the span port via pin 1 and 2 on the solenoid activation barrier strip. Perform the following steps:

1. Disconnect the calibrator line from the span port on the 43C TLE and connect the line above the filter where the sample line was. Block off the span port on the back of the 43C-TLE with the leak-tight cap.
2. Press **Menu** and move ↑ and ↓ buttons and 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. Proceed to “multi point calibration”. Document in the logbook. If leak check fails, troubleshoot the instrument and conduct any necessary repairs and repeat the leak check.

- **Multi-Point Calibration**

Conduct a manual full calibration along with linearity checks over the course of a few days to indicate instrument stability and repeatability. Although the trace level sulfur dioxide monitoring system is very similar to the standard compliance-type systems (TEI 43C), 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.

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 SO<sub>2</sub> 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 43C TLE, 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, version 4 and below with an example provided in Appendix A:

Method Detection Limit Procedure

- 1) Each trace level SO<sub>2</sub> monitor that is placed in service at a 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 regional office. However, the ECB 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 spread sheet to a disk and provide to the PPB/DMSSB 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 SO<sub>2</sub> the precision is required to be ±15% at the 95 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. ( $X_{0.1, n-1}$  is the 10th percentile of a chi-squared distribution with  $n-1$  degrees of freedom)

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{n(n-1)}} \cdot \sqrt{n-1 / X^2_{0.1, n-1}}$$

also described as,

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1, n-1}}}$$

The initial ECB bench tests of the 43C-TLE 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 SO<sub>2</sub> molecules colliding with N<sub>2</sub>, O<sub>2</sub> 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.

$$| \textit{bias} | = AB + t_{0.95, n-1} \cdot [ AS / \sqrt{n} ]$$

The term *AB* is the mean of the absolute values of the individual *d<sub>i</sub>* 's. The number of comparisons is *n*. The value *t<sub>0.95, n-1</sub>* is the 95<sup>th</sup> quantile of a t-distribution with n-1 degrees of freedom. The quantity *AS* is the standard deviation of the absolute values of *d<sub>i</sub>*'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 25<sup>th</sup> and 75<sup>th</sup> percentiles. If the signs of the 25<sup>th</sup> and 75<sup>th</sup> 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 43C-TLE resulted in bias calculations of less than 5% at all levels. If the bias is greater than ± 15%, then trouble-shoot the instrument and/or return it to the manufacturer.

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

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

**Linearity:** The EPA recommends that the trace level SO<sub>2</sub> 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 SO<sub>2</sub> 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 SO<sub>2</sub>.

- **Inventory**

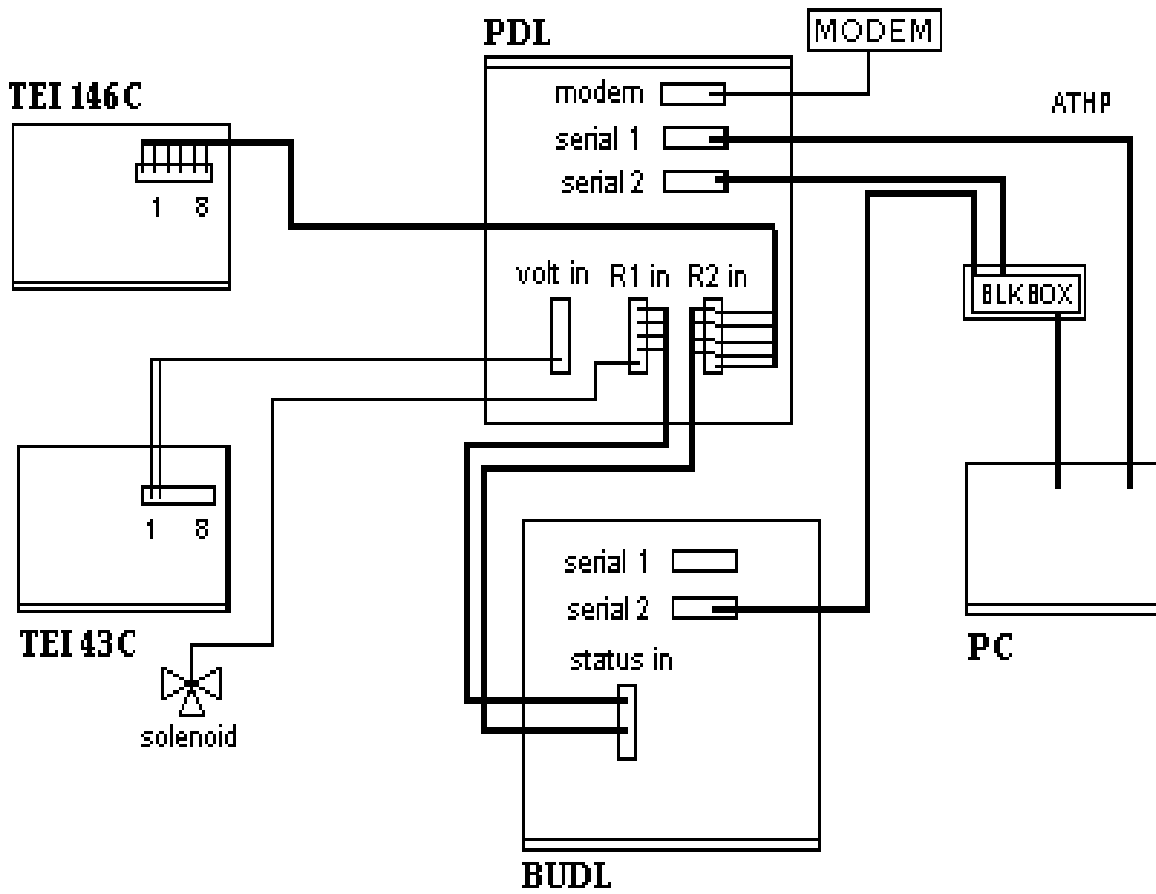
After the ECB personnel have tested and approved the unit, the unit shall be added to the fixed asset system. For each monitor, apply an inventory decal FAS # and complete an inventory load sheet showing the planned monitor location. Submit the inventory load sheet to the Branch Supervisor.

