

4.06 METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE (SO₂) by ULTRAVIOLET FLOURESCENCE

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4.06 SULFUR DIOXIDE BY PULSED ULTRAVIOLET FLOURESCENCE

4.06.0 METHOD SUMMARY

This principle is based on detection of the characteristic fluorescence released by the sulfur dioxide molecule when it is radiated by ultraviolet light. This fluorescent light is also in the ultraviolet region of the spectrum, but at a different wavelength than the incident radiation. The fluorescent wavelengths usually monitored are between 190 and 230 nm. In this region of the spectrum, there is relatively little quenching of the fluorescence by other molecules occurring in ambient air. As in flame photometry, the light is detected by a photo multiplier tube (PMT) that, through the use of electronics, produces a voltage proportional to the light intensity and SO₂ concentration.

The fluorescent light reaching the PMT is usually modulated to facilitate the high degree of amplification necessary. Some analyzers mechanically "chop" the incident irradiation before it enters the reaction chamber. This process is accomplished by a fan-blade-like chopper rotating at a constant speed, which alternately blocks and passes the light to the chamber. Other instruments electronically pulse the incident light source at a constant rate.

Potential interferences to the fluorescent technique include any species that either quench or exhibit fluorescence. Both water vapor and oxygen strongly quench the fluorescence of SO₂ at some wavelengths. Where water vapor presents a problem, it can be removed by a dryer within the instrument. In most analyzers, the water interference is minimized by careful selection of the incident radiation wavelength. Difference in oxygen concentrations between the two matrices can become significant if a low-level SO₂-in-nitrogen cylinder gas is diluted to prepare a calibration standard. In such a case, the nitrogen in the pollutant flow stream may "dilute" the oxygen in the dilution air stream, significantly decreasing the oxygen concentration. This situation can be avoided by keeping the concentration of SO₂ in the cylinder gas high enough that the nitrogen contributed by the pollutant flow stream is insignificant with respect to the total flow volume.

Aromatic hydrocarbons such as naphthalene exhibit strong fluorescence in the same spectral regions as SO₂ and are major interferences. These aromatics must be removed from the sample gas stream by an appropriate scrubber upstream of the reaction chamber. The scrubbers may operate at ambient or elevated temperature. Certain elevated-temperature scrubbers, however, have the potential for converting ambient hydrogen sulfide (which normally does not interfere with the fluorescent technique) into SO₂. In these cases, the hydrocarbon scrubber must be preceded by a scrubber for H₂S.

The operating range for this method is 0-0.5ppm or 0-1.0ppm, depending upon each analyzer's "EPA Designated Reference or Equivalent Method" operating range.

Analyzers used for monitoring SO₂ in the ambient air must be USEPA-designated reference or equivalent method SO₂ analyzers.

The method detection limit is 2% of full scale (i.e., 0.01ppm for 0-0.5ppm range and 0.02ppm for 0-1.0ppm range).

4.06.1 SAMPLE PROBE AND SHELTER CRITERIA

4.06.1.A SITING REQUIREMENTS

The probe siting criteria as discussed below must be followed to the maximum extent possible. It is recognized that there may be situations when the probe siting criteria cannot be followed. If the siting criteria cannot be met, this must be thoroughly documented with a written request for a waiver which describes how and why the siting criteria differs. This documentation should help to avoid later questions about the data. These siting criteria are discussed in 40 CFR Part 58, Appendix E.

The spatial scales of representativeness used in this appendix (i.e., micro, middle, neighborhood, urban, and regional) are defined and discussed in 40 CFR Part 58, Appendix D. Pollutant-specific probe siting criteria generally apply to all spatial scales except where noted otherwise. Specific siting criteria that are prefaced with a "must" are defined as a requirement, however, exceptions may be applied through other provisions found in 40 CFR Part 58, Appendix E. Siting criteria that are prefaced with a "should" are defined as a goal to meet for consistency, but are not a requirement.

Horizontal and Vertical Probe Placement--The height of the SO₂ inlet probe must be 3 to 15 meters above ground. The distance of the inlet probe from any supporting structures must be greater than one meter vertically or horizontally.

Spacing from Obstructions--No furnace or incineration flues or other minor sources of SO₂ should be nearby. The separation distance is dependent on the height of the flues, type of waste or fuel burned, and sulfur content of the fuel. If the inlet is located on a roof or other structure, it must be at least 1 meter from walls, parapets, penthouses, etc.

The inlet probe must be located away from obstacles and buildings. The distance between the obstacle(s) and the inlet probe must be at least twice the height that the obstacle protrudes above the inlet probe. Sampling stations that are located closer to obstacles than this criteria allows should not be classified as a neighborhood scale, since the measurements from such a station would closely represent middle scale stations. Therefore, stations not meeting this criteria should be classified as middle scale.

Airflow must be unrestricted in an arc of at least 270 degrees around the inlet probe, and the predominant wind direction for the season of greatest pollutant concentration must be included in the 270 degree arc. If the probe is located on the side of a building, 180 degrees of clearance is required.

Spacing from Trees and Other Considerations--The inlet probe should be at least 20 meters from the dripline of trees. However, where trees can be classified as an

obstruction (i.e., the distance between the tree(s) and the sampler is less than twice the height that the tree(s) protrude above the sampler), the sampler must be placed at least 10 meters from the dripline of the obstructing tree(s).

4.06.1.B SAMPLE TRAIN (PROBE AND GAS LINE) MATERIALS

Sampling train (probes, gas lines, manifolds) must be constructed of borosilicate glass, stainless steel (s.s.316 or better), FEP Teflon, or equivalent material, to minimize possible reaction(s) and degradation of SO₂. The use of integrating flasks on the sample manifold is strongly discouraged. Even with nonreactive gas line materials, reactive particulate matter is deposited on sample train walls over time. Therefore, the time it takes the gas to transfer from the probe inlet to the sampling device is also critical. Residence times should not exceed 20 seconds. In addition, other sample train specifications are listed below:

Sample Probe and Gas Manifold Material-Borosilicate Glass, FEP Teflon (or equivalent), stainless steel (s.s.316 or better).

Filter--Particulate filter(s), if used, must be borosilicate glass, FEP Teflon, stainless steel (s.s. 316 or better), or equivalent material. The use of particulate filters on the sample manifold and inlet line is optional and left to the discretion of the user. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. The user is cautioned, however, that particulate matter concentrated on a filter may cause erroneous SO₂ measurements. For this reason, filters should be changed frequently. In addition, a particulate filter may only be used in the sample line (between the gas manifold and the analyzer). Prior to routine use, it is incumbent on the user/manufacturer to prove that an in-line filter does not bias the reliability of the analyzer to measure actual concentrations of SO₂ in ambient air. These checks must be conducted at calibration, and at periodic intervals thereafter, to test the integrity of the sample introduction system. It is up to the agency operating these monitors to design and implement these checks. As with all instrument checks, documentation is a required QA activity.

Valve(s) Material-pyrex glass, FEP Teflon, or stainless steel (s.s.316 or better).

Gas Lines--Gas lines, including sample, span, and calibration lines, must be either borosilicate glass, FEP Teflon, or stainless steel (s.s.316 or better). Sample lines should be kept as short as possible to reduce sample gas residence time. All fittings must be compatible (e.g., both male and female ends either stainless steel or Teflon). Sample Train Gas Residence Time (from test gas introduced at sample inlet to first upscale analyzer response)-10 seconds preferred, 20 seconds acceptable. Demonstration of compliance may be physical testing or calculated. The residence time within the sampling line should be minimized to: 1) reduce the possibility of reactive gas interactions, and 2) to minimize SO₂ adsorption on the surface of the lines.

Further information and requirements regarding probe and manifold materials and designs can be found in "*Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, Ambient Air Specific Methods, Section 2.0.2.2.1 Design of Probes and Manifolds.*"

4.06.1.C SHELTER

The monitoring shelter's role in quality assurance is to provide a temperature-controlled environment in which the sampling equipment can operate at optimum performance. The mean shelter temperature should be within 15 to 30°C. Daily fluctuations should not exceed $\pm 2^\circ\text{C}$ ($\pm 4^\circ\text{F}$). A continuous recording thermograph should be installed at the shelter to continuously record daily fluctuations in temperature. Fluctuations greater than $\pm 2^\circ\text{C}$ may cause the electronic components of the analyzer to drift and may introduce error into the data. For this reason, excursions outside the specifications should be flagged to indicate possible questionable data.

In addition to a temperature-controlled environment, it is highly recommended that all power supplied to sensitive monitoring equipment be conditioned. Appropriate selection of a power conditioner for the monitoring area will minimize equipment failure and loss of data.

4.06.2 SO₂ INSTRUMENT CALIBRATION

The accuracy and validity of measurement data recorded by air monitoring equipment depends on the quality assurance procedures used. The primary procedure is dynamic calibration, which determines the relationship between the observed and the actual values of the variable being measured.

In dynamic multi-point calibration, an instrument's responses are related to successive gas samples of known concentrations. A minimum of four reference points and a zero point are recommended to derive the calibration relationship. The "true" value of each SO₂ cylinder gas or SO₂ permeation tube must be traceable to a National Institute of Standards and Technology-Standard Reference Material (NIST-SRM), Certified Reference Material (CRM), or NIST Traceable Reference Material (NTRM).

4.06.2.A STANDARD REFERENCE MATERIALS

To assure data of desired quality, the SO₂ measurement process must be under defined control limits, and any systematic errors, when combined with random variations in the measurement process, must result in a small level of uncertainty.