#### **2.34.1.4 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. Phone service and electrical power should be secured by the regional office, 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 2.34.1-4 - Wiring Diagram for Monitoring Setup' and 'Figure 2.34.1-5 - Plumbing Diagram for Monitoring Setup'; for general schematic of the set-up.

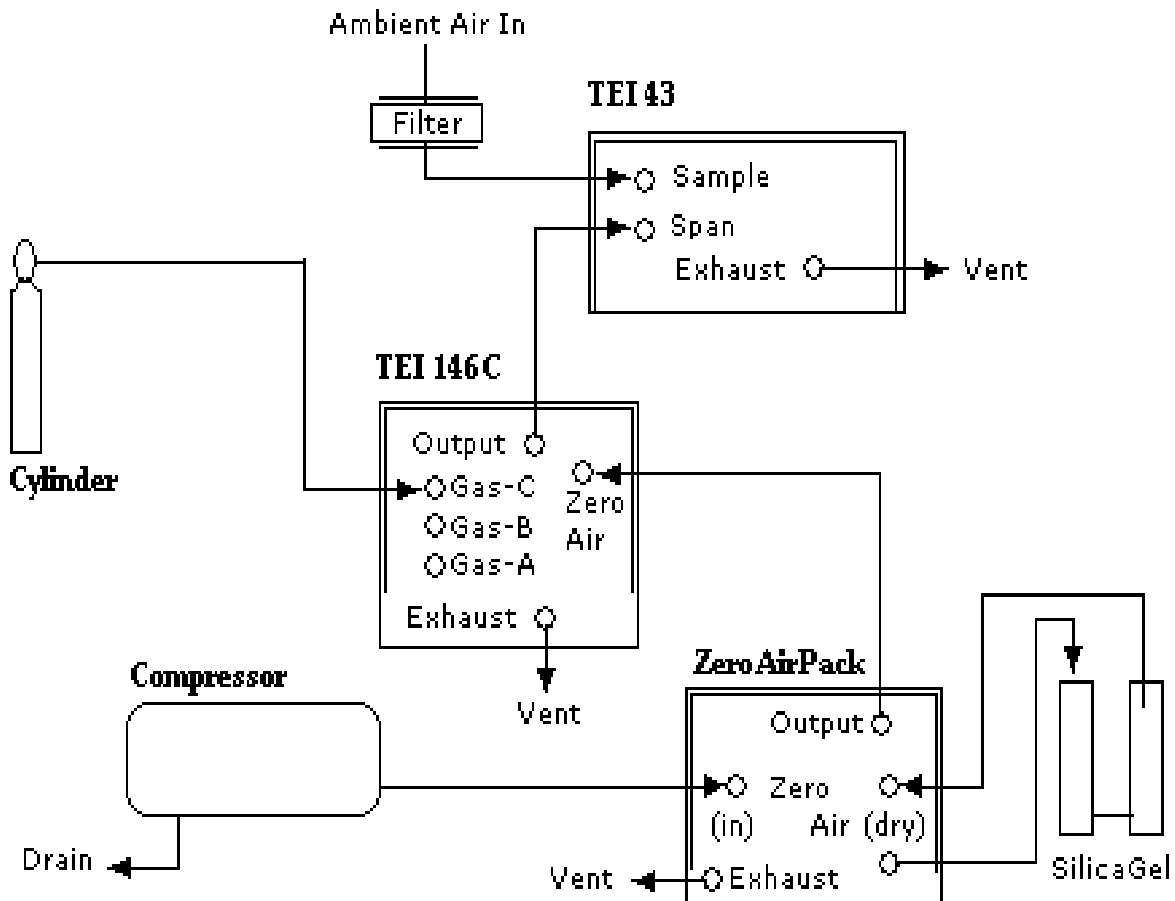
**Wiring Diagram for Monitoring Setup**

(Figure 2.34.1-4)



**Plumbing Diagram for Monitoring Setup**

(Figure 2.34.1-5)



• **Installation**

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).

Install one end of a short piece of vent line (any type of ¼" tubing) to the 43C TLE 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.**

Connect the monitor, modem, data logger, backup data logger, and computer as shown in 'Figure 2.34.1-4; Wiring Diagram' and 'Figure 2.34.1-5; Plumbing Diagram. 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.

Configure the modem to auto answer on the first ring and to operate at 2400 bps. Configure the data loggers and PC software, including the scheduler, to run auto poll/cal. Primary and Backup data loggers can be ESC Model 8816's or 8832's. The ECB verifies that the system can be accessed remotely by phone from the ECB lab. (It is the responsibility of the region to program the E:DAS for the polling of information that is specific to the needs of the region.)

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 SO<sub>2</sub> cylinders into service. The *regulator* must be *fully purge* to avoid any chance of moisture affecting the delivery of SO<sub>2</sub> from the cylinder. Check the analog outputs on the instrument after performing the operational checks.

- **Set Data Loggers and Computer Time and Date**

The times for the PDL, BUDL, and computer must be EASTERN STANDARD TIME. The "synchronization" function in the ESC data logger software will not be employed by the central EDAS computer or the regions' polling computers in order to avoid possibly short-changing data sets by constantly resetting clocks before a full hour can be polled.

**NOTES: The BUDL and PDL must have the same time and be synched to the NIST time provider in Colorado (± 1 minute). Sources of the NIST time include: cell phones-most automatically synch to local NIST time; calling Colorado (303-499-7111); setting a watch to the NIST website (<http://nist.time.gov/>) within 24hrs of visiting the site. The site computer must be set 5 minutes *slower* than the data loggers to ensure that a full hour of data is retrieved/stored during regularly scheduled polling.**

- **Leak Check the System**

Before running an installation zero or span, leak check the SO<sub>2</sub> sampling system as described earlier under “Leak Check and Calibration” (see page 13 of 28).

- **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 2.34.1.3). 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, SO<sub>2</sub> 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 primary data logger and checking and adjusting the low-output engineering units to the back-up data logger. The Span point check will include checking the analog output (SP1) to the primary data logger and checking high-output engineering units to the back-up data logger. Whenever possible the PDL (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:

- Monitor replacement/repair
- Calibrator replacement/repair
- Zero air system replacement/repair
- Cylinder swap-out
- 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).

- **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.

### **2.34.1.5 Routine Maintenance**

- **TEI 43C TLE Analyzer**

Periodic maintenance procedures should be performed when necessary to ensure proper operation of the 43C TLE. Maintenance includes preventive, routine, and corrective tasks. Refer to the TEI 43C TLE operation manual for preventive maintenance details (see Sections 5 and 7 of the manual). 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 SO<sub>2</sub> Analyzer", P/N 13399, August 23, 2004). Always down / disable the PDL and BUDL data channels.

Items requiring maintenance by ECB are:

- Replacing the UV lamp (performed when lamp voltage approaches 1200 volts);
- Replacing the printed circuit boards (performed when operational problem is traced to a particular component);
- Leak Checks (performed after filter changes or when sample flow drops below 0.35 LPM as determined during bi-weekly QC checks);
- 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);
- Clean Optic Bench as needed;
- Replace PMT as needed; and
- Clean/Replace capillary (if sample flow falls below 0.35 LPM).