Good data quality requires documentation of the quality control checks and performing independent audits of the measurement process. These tasks necessitate maintaining good data recording practices and using materials, instruments, and measurement procedures traceable to reference standards of known quality. To establish traceability, multiple measurements must be made of standard reference materials (primary,

secondary, and/or working standards), and process control procedures must be established. More specifically, working calibration standards must be traceable to standards of higher accuracy, such as NIST-SRM, CRM, or NTRM. Procedures for certification of an SO₂ working standard against NIST-SRM, CRM, or NTRM are found in section 4.06.2.C, Certification of SO₂ Working Standards.

4.06.2.A.1 ZERO AIR

Dry zero air, verified to be free of contaminants that would cause detectable responses in the SO₂ analyzer, may be purchased in high-pressure gas cylinders or generated with commercially available clean air systems. Care should be taken to ensure that an ambient concentration of carbon dioxide (CO₂), approximately 350 ppm CO₂, is maintained in any zero air source used.

4.06.2.A.2 SULFUR DIOXIDE (SO₂) CYLINDER GAS

SO₂ Concentration Standard--SO₂ cylinder gas must contain a known concentration of SO₂ in Nitrogen (N₂). SO₂ cylinder calibration gases must be certified traceable to either a NIST-SRM, CRM, or NTRM cylinder gas.

4.06.2.A.3 SULFUR DIOXIDE (SO₂) PERMEATION DEVICES

SO₂ Concentration Standard--SO₂ permeation device(s) suitable for generating SO₂ concentrations at the required flowrates over the required concentration range. The SO₂ permeation devices must be certified traceable to either a NIST-SRM, CRM, or NTRM source.

4.06.2.B CALIBRATION PROCEDURES

Either of two methods may be used for dynamic multi-point calibration of the analyzer. These are:

Method A: Calibration by Dynamic Dilution of a High Concentration SO₂ Gas Cylinder, or

Method B: Calibration by Dynamic Dilution of an SO₂ Permeation Tube.

NOTE: Analyzers used for monitoring SO₂ in the ambient air must be USEPA-designated reference or equivalent method SO₂ analyzers.

The SO₂ analyzer will require a new calibration whenever one of the following conditions occur:

- six months has elapsed since the last calibration;

- replacement of any major component(s) of the SO₂ analyzer and monitoring system;
- the monitor fails a performance audit;
- a level 1 zero/span SO₂ gas check is not within tolerance of the corresponding zero/span gas concentration.

NOTE: If the monitor fails a precision quality control (QC) check, the instrument response should be used only as an indicator of the analyzer's performance (no analyzer adjustment can be taken based solely on an analyzer's response to a precision gas). A level 1 zero/span QC check must be performed immediately thereafter to determine if the analyzer is within calibration tolerance.

- physical relocation of the monitor;
- an interruption of more than three days in analyzer operation; and
- any other indication such as excessive zero or span drift, or malfunction of the SO₂ monitoring system.

4.06.2.B.1 CALIBRATION FREQUENCY

To ensure accurate measurements of SO₂ concentrations, calibrate the analyzer at the time of installation, and recalibrate it:

1. no later than three months after the most recent calibration or performance audit which indicated analyzer response to be acceptable; or
2. following any repairs which might affect its calibration.

Following any repairs which might affect the analyzer's calibration, the zero and span should be checked to determine if a calibration is necessary. If the analyzer zero and span drifts do not exceed the calibration limits in figure 4.06-9 (located at the end of section 4.06.3), a calibration need not be performed. If either the zero or span drift exceeds its respective calibration limit, investigate the cause of the drift, take corrective action, and calibrate the analyzer.

An activity matrix for calibration procedures is presented in figure 4.06-6 at the end of this section.

4.06.2.B.2 CALIBRATION METHOD A

Calibration by Dynamic Dilution of a High Concentration SO₂ Gas Cylinder

In this method, a high concentration certified SO₂ in N₂ cylinder is diluted with dry zero air to generate incremental concentrations of SO₂ to calibrate the analyzer's SO₂ responses.

Before using the assembled and/or purchased systems for SO₂ calibrations, your system must:

1. Use an SO₂ standard gas traceable to a NIST-SRM, CRM, or NTRM. This high concentration SO₂ gas cylinder (preferably in the range of 30-50 ppm and the remaining balance N₂) is the primary sulfur dioxide (SO₂) calibration source from which all subsequent SO₂ dilutions (calibration standards) are made;

NOTE: All regulators used in a calibration system (zero air and standard gases) should be cleaned prior to initial use to remove potential manufacturing residues that may contaminate the calibration system.

2. Have a minimum total flow output that exceeds the analyzer flow demand by at least 10 percent;
3. Be capable of generating an SO₂ concentration that is approximately 80% of the upper range limit (URL) of the SO₂ range to be calibrated;
4. For a gas dilution calibrator, be able to generate a series of dilute SO₂ gas standards by diluting the SO₂ output of the SO₂ gas tank (via a system of mass-flow-controllers that regulate both the pollutant and the dilution (zero) air) to the desired SO₂ concentration(s);
5. Have a gas dilution calibration system capable of controlling and regulating flow rates to $\pm 1\%$. Flow rates must be measured with an accuracy of $\pm 2\%$ of stated flow. All parts of the gas dilution calibrator in contact with the SO₂ output must be glass, Teflon (and to a limited amount), s.s. 316 or better quality stainless steel;
6. Have dry dilution (zero) air which is free of interferants that would cause a detectable response in the SO₂ analyzer. This air may be used in generating multi-point calibrations, precision checks, and span checks. This zero air is used to establish and check the analyzer's zero baseline and to dilute the SO₂ gas to the desired concentrations. Zero air may be supplied from cylinders or from a clean air generator;

7. Have pressure regulator(s) for standard SO₂ cylinders that have a nonreactive diaphragm and internal parts, and a suitable delivery pressure;
8. Have a mixing chamber designed to provide thorough mixing of SO₂ and diluent air; and
9. have an output manifold of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

Assemble a dynamic calibration system (consult the manufacturer's manuals for proper set up and operations). See figure 4.06-1 (following section 4.06.2.C.4) for a schematic diagram of a typical calibration system. Ensure that all flow meters are calibrated under conditions of use against a NIST-traceable intermediary primary standard (e.g., soap bubble meter, laminar flow element (LFE), wet test meter.) Correct all volumetric flow rates to 25°C (298°K, 78°F) and 760 mm (29.92 in.) Hg. Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual).

Precautions must be taken to remove O₂ from the SO₂ pressure regulator and delivery system prior to the start of calibration. Failure to do so can cause significant errors in calibration. This problem may be minimized by:

- a. carefully evacuating the regulator after it has been connected to the cylinder, but before opening the cylinder valve;
- b. thoroughly flushing the regulator and delivery system with cylinder gas after opening the cylinder valve; and
- c. not removing the regulator from the cylinder between calibrations unless absolutely necessary.

Connect the strip chart recorder and the data acquisition system (DAS) output cables of the analyzer to the input cables of the strip chart recorder and DAS. All adjustments to the analyzer should be performed based on the appropriate DAS and strip chart recorder readings. References to analyzer responses in the procedures given below refer to DAS and recorder responses.

Prior to calibrating the SO₂ analyzer, verify the accuracy of the DAS and strip chart recorder with a power supply and a volt meter of known accuracy. At a minimum, 80%, 20%, and 0% of analyzer full scale responses should be verified. Both chart recorder and DAS readouts should be within ±2% full scale volts of the analyzer output.

During the calibration, the analyzer must be operating in its normal sampling mode, and the test atmosphere must pass directly to the sample inlet of the analyzer. Ensure that calibration gases are introduced to the analyzer at atmospheric pressure.

Note: During a calibration, the analyzer's response(s) is set to equal the calibration gas concentration. Any external filters, scrubbers, conditioners, etc., may introduce bias to the measurement system. After completing the calibration, conduct a level 1 zero/span quality control check and measure the responses. Reconnect all in-line sample conditioning equipment and repeat the same level 1 zero/span quality control check. The differences between the two measured level 1 zero/span checks should be zero. If not, the in-line conditioners are introducing bias to the measurement system.

1. Record the station name and address on a calibration data form/log book. Identify individual stations by their official names and addresses. Where appropriate, station name and address should be the same as those appearing on the SAROAD or AIRS site identification form for that station. This will help to eliminate any confusion by persons not familiar with the station;
2. Identify the person performing the calibration and record the date of calibration;
3. Identify the analyzer being calibrated. The manufacturer's name, model, and serial number should be recorded;
4. Identify the calibration apparatus used. If the calibrator was purchased, record the manufacturer's name, model, and serial number. Calibrators assembled by the user should be assigned an identification number so that calibrations can be referenced to that particular apparatus;
5. Identify, by supplier and cylinder number, the reference standard to be used. Record the concentration of the calibration gas(es). Do not use cylinders with pressures < 200 psig for calibration. Provide a record of NIST traceability for any cylinder used in a calibration. Include the date, and the name of the person who conducted the reference testing;
6. Select the operating range of the SO₂ analyzer to be calibrated;
7. Record the zero and span knob settings after the calibration is complete so that these settings can be used at a later date to determine changes in the instrument performance characteristics;
8. Record the shelter temperature and barometric pressure at the time of calibration;
9. Use the SO₂ calibration data form (figure 4.06-3) for the systematic recording of data determined during the calibration of the analyzer. Because zero and

calibration adjustments differ between analyzers, consult the manufacturer's manual before calibrating the analyzer;

10. Adjust diluent air (zero air) to provide zero air to the input of the analyzer. Ensure that the total air flow exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the atmospheric dump. For safety concerns, ensure that the atmospheric dump vents to ambient air (outside the monitoring shelter). Measure the diluent air flow using a NIST-traceable intermediate primary standard. Consult the respective manufacturer's standard operating procedures manual for specific directions. Measure and record temperature and pressure of the (in-line) diluent air flow. Correct the actual measured air flow to standard temperature and pressure conditions (STP: i.e., $T_{std} = 298^{\circ}\text{K}$ (25°C , 78°F) and $P_{std} = 760\text{mm Hg}$ (29.92 in.Hg)). Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). Record the standardized diluent air flow (F_D) in column 1 of page 2 (figure 4.06-3);

NOTE: When installing an atmospheric dump, take care not to create a back pressure problem.