- **TEI 146C Site Calibrator**

Periodic maintenance and/or adjustment to the Model 146C is required to ensure proper operation. Refer to the "Thermo Model 146C Calibrator" QA/Operational guidelines (as separate document, Section 2.3.4.1). Except for mass flow controller re-certification, which occurs every 9 months, the following maintenance activities are performed only when the calibrator malfunctions as determined by the site operator:

- Leak Checking
- Solenoid Replacement
- Circuit Board Replacement
- Mass Flow Controller Replacement
- Replacement of DVM
- Internal Adjustments

- Certification of Mass Flow Controllers (see section 2.3.4.1 of the 146C Calibrator QA Manual)

After conducting any maintenance, “up” the PDL and BUDL channels (enable/mark channels online), document the work done in the site logbook (and instrument logbook if appropriate), and flag the data.

### **2.34.1.6 Accuracy Auditing**

Each analyzer must be audited by the ECB at least once per year. At least ¼ 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. Several routine items that shall be included in the audit are:

- Security of the Building
- Site / Building Temperature
- Condition of the Sample Line, Probe, and Funnel (replace as required)
- Normal Operating Status of the Monitoring System

**The audit calibrator must be certified against a primary standard quarterly.** 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.

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 SO<sub>2</sub> concentration for the day (never conduct an audit during an ambient SO<sub>2</sub> exceedance or a potential ambient SO<sub>2</sub> exceedance). Down (disable) the SO<sub>2</sub> channel.

Connect the audit calibrator at the analyzer inlet. 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 red indicator light and by listening for the pump.
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. These concentrations must be between :
  - 60 - 80 ppb,*
  - 30 - 50 ppb,*
  - 6 - 10 ppb,*

*3 –5 ppb and  
a zero (0.0) ppb.*

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 (PDL & BUDL).
5. If the audit results are greater than  $\pm 15\%$  of the expected value, contact the ECB supervisor and print out the last available auto calibration routine.

Reconnect the ambient sample line to the filter on back of analyzer, “up” the data loggers, reset the scheduler, and sign out.

Calculate the percent difference ( $d_2$ ) at each concentration level (except zero) using the following equation:

$$d_2 = \frac{C_m - C_{ACT}}{C_{ACT}} \times 100$$

where:  $C_m$  = SO<sub>2</sub> concentration measured (average of 5 reading from the SO<sub>2</sub> channel, in ppb)  
 $C_{ACT}$  = Actual Concentration of audit gas produced by the audit calibrator (Output ppb). If  $d_2$  exceeds  $\pm 15\%$ , the regional auditor must initiate checks, troubleshooting, and recalibration.

Record  $d_2$  on the audit form/worksheet and in the instrument logbook. Verify that the form is correct and complete, and forward to the ECB supervisor. 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. Investigation can include, but is not limited to:

- Examination of the audit equipment
- Review of the calibration records (both auto and manual)
- Confirming the audit results with a follow-up audit

#### **2.34.1.7 Trouble Shooting**

High sensitivity SO<sub>2</sub> 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 SO<sub>2</sub> Analyzers**

<b>Problem</b>	<b>Possible Cause</b>	<b>Possible Solution</b>
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

**Appendix A**

EXAMPLE OF MDL CALCULATION PROCEDURE

	1	2	3	4	5	6	7	8	9	10
	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
21	0.2701	0.25	0.2513	0.2707	0.2515	0.2254	0.2403	0.2607	0.2503	0.2029
22	0.261	0.2528	0.2109	0.2301	0.2575	0.269	0.235	0.2635	0.2582	0.2555
23	0.2197	0.2557	0.2687	0.2272	0.2414	0.2608	0.2248	0.2331	0.2812	0.2484
24	0.1807	0.2094	0.2624	0.2557	0.2793	0.2395	0.2291	0.2294	0.2816	0.2399
25	0.2366	0.2991	0.2524	0.2333	0.2216	0.268	0.2707	0.215	0.2651	0.2475
Avg	0.240	0.237	0.249	0.246	0.251	0.237	0.238	0.243	0.242	0.228

avg of avgs= 0.241

stdev of avgs=0.007

MDL = student t (n-1) x STDEV

student t for n-1 readings = 2.821

MDL= 2.821x 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.