11. Allow the analyzer to sample zero air until a stable response is obtained (a response that does not vary by more than $\pm 1\%$ of full scale over a 5 minute time period); then adjust the analyzer zero control to read zero. For a strip chart recorder, offset the analyzer zero to $+5\%$ of the strip chart scale. This facilitates observing negative zero drift. Record the stable zero air response;
12. Determine the 80% upper range limit (URL) SO_2 cylinder gas flow (F_{SO_2}) by solving equation 4.06-1 for F_{SO_2} . Adjust F_{SO_2} to generate an SO_2 concentration of approximately 80% of the URL of the analyzer. Measure the SO_2 flow (F_{SO_2}) using a NIST-traceable intermediate primary standard. Measure and record the SO_2 air stream (in-line) temperature and pressure. Correct the actual measured flow to STP conditions. Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). Record F_{SO_2} under column 2 on the 80% URL line (figure 4.06-3).

$$F_{\text{SO}_2} = \frac{(F_D \times [\text{SO}_2]_{\text{out}})}{([\text{SO}_2]_{\text{std}} - [\text{SO}_2]_{\text{out}})} \quad \text{eqn. 4.06-1}$$

where: $[\text{SO}_2]_{\text{out}} =$ 80% URL SO_2 gas concentration

$[\text{SO}_2]_{\text{std}} =$ SO_2 cylinder gas concentration

$F_{\text{SO}_2} =$ flow rate of SO_2 cylinder gas, sccm

$F_D =$ flow rate of dilution air, sccm;

13. Calculate the exact SO₂ concentration [SO₂]_{OUT} by solving equation 4.06-2.

$$[\text{SO}_2]_{\text{OUT}} = F_{\text{SO}_2} \times [\text{SO}_2]_{\text{STD}} / (F_{\text{SO}_2} + F_0) \quad \text{eqn. 4.06-2}$$

Record the [SO₂]_{OUT} under column 3 on the 80% line (figure 4.06-3);

14. Sample the generated concentration until the SO₂ response has stabilized. Adjust span response for the analyzer SO₂ channel for a balanced output equal to the SO₂ calibration gas.

If substantial adjustment of the SO₂ span control is necessary, recheck the zero and span adjustment in steps 11 and 14. Record the analyzer's SO₂ response under columns 4 and 5 on the 80% URL line (figure 4.06-3);

15. Generate four more, evenly spaced, SO₂ gas concentrations by decreasing F_{SO₂} or increasing F₀. Use equation 4.06-1 to calculate F_{SO₂} flows for 60% URL, 40% URL, 20% URL, and 10% URL SO₂ gas concentrations. Measure SO₂ and diluent flows for the 60% URL, 40% URL, 20% URL, and 10% URL SO₂ gas concentrations as described in steps #10 and #12. Correct all flows to STP conditions. Record the calibration data for each point under the appropriate column in the SO₂ table of figure 4.06-3;
16. Plot the analyzer's SO₂ responses against the corresponding SO₂ calibration gas concentrations. Determine the best straight line by the method of least squares. This can be done with a programmed calculator with this ability, or with the calculation data form presented in figure 4.06-4. Because the time required to perform the calculation manually (using the data form) is considerably longer than that using a programmed calculator, it is suggested that the latter be used when possible; and
17. Calculate the SO₂ linear regression calibration curve. Record the slope (m), y intercept (b), and correlation coefficient (r) for the SO₂ curve. To be considered linear, the correlation coefficient (r) must be ≥ 0.995.

4.06.2.B.3 CALIBRATION METHOD B

Method B: Calibration by Dynamic Dilution of an SO₂ Permeation Tube

The principle: In a permeation device, an easily liquefiable gas such as SO₂ is condensed inside an inert container, all or part of which is constructed from a polymeric material (often Teflon). Gas from the container permeates and passes through the polymer walls at a temperature-dependent rate. The rate of gas effusion (in µg/min) at a constant temperature can be established by gravimetric determination of the weight loss of the permeation device over a known period of time.

In this calibration procedure, the SO₂ analyzer's responses are calibrated with accurately known concentrations of SO₂ that are dynamically produced by diluting the effusion from an SO₂ permeation device, with various flows of clean air to obtain a calibration for SO₂. The SO₂ permeation device used must be certified traceable to either a NIST-SRM, CRM, or NTRM source.

Figure 4.06-2 depicts a diagram of a typical permeation device calibration system. Such systems are also commercially available. All connections between components in the system should be glass, Teflon, or other non-reactive material. The system consists of three functional sections:

1. A controlled-temperature section that houses the SO₂ permeation device and is flushed continuously with purified, dry zero air or nitrogen.
2. A regulated source of clean, dry zero air for dilution of the SO₂ effluent from the permeation device.
3. A dilution-mixing, sampling and exhaust system.

Temperature control is the primary concern in using an SO₂ permeation device to generate known accurate SO₂ calibration standards. For example, a change in temperature of about 0.5°C effects a change in the permeation rate of the device of about four percent. For this reason, it is important that the temperature of the device be maintained at a constant value within ±0.1°C, and that it be closely monitored when the device is in use.

Generally, the SO₂ permeation device is housed in a temperature-controlled glass container that has an entrance and exit port at opposite ends; a glass thermometer accurate to ±0.05°C may be placed beside the device to monitor its temperature. A small fixed zero air or nitrogen flow (about 100 cm³/min) that is maintained at the same temperature as the permeation device flushes the SO₂ out of the device housing into a mixing chamber where the SO₂ is diluted with clean, dry zero air. A valve, e.g., a three-way stopcock, placed at the exit of the device housing, may be used to divert the SO₂ stream to a vent when clean air is required at the manifold for making the necessary zero adjustments to the analyzer.

To maintain the temperature of the permeation device to within ±0.1° C of the desired value, the device and housing may be either placed physically inside a constant temperature chamber, or they can be located externally to the constant temperature chamber with the heat transfer medium circulated around the device housing. The flushing zero air or nitrogen passes through a heat exchanger, e.g., a coil of copper tubing, contained in the constant temperature chamber before passing over the device to adjust its temperature to that of the device.

The diffusion properties of SO₂ have made the construction of stable, accurate SO₂ permeation devices no easy feat. For this reason, due care must be given to their

handling for reliable use. Permeation devices are available from commercial sources and from NIST as a Standard Reference Material (SRMs 1625, 1626 and 1627). These NIST devices have certified permeation rates of approximately 3.7, 2.1, and 0.8 ug/min at about 30°C. Permeation rates of commercial devices vary according to size and recommended operating temperature. Both NIST and commercial manufacturers provide explicit instructions on the use of their respective devices which the user should follow for accurate measurements.

Most permeation devices must equilibrate for at least 24 hours at the certified or operating temperature before the permeation rate stabilizes. Equilibration times may be longer and the permeation rate may be erratic if the device is subjected to extreme temperature variations when not in use. It was mentioned above that the flush gas over the permeation device must be extra dry. This is especially true of the NIST devices and many others which have a large surface for SO₂ permeation. Some commercial devices which have a very small permeating area and are designed to operate at elevated temperatures (40 to 60°C) may not be as susceptible to trace moisture in the flush gas.

If the SO₂ permeation device is to be used as the reference standard for calibration, the permeation rate of the device must be traceable to a NIST SO₂ in N₂ cylinder gas standard SRM or SO₂ permeation device SRM. Procedures for certifying the reference standard against NIST-traceable SO₂ in N₂ or SO₂ permeation standards and for inter-comparing SO₂ working standards are found in section 4.06.2.C.

The dynamic permeation tube dilution calibrator is required to dilute the output from the temperature-controlled permeation system to the desired concentration. All parts in contact with the SO₂ output must be glass or Teflon. The system must be capable of controlling and measuring flow rates to within ±2 percent of stated flow. A small portion of this dried zero air (approximately 100 sccm) is used as the flush gas for the permeation device.

In figure 4.06-2, the zero air stream is split to allow a small air flow to pass continuously over the permeation device. Alternatively, the flush gas could be supplied from a cylinder of pre-purified dry air or nitrogen. Whatever its source, it is extremely important that the flushing stream be extra dry so that moisture does not condense on the surface of the device. Water condensate could react with the effusing SO₂ to form an acid mist, thus changing the SO₂ concentration. A transparent drying column containing a mixture of molecular sieve (e.g., 6-16 mesh, type 4A) and indicating calcium sulfate (e.g., Drierite) has been used effectively as a moisture scrubber on the flush gas line.

Assemble a dynamic calibration system (consult the manufacturer's manuals for proper set up and operations). See figure 4.06-2 (at the end of this method B) for a schematic diagram of a typical calibration system using a dynamic dilution permeation device system. Ensure that all flow meters are calibrated under conditions of use against a NIST-traceable intermediary or primary standard (e.g., soap bubble meter, laminar flow element (LFE), or wet test meter). Correct all volumetric flow rates to 298°K (25°C).

78°F) and 760 mm Hg (29.92 in.Hg). Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). For the permeation calibrator, ensure that the permeation chamber temperature indicator is calibrated under conditions of use to a NIST-traceable intermediary or primary standard. Also ensure that the permeation chamber maintains a stable set point temperature within $\pm 0.1^\circ\text{C}$.

Connect the recorder and DAS output cables of the analyzer to the input cables of the strip chart recorder and DAS. All adjustments to the analyzer should be performed based on the appropriate DAS and strip chart recorder readings. References to analyzer responses in the procedures given below refer to DAS and recorder responses.

Prior to calibrating the SO_2 analyzer, the DAS and strip chart recorder accuracy should be verified with a power supply and a volt meter of known accuracy. At a minimum, 80%, 20%, and 0% of analyzer full scale responses should be verified. Both chart recorder and DAS readouts should be within ± 2 percent full scale volts of the analyzer output.

Calibration gases must be introduced directly to the sample inlet port of the analyzer. Ensure that calibration gases are introduced to the analyzer at atmospheric pressure.

Dynamic calibration systems based upon SO_2 permeation tube dilution systems may be used to calibrate an SO_2 analyzer provided they meet the following requirements:

1. Air flow controllers capable of maintaining constant air flows within ± 2 percent of the required flow rate;
2. Component parts in contact with SO_2 gases of non-reactive and non-adsorbent material (i.e., borosilicate glass, FEP Teflon, or equivalent material);
3. Air flow indicator capable of measuring and monitoring flows with an accuracy of ± 2 percent of the measured flow rate. In addition, each flow meter must be calibrated to a NIST-traceable source (i.e., laminar flow element, soap bubble meter, or wet test meter);
4. Constant temperature chamber (constructed of non-reactive and non-adsorbent material) capable of housing the SO_2 permeation device(s) and maintaining its temperature to within $\pm 0.1^\circ\text{C}$;
5. Temperature measuring device capable of measuring and monitoring the temperature of the SO_2 permeation chamber with an accuracy of $\pm 0.05^\circ\text{C}$;
6. Drier and scrubber(s) to remove moisture and contaminants from the permeation device air system. The use of the drier is optional with SO_2

permeation devices not sensitive to moisture (refer to the supplier's instructions for use of the permeation device);

7. Valve(s) to divert the SO₂ from the permeation device when zero air is required at the manifold. Valve(s) must be constructed of borosilicate glass, Teflon, or other non-reactive material;
8. Mixing chamber, designed to provide thorough mixing of reaction products and diluent air, is constructed of borosilicate glass (preferred) or other non-reactive and non-adsorbent material; and
9. Output manifold constructed of borosilicate glass (preferred), Teflon, or non-reactive and non-adsorbent material. The manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

During the calibration, the analyzer must be operating in its normal sampling mode, and the test atmosphere must pass directly to the sample inlet of the analyzer.

NOTE: During a calibration, the analyzer's response(s) is set to equal the calibration gas concentration. Any external filters, scrubbers, conditioners, etc., may introduce bias to the measurement system. After completing the calibration, conduct a level 1 zero/span quality control check and measure the responses. Reconnect all in-line sample conditioning equipment and repeat the same level 1 zero/span quality control check. The differences between the two measured level 1 zero/span checks should be zero. If not, the in-line conditioners are introducing bias to the measurement system.

1. Record the station name and address on a calibration data form/log book. Identify individual stations by their official names and addresses. Where appropriate, station name and address should be the same as those appearing on the SAROAD or AIRS site identification form for that station. This will help to eliminate any confusion by persons not familiar with the station.
2. Identify the person performing the calibration and record the date of calibration.
3. Identify the analyzer being calibrated. The manufacturer's name, model, and serial number should be recorded.
4. Identify the calibration apparatus used. If the calibrator was purchased, record the manufacturer's name, model, and serial number. Calibrators

assembled by the user should be assigned an identification number so that calibrations can be referenced to that particular apparatus.

5. Identify, by supplier and permeation device number, the reference standard to be used. Record the permeation rate of the calibration standard. Provide a record of NIST traceability for any permeation device used in a calibration. Include the date and name of the person who conducted the referencing.
6. Select the operating range of the SO₂ analyzer to be calibrated.
7. Record the zero and span knob settings after the calibration is complete so that these settings can be used at a later date to determine changes in the instrument performance characteristics.
8. Record the shelter temperature and barometric pressure at the time of calibration.
9. Use the SO₂ calibration data form (figure 4.06-5) for the systematic recording of data determined during the systematic calibration of the SO₂ analyzer. Because zero and calibration adjustments differ between analyzers, the manufacturer's manual should be consulted before calibration is performed.
10. Select sample zero air. Adjust the diluent air flowrate (F_D) to provide zero air to the analyzer sample inlet. Ensure that the total air flow exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the atmospheric dump. For safety concerns, ensure that the atmospheric dump vents to ambient air (outside the monitoring shelter). Measure the diluent air flow (F_D) using a NIST-traceable intermediate primary standard. Consult the respective manufacturer's standard operating procedures manual for specific directions. Measure and record temperature and pressure of the (in-line) diluent air flows. Correct the actual measured air flows to standard temperature and pressure conditions (STP: i.e., $T_{std} = 298^\circ\text{K}$ and $P_{std} = 760\text{mmHg}$). Record the standardized diluent air flow (F_D) in column 1 of figure 4.06-6.

NOTE: When installing an atmospheric dump, take care not to create a back pressure problem.

11. Allow the analyzer to sample zero air until a stable response is obtained (a response that does not vary by more than $\pm 1\%$ of full scale over a 5-minute time period); then adjust the analyzer zero control to read zero. For a strip chart recorder, offset the analyzer zero to -5% of the strip chart scale. This facilitates observing negative zero drift. Record the stable

zero air response under columns 4 and 5 of calibration data form/figure 4.06-5.

12. Select and provide SO₂ gas to the analyzer sample inlet. Adjust F_D to generate an SO₂ concentration approximately 80% URL of the analyzer. Ensure that the total air flow exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the atmospheric dump. Measure the dilution and SO₂ permeation gas flows (F_D and F_P) using a NIST-traceable intermediate primary standard. Measure and record the dilution and SO₂ air streams (in-line) temperatures and pressures. Correct the actual measured flows to STP conditions. Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). Record F_P and F_D under columns 1 and 2 on the 80% URL line (figure 4.06-5).

Determine the 80% upper range limit (URL) dilution gas flow (F_D) by solving equation 4.06-3 for F_D.

13. Calculate the SO₂ concentration using equation 4.06-3 below:

$$[\text{SO}_2]_{\text{out}} = (P \times \text{Km}) / (F_P + F_D) \quad \text{Eqn. 4.06-3}$$

where: $[\text{SO}_2]_{\text{out}}$ = diluted SO₂ concentration supplied to the analyzer

P = permeation rate, µg/min

Km = molar constant for SO₂

= 0.382 (@ 30°C and 760 mmHg)

F_P = air flow across permeation device, sccm

F_D = diluent air flowrate, sccm

Record the 80% URL value in column 3, $[\text{SO}_2]_{\text{OUT}}$

14. Allow the analyzer to sample this 80% URL SO₂ concentration until a stable response is obtained (a response that does not vary by more than ±1% of full scale over a 5-minute time period); then adjust the analyzer's span control to read actual $[\text{SO}_2]$ concentration.

Sample this 80% URL SO₂ concentration until the analyzer's responses have stabilized. Record these values in columns 4 and 5.

15. Adjust F_D to generate four more evenly-spaced SO_2 gas concentrations. Use equation 4.06-3 to calculate F_D flows for 60% URL, 40% URL, 20% URL, and 10% URL SO_2 gas concentrations. Measure F_p and F_D using a NIST-traceable intermediate primary standard. Measure and record the F_p and F_D air stream (in-line) temperature and pressure. Correct the actual measured flows to STP conditions. Record the analyzer's measured $[SO_2]$ response for each concentration. Calculate the SO_2 concentration using equation 4.06-3. Record the values in columns 4 and 5 of figure 4.06-5.

NOTE: An equilibration time of a least fifteen minutes is recommended between concentration changes.

16. Plot the analyzer's $[SO_2]$ responses against the corresponding SO_2 calibration gas concentrations. Calculate the $[SO_2]$ linear regression calibration curve. Record the slope (m), y intercept (b), and correlation coefficient (r) for each calibration curve. The correlation coefficient for each curve must be ≥ 0.995 . If not, correct the problem and recalibrate the analyzer.

4.06.2.C CERTIFICATION OF SO_2 WORKING STANDARDS

NIST-SRM or CRM Sulfur Dioxide (SO_2) in N_2 gas cylinders are typically certified for 2 years. After the certification date has expired, the standard in question must be recertified against currently certified SO_2 NIST-SRMs or CRMs. The SO_2 content of the SO_2 working standard must be periodically assayed against NIST-traceable SO_2 standards. Certification of the SO_2 working standard should be made on a quarterly basis, or more frequently, if required. The following procedures may be used to recertify working SO_2 standards.

4.06.2.C.1 Certification of SO_2 Cylinder Gas Working Standard Against a NIST-traceable SO_2 Standard Cylinder Gas

Use a NIST-traceable standard cylinder gas and the gas dilution calibration procedure (method A) to calibrate the SO_2 responses of the analyzer. Refer to the calibration procedure for exact details; ignore the recommended zero offset adjustments.

Generate several SO_2 concentrations by dilution of the SO_2 cylinder gas working standard. Use the nominal SO_2 concentration of the working standard, $[SO_2]_{NOM}$, to calculate the diluted concentrations. Plot the analyzer SO_2 response (in ppm) versus the nominal diluted SO_2 concentration and determine the slope, S_{NOM} . Calculate the SO_2 concentration of the working standard, $[SO_2]_{STD}$, from equation 4.06-4.

$$[SO_2]_{STD} = [SO_2]_{NOM} \times S_{NOM} \qquad \text{Eqn. 4.06-4}$$

where: $[\text{SO}_2]_{\text{NOM}}$ = expected concentration of the SO_2 cylinder to be certified

If the nominal SO_2 concentration of the working standard is unknown, generate several SO_2 concentrations to give on-scale SO_2 responses. Measure and record the SO_2 cylinder gas flow (F_{SO_2}) and the total flow (F_T) for each SO_2 concentration generated. Plot the analyzer SO_2 response versus F_{SO_2}/F_T and determine the slope which gives $[\text{SO}_2]_{\text{STD}}$ directly.

4.06.2.C.2 Certification of SO_2 Cylinder Gas Working Standard Against a NIST-traceable SO_2 Standard Permeation Device

The SO_2 analyzer need not be in calibration for these measurements. Generate several SO_2 concentrations by dilution of the NIST-traceable SO_2 standard permeation device (method B). Plot the analyzer SO_2 response versus the SO_2 concentration and determine the slope, S_{NIST} . Generate several SO_2 concentrations by dilution of the working SO_2 cylinder gas standard (method A) to give on-scale SO_2 responses. Measure the total flow at the manifold, F_T , for each SO_2 concentration generated. Plot the analyzer SO_2 response versus $1/F_T$ and determine the slope, S_{STD} .

4.06.2.C.3 Certification of a Working SO_2 Standard Permeation Device Against an SO_2 NIST-traceable Cylinder Gas Standard

The SO_2 analyzer need not be in calibration for these measurements. Generate several SO_2 concentrations by dilution of the NIST-traceable SO_2 standard cylinder gas (method A). Plot the analyzer SO_2 response versus the SO_2 concentration and determine the slope, S_{NIST} . Generate several SO_2 concentrations by dilution of the working SO_2 permeation device standard (method B) to give on-scale SO_2 responses. Measure the total flow at the manifold, F_T , for each SO_2 concentration generated. Plot the analyzer SO_2 response versus $1/F_T$ and determine the slope, S_{STD} . Calculate the permeation rate, P , from equation 4.06-5:

$$P = S_{\text{STD}} / (K_m \times S_{\text{NIST}}) \quad \text{Eqn. 4.06-5}$$

where: $K_m = (0.382 \mu\text{l SO}_2) / (\mu\text{g SO}_2)$ at 30°C^* and 760 mmHg

4.06.2.C.4 Certification of a Working SO_2 Standard Permeation Device Against an SO_2 NIST-traceable Permeation Device Standard

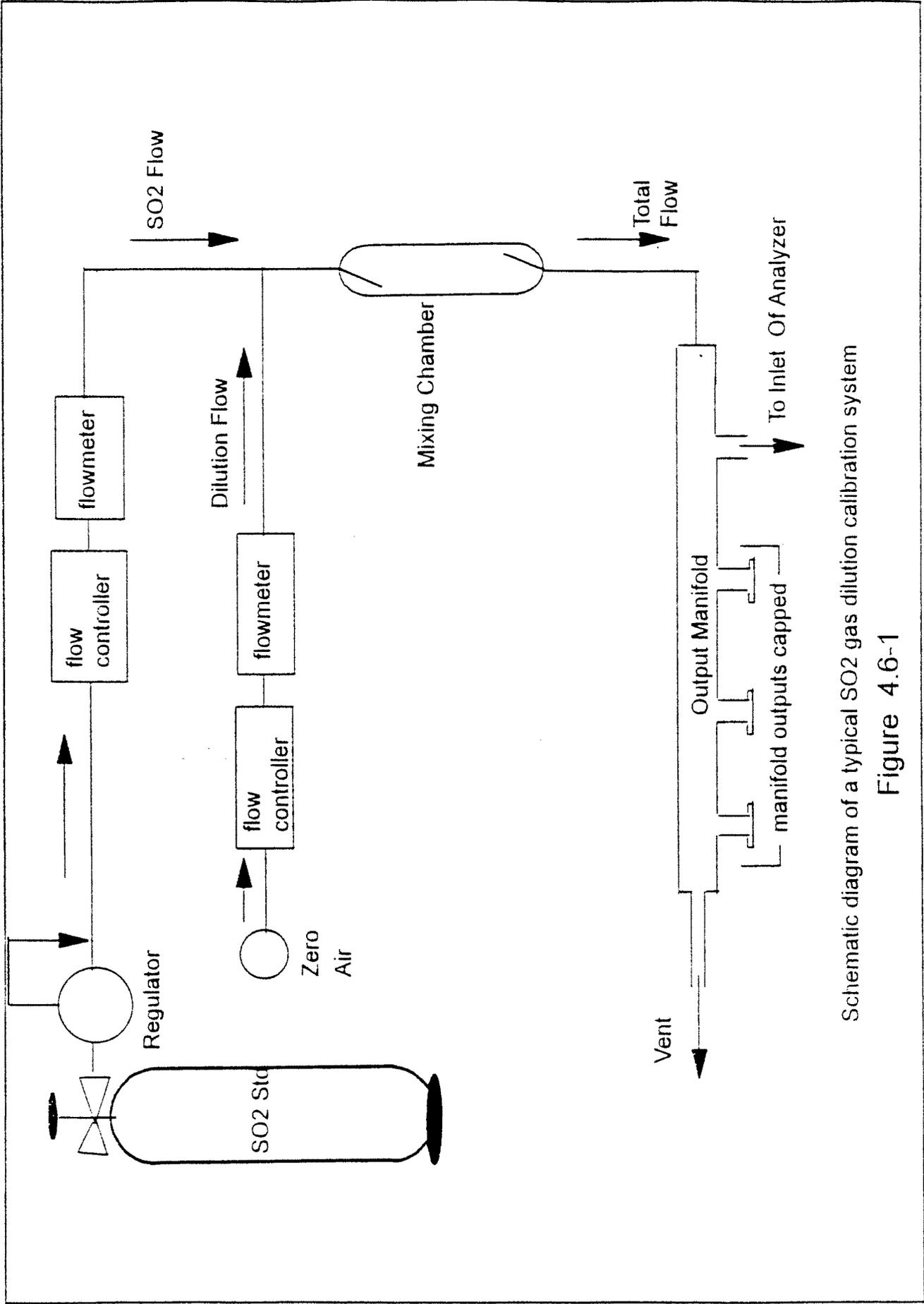
The SO_2 analyzer need not be in calibration for these measurements. Generate several SO_2 concentrations by dilution of the NIST-traceable SO_2 standard permeation device (method B). Plot the analyzer SO_2 response versus the SO_2 concentration and determine the slope, S_{NIST} . Generate several SO_2 concentrations by dilution of the working SO_2 permeation device standard (method B) to give on-scale SO_2 responses. Measure the total flow at the manifold, F_T , for each SO_2 concentration generated. Plot

the analyzer SO₂ response versus 1/F_T and determine the slope, S_{STD}. Calculate the permeation rate, P, from equation 4.06-5:

$$P = S_{STD} / (K_m \times S_{NIST}) \quad \text{Eqn. 4.06-5}$$

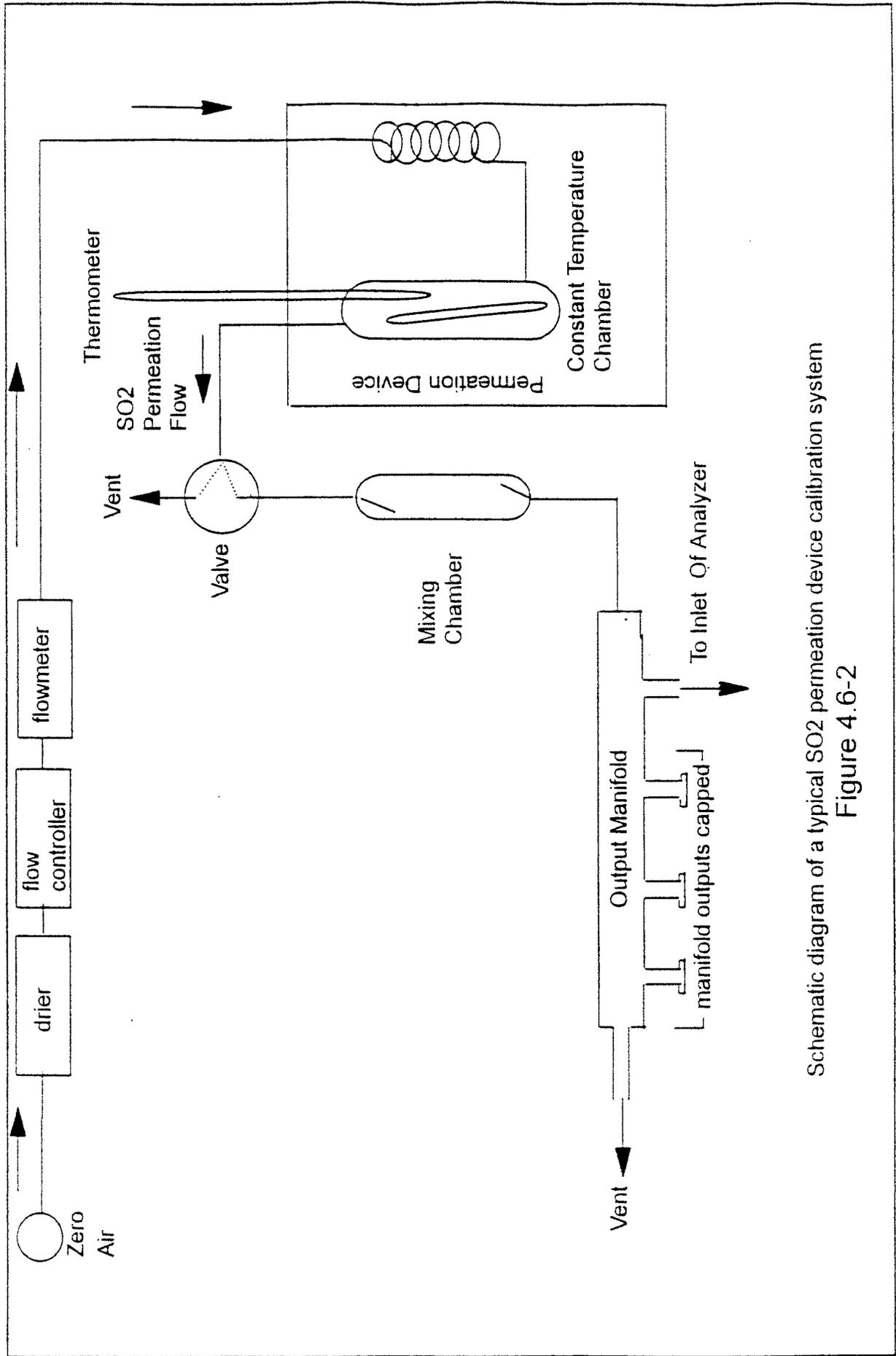
where: $K_m = (0.382 \mu\text{l SO}_2) / (\mu\text{g SO}_2)$ at 30°C* and 760 mmHg

* = temperature at which permeation rate of the permeation device is certified at.



Schematic diagram of a typical SO₂ gas dilution calibration system

Figure 4.6-1



Schematic diagram of a typical SO₂ permeation device calibration system
 Figure 4.6-2

SO₂ CALIBRATION DATA FORM BY GAS DILUTION (Method A)

1. Station _____

2. Calibrated by _____ Date _____
3. Analyzer Mfr. _____ 4. Calibrator Mfr. _____
 Model _____ Model _____
 S/N _____ S/N _____
5. SO₂ Reference Standard _____
 Supplier _____ Cylinder Number _____
 Concentration [SO₂]_{Std} _____ Cylinder Pressure _____
 Reference to NIST-SRM, CRM, or NTRM _____
 By _____ Date of Reference _____
6. Zero Air Make/Model # _____ Serial Number _____
7. Flow Rate Calibrator Reference Standard _____
 Make/Model # _____ Serial Number _____
8. Zero Knob Setting _____ Span Knob Setting _____
9. Temperature _____ Barometric Pressure _____

Equations Used for SO₂ Calibration

Equation 4.06-1

$$F_{SO_2} = (F_D \times [SO_2]_{OUT}) / ([SO_2]_{STD} - [SO_2]_{OUT})$$

F_{SO_2} = flow rate of SO₂ standard, sccm

Equation 4.06-2

$$[SO_2]_{OUT} = F_{SO_2} \times [SO_2]_{STD} / (F_{SO_2} + F_D)$$

F_D = flow rate of zero air, sccm

URL = upper range limit

[SO₂]_{STD} = concentration of the

[SO₂]_{OUT} = concentration at the output manifold undiluted SO₂ standard

Figure 4.06-3 (page 1 of 2)

SO₂ CALIBRATION DATA FORM BY GAS DILUTION

Calibrations Points SO ₂	1 F _{O₂} , sccm	2 F _{SO₂} , sccm	3 [SO ₂] _{OUT} , ppm	4 SO ₂ DAS reading	5 SO ₂ recorder reading
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					

Figure/Form 4.06-3 (page 2 of 2)

**SO₂ CALIBRATION AND LINEARITY CHECK
CALCULATION FORM FOR THE METHOD OF LEAST SQUARES**

Calibration Point	Concentration, [SO ₂ ppm] x	x ₂	DAS or Recorder reading y	y ²	xy
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					

$\Sigma x = \underline{\hspace{2cm}}$, $\Sigma x^2 = \underline{\hspace{2cm}}$, $\Sigma y = \underline{\hspace{2cm}}$, $\Sigma y^2 = \underline{\hspace{2cm}}$, $\Sigma xy = \underline{\hspace{2cm}}$

$x_{avg.} = \Sigma x/n = \underline{\hspace{2cm}}$, $y_{avg.} = \Sigma y/n = \underline{\hspace{2cm}}$, and

n = number of calibration points

The equation of the line fitted to the data is written as:

$$Y = y_{avg.} + b(x - x_{avg.}) = (y_{avg.} - bx_{avg.}) + bx = a + bx,$$

where Y = predicted mean response for corresponding x,

b = slope of the fitted line, and

a = intercept where the line crosses the y-axis.

$$b = \frac{\{\Sigma xy - [(\Sigma x)(\Sigma y)]/n\}}{[\Sigma x^2 - (\Sigma x)^2/n]}$$

$$a = y_{avg.} - bx_{avg.}$$

Figure/Form 4.06-4

SO₂ CALIBRATION DATA FORM BY PERMEATION DEVICE (Method B)

1. Station _____

2. Calibrated by _____ Date _____
3. Analyzer Mfr. _____ Model _____
 S/N _____
4. SO₂ Reference Standard Supplier _____ Permeation Tube Number _____
 SO₂ Permeation Rate at _____ °K P = _____ ng/min.
 Reference to NIST-SRM _____ By: _____
 Date of Certification _____
5. Zero Air Source Supplier _____ Cylinder Number _____ Date _____
 Make/Model # _____ Serial # _____
6. Zero Potentiometer Setting _____ Span Potentiometer Setting _____
7. Temperature _____ Barometric Pressure _____

Equations Used for SO₂ Calibration

Equation 4.06-3

$$[\text{SO}_2]_{\text{OUT}} = (P \times \text{Km}) / (F_p + F_D)$$

F_D = flow rate of dilution air, sccm

$[\text{SO}_2]_{\text{OUT}}$ = concentration at the output manifold

F_p = air flow across permeation device, sccm

P = Permeation rate @ known °C, mmHg

URL = upper range limit

Km = molar constant for SO₂ = 0.382 @ 30°C

SO ₂ Calibrations Points	1 F _D , sccm	2 F _D , sccm	3 [SO ₂] _{OUT} (ppm)	4 SO ₂ recorder (chart div)	5 SO ₂ DAS (ppm)
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					

Figure/Form 4.06-5

ACTIVITY MATRIX FOR CALIBRATION PROCEDURES			
Calibration Activities	Acceptance Limits	Frequency and Method of Measurements	Action if Requirements Are Not Met
Calibration gases	Cylinder gases certified to NIST-SRM, CRM, or NTRM standard, cylinder pressure >200 psig, also U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.0.7, Subsec. 7.1.	Assayed against a NIST-SRM, CRM, or NTRM quarterly, Method 4.06.2.C also U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.0.7.	Working gas standard is unstable and/or measurement method is out of control; take corrective action, e.g., obtain new calibration gases. Repeat the calibration.
Dilution gas	Dry zero air, free of contaminants; U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.0.7, Subsec. 7.1.	Compare new zero air against a source known to be free of contaminants.	Return to supplier, or take appropriate corrective action with generation system as appropriate.
Multi-point calibration	Use calibration procedures in Subsec. 4.06.2.B; also U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.9, Subsec. 2.0.	4.06.2.B, U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.9, Subsec. 2.0.	Repeat the calibration.

Figure/Form 4.06-6

4.06.3 SO₂ EQUIPMENT STANDARD OPERATING PROCEDURES

Essential to quality assurance (QA) are scheduled quality control (QC) checks for verifying the operational status of the monitoring system. The operator should visit the site at least once per week. Every two weeks a Level 1 zero/span QC check must be conducted on the analyzer. In between the Level 1 zero/span checks, Level 2 zero/span QC checks should be conducted on the analyzer at a frequency desired by the user. Both Level 1 and Level 2 zero/span checks must be conducted at a level between 70% and 90% of the analyzer's operating measurement range.

NOTE: It is strongly encouraged that an automatic system for the remote-controlled activation and recording of Level 1 zero/span checks be installed so that more frequent (e.g., daily) systematic zero/span checks could be conducted. Acceptable checks could then be used to bracket acceptable time blocks of data to limit invalidating larger time blocks of data when the instrumentation malfunctions.

In addition, an independent precision check at a concentration between 16% and 20% of the SO₂ analyzer's upper range limit (URL) must be carried out at least once every two weeks. Figure 4.06-7, at the end of this section, summarizes the QA activities for routine operations. Each activity is discussed in the following subsections.

To provide for documentation and accountability of activities, it is recommended that a checklist be compiled and then filled out by the field operator as each activity is completed. The completed checklist can then be filed with other site operational information (e.g., calibrations, maintenance, etc.) to provide complete documentation for the site. An example checklist is Figure 4.06-8, at the end of this section.

4.06.3.A EQUIPMENT

4.06.3.A.1 MONITORING SHELTER

The monitoring shelter's role in quality assurance is to provide a temperature-controlled environment in which the sampling equipment can operate at optimum performance. The mean shelter temperature should be within 15 to 30 degrees C. Daily fluctuations should not exceed ± 2 degrees C (± 4 degrees F). A continuous recording thermograph should be installed at the shelter to record daily fluctuations in temperature. Fluctuations greater than ± 2 degrees C may cause the electronic components of the analyzer to drift and may introduce error into the data. For this reason, excursions outside the specifications should be flagged to indicate possible questionable data.

4.06.3.A.2 SAMPLE INTRODUCTION SYSTEM

The sample introduction system consists of:

- intake port;

- particulate and moisture traps;
- sampling manifold;
- sampling blower; and
- sampling line to the analyzer.

As part of the QA program, the field operator should inspect the above components on a predetermined schedule for:

- breakage;
- leaks;
- particulates or foreign matter;
- moisture deposition in sample line or manifold; and
- sample line connected to sample manifold.

Any component of the sample introduction system that is not within tolerance needs to be either cleaned, repaired, or replaced immediately.

4.06.3.A.3 ANALYZER INSPECTION

On each site visitation, the field operator should inspect the following external operating parameters of the analyzer. These will vary from instrument to instrument, but in general they will include the following:

- correct settings of flow meters and regulators;
- cycling of temperature control indicators;
- verification that the analyzer is in the sampling mode rather than the zero or the calibration mode; and
- zero and span potentiometers are locked and set at the proper values.

4.06.3.A.4 CHART RECORDER

During each visit to the monitoring site, the field operator should check the recorder against the following list:

- legibility of the ink trace;

- ink supply in the reservoir;
- chart paper supply;
- chart speed control setting;
- signal input range switch; and
- time synchronization (mark chart with correct time, date, and operator's signature).

At least once per week, the operator must note the exact pen position on the chart paper with a tick mark. Place the time, date, and the operator's initials beside the mark. Due to the variety of strip chart recorders available, specific operator instructions for these recorders are not incorporated in this document. Consult the respective manual(s) for each recorder model used.

4.06.3.A.5 SIGNAL AVERAGER

The signal averager time should be checked during each site visit (at least weekly). Document, sign, and date these observations in the station log book.

After a power outage, the signal averager must be cleared and reset on the hour. The average for the previous hour will be lost so that average must be manually averaged from the strip chart. Any changes to the signal averager must be documented in the station log book and on the corresponding section of the chart recorder paper.

Correct any problems so that normal routine operations are reestablished. Sign and date the documented problems/corrections.

NOTE: If an electronic data logger is used in conjunction with a strip chart recorder, a signal averager may not be desirable.

For operational procedures of specific signal averagers, please consult the manufacturer's manual.

4.06.3.A.6 DATA ACQUISITION SYSTEM (DAS)

The DAS should be checked during each site visit (at least weekly) for the following:

- correct synchronization of time;
- correct synchronization of date;

- any error-indicator messages; and
- DAS is in normal operating mode.

Note observations in the site log book and on the corresponding section of the chart recorder. Sign and date these observations.

Correct any problems so that normal routine operations are reestablished. Sign and date the documented problems/corrections.

For operational procedures of a specific DAS, please consult the manufacturer's manual.

4.06.3.A.7 ZERO AIR

During each site visit, visually inspect the zero air system and service as needed.

4.06.3.A.8 GAS CYLINDER PRESSURE

Once per week, note and record the span and precision SO₂ gas tank pressures in the station log book. If the pressure for either the span SO₂ gas tank or precision SO₂ gas tank is below 300 psig, it should be replaced with an SO₂ gas tank of higher pressure. A new SO₂ gas tank should be ordered when the pressure falls to 500 psig. When an SO₂ span gas tank is changed, the new SO₂ span gas concentration must be checked with the analyzer's calibrated output (DAS, chart recorder) for verification of the specified SO₂ span gas concentration. The new SO₂ span value must be entered into the DAS; adjustment to the analyzer may be needed by adjusting the span potentiometer to correct the analyzer's reading.

4.06.3.B QUALITY CONTROL (QC) PERFORMANCE CHECKS

Zero and SO₂ span checks are required to document within-control conditions. The purpose of the zero and span checks are to provide interim checks on the response of the instrument to known concentrations. If an analyzer's response falls outside the prescribed limits, the analyzer is out of control, and the cause must be determined and corrected. Maintenance of a quality control chart is highly recommended to provide a visual check to determine:

1. if the analyzer is within control conditions; and
2. the trend of the analyzer's bias so corrections can be planned and made to improve control over the SO₂ measurement process before an out-of-limits situation occurs. Please refer to *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems: Volume 1. Principles, Appendix H, Control Charts* for specifics on the use of control charts.

Every two weeks, a Level 1 zero/span check must be made on the analyzer. Level 2 zero/span checks should be conducted between the Level 1 zero/span checks at a frequency desired by the user.

Standard(s) used for multi-point calibration may be used for conducting zero and span checks.

It is essential that the same SO₂ gas be used each time a zero/span check is conducted. This provides a means to track the analyzer's reliability to measure the same gas over a long period.

Figure 4.06-9 (SO₂ Zero/Span Drift Control Limits) summarizes the required quality control actions for the use of zero and span checks to determine SO₂ analyzer calibration control. This figure is at the end of this section.

4.06.3.B.1 LEVEL 1 ZERO/SPAN CHECK

A level 1 SO₂ zero/span check must be conducted every two weeks. An SO₂ gas used for the multi-point calibration may be used to conduct a level 1 zero/span check. The SO₂ span gas must be a NIST-traceable certified SO₂ standard within the 70% to 90% URL of the analyzer.

To conduct a level 1 zero/span check, the analyzer should be operating in its normal sampling mode with the test concentrations passing through as much of the inlet and sample conditioning system as is practicable. Wet or dirty inlet lines can cause changes in the SO₂ pollutant concentrations. Efforts should be made to introduce the span gas into as much of the sample train as possible. **The span gas must pass through all sample conditioning components used in the sample train.** The calibration response can then be compared to the response when the span concentration is introduced at the analyzer, downstream of the sample inlet components, as a check of the entire sample inlet system.

No adjustment(s) to the analyzer may be made during the zero and span calibration. Analyzer response readings must be obtained "as is" before any adjustments are made to the analyzer. These unadjusted zero and span readings provide valuable information for:

- confirming the validity (or invalidating) the measurements obtained immediately preceding the calibration;
- monitoring the analyzer's calibration drift; and
- determining the frequency of recalibration.

To conduct a Level 1 zero and span check, perform the following:

1. Disconnect the analyzer's inlet from the ambient sample probe at the junction of the probe manifold and the sample line, and connect it to the SO₂ gas or permeation device dilution calibration system. Ensure that the zero/span gas is delivered to the analyzer at atmospheric pressure. Leave the analyzer in its normal sampling mode. Make no other adjustments to the analyzer;
2. Sample and measure the span test concentration and record the unadjusted, stable ("as is") span response reading in the station log book, on the strip chart recorder, span check data form/figure 4.06-10 (at the end of this section), and on an X-S control chart used for recording Level 1 zero/span checks;

NOTE: All analyzer response readings must be recorded in the analyzer's normal output units (e.g., millivolts, % of scale, etc.--the same units used for the calibration curve). If these units are concentration units, they should be identified as "indicated" or "uncorrected" to differentiate them from the "actual" concentration units that are used for reporting the reference span gas concentration measurements.

3. Sample and measure the zero test concentration standard and record the unadjusted, stable zero reading in the station log book, on the strip chart recorder, and on an X-S control chart used for recording Level 1 zero/span checks;
4. Perform any needed analyzer adjustments (flow, pressure, etc.) or analyzer maintenance;
5. If adjustment of the zero is needed or if any adjustments have been made to the analyzer, adjust the zero to the desired zero reading. Offsetting the zero reading (e.g., to 5% of scale) may help to observe any negative drift that may occur. Record the adjusted, stable zero reading in the station log book, on the strip chart recorder, and on an X-S control chart used for recording Level 1 zero/span checks;
6. Sample and measure the span test concentration. If span adjustment is needed, adjust the span response to the desired value, allowing for any zero offset used in the previous step. Record the final adjusted, stable span reading in the station log book, on the strip chart recorder, and on an X-S control chart used for recording Level 1 zero/span checks; and
7. If any adjustments were made to the zero, span, or other parameters, or if analyzer maintenance was carried out, allow the analyzer to restabilize at the new settings, then recheck the zero and span readings. Record the new zero/span settings as well as the actual zero and span readings on the chart recorder, on the X-S control chart, and in the station log book.

When the response from a span check is outside the control limits, the cause for the extreme drift should be determined and the appropriate corrective action(s) must be taken. Some of the causes for drift are listed below:

- a. lack of preventive maintenance;
- b. fluctuations in the electrical power supply;
- c. fluctuations in flow;
- d. changes in zero air source;
- e. change in span gas concentration;
- f. degradation of photomultiplier tube;
- g. electronic and physical components not within manufacturer's specifications; and/or
- h. change in environmental temperature control.

For specific and detailed corrective actions to be taken, please consult the manufacturer's instruction/operations manual.

4.06.3.B.2 LEVEL 2 ZERO / SPAN CHECK

A Level 2 zero/span check is an unofficial quality control check of an analyzer's response. Level 2 zero/span checks should be conducted on a more frequent and pre-determined schedule between level 1 zero/span checks. It may include dynamic checks made with uncertified test concentrations, artificial stimulation of the analyzer's detector, electronic, or other types of checks of a portion of the analyzer, etc.

Level 2 zero and span checks are not to be used as a basis for analyzer zero or span adjustments, calibration updates, or adjustment of ambient data. They are intended as quick, convenient checks to be used between zero and span calibrations to check for possible analyzer malfunction or calibration drift. Whenever a Level 2 zero and span check indicates a possible calibration problem, a Level 1 zero and span (or a multi-point) calibration should be conducted before any corrective action is taken.

If a Level 2 zero and span check is to be used in the quality control program, a reference response for the check must be obtained immediately following a zero and span (or multi-point) calibration while the analyzer's calibration relationship is accurately known. Subsequent Level 2 check responses are compared to the most recent reference response to determine if a change in response has occurred. Like level 1 zero/span checks, all level 2 zero and span checks are recorded/plotted on a zero/span check form (figure/form 4.06-11) and on an X-S quality control chart.

NOTE: Keep in mind that any Level 2 check that involves only part of the analyzer's measurement system cannot provide information about the portions of the system not checked and, therefore, cannot be used as a verification of the overall analyzer's calibrated measurement system.

It is further recommended that level 2 zero/span checks be automated to remotely activate every 24 hours.

DAILY ACTIVITY MATRIX			
Characteristic	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
Shelter temperature	Mean temperature between 15 to 25°C, daily fluctuations not greater than $\pm 2^{\circ}\text{C}$ (4°F)	Edit thermograph chart daily for variations greater than $\pm 2^{\circ}\text{C}$ (4°F)	<ol style="list-style-type: none"> 1. Mark strip chart for the affected time period 2. Repair or adjust temperature control system
Sample introduction system	No moisture, foreign material, leaks, obstructions; sample line connected to manifold	Weekly visual inspection	Clean, repair, or replace as needed
Recorder	<ol style="list-style-type: none"> 1. Adequate ink supply and chart paper 2. Legible ink traces 3. Correct settings of chart speed and range switches 4. Correct time 	Weekly visual inspection	<ol style="list-style-type: none"> 1. Replenish ink and chart paper supply 2. Adjust recorder time to agree with clock; note on chart
Analyzer operational settings	<ol style="list-style-type: none"> 1. Flow and regulator indicators at proper settings 2. Temperature indicators cycling or at proper levels 3. Analyzer set in sample mode 4. Zero and span controls locked 	Weekly visual inspection	Adjust or repair as needed
Analyzer operational check	Zero/span checks within tolerance limits as described in Subsection 4.06.3.B.1	Level 1 zero/span checks every 2 weeks; Level 2 between Level 1 checks at frequency desired by user	<ol style="list-style-type: none"> 1. Isolate source of error, and repair 2. After corrective action, recalibrate analyzer
Analyzer precision check	Precision checks within tolerance limits as described in Subsection 4.06.7.A.	every 2 weeks	Precision check criteria not met, conduct level 1 zero/span check to substantiate problem.

Figure 4.06-7

OPERATIONAL CHECKLIST

Site ID _____ Date _____

Site Location _____ Technician _____

Site Address _____

1. Inspect thermograph for temperature variations greater than $\pm 2^{\circ}\text{C}$ (4°F). Identify time frame of any temperature level out of tolerance.

Comments: _____

2. Inspect sample introduction system for moisture, particulate buildup, foreign objects, breakage, leaks.

Comments: _____

3. Is sample line connected to manifold?

Comments: _____

4. Inspect data recording system.

	OK	Corrective Action Taken
◦ Legibility of trace	_____	_____
◦ Ink supply	_____	_____
◦ Paper supply	_____	_____
◦ Chart speed selector	_____	_____
◦ Signal range switch	_____	_____
◦ Time synchronization	_____	_____

Comments: _____

Figure 4.06-8A

OPERATIONAL CHECKLIST (continued)

__ 5. Inspect analyzer operational parameters.

	OK	Corrective Action Taken
o Sample flow rate	_____	_____
o Analyzer in sample mode	_____	_____
o Zero and span potentiometers locked at correct setting	_____	_____

Comments: _____

__ 6. Zero the analyzer
__ 7. Is unadjusted zero within tolerance?

Comments: _____

__ 8. Span the analyzer
__ 9. Is unadjusted span within tolerance?

Comments: _____

__ 10. Enter zero and span values on span check data form
__ 11. Return to sample mode
__ 12. Record cylinder pressure of zero and span tanks

Zero air _____
Span air _____

__ 13. Close valve on zero and span tanks.

Signature Date

Figure 4.06-8B

SO₂ ZERO/SPAN DRIFT CALIBRATION LIMITS

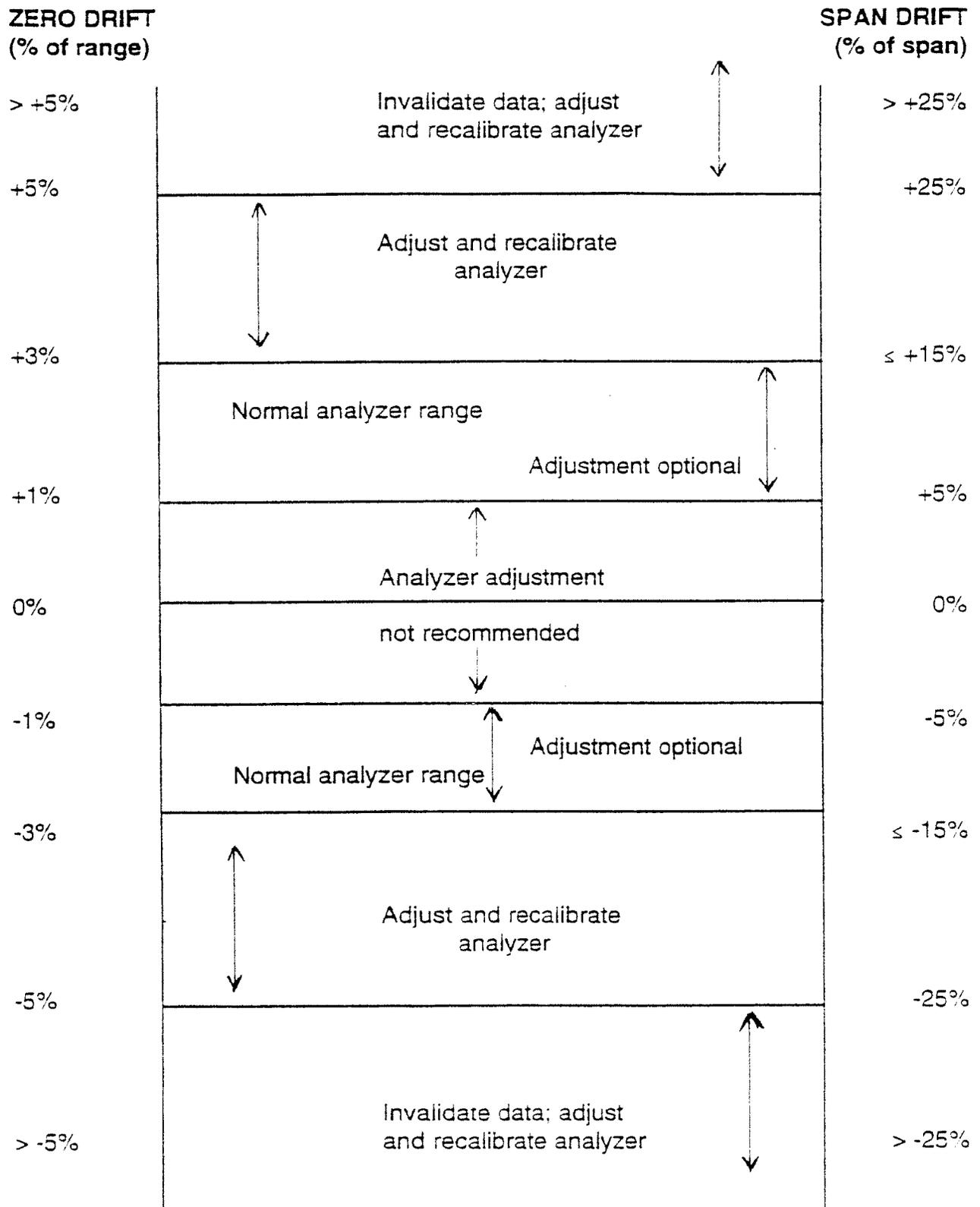


Figure 4.06-9

4.06.4 PREVENTIVE MAINTENANCE

Because preventive maintenance requirements vary from instrument to instrument, the manufacturer's manual should be consulted for a specific analyzer. From these instrument-specific maintenance requirements a suitable preventive maintenance schedule should be developed for each instrument. A detailed preventive maintenance record of the preventive actions taken on each analyzer must be documented. This documentation must be kept on file at the site to identify recurring malfunctions. A maintenance log appears in figure 4.06-11.

4.06.5 AUDIT PROCEDURES

The quarterly audit is the responsibility of the agency conducting the monitoring program. At any time, ADEC may choose to conduct oversight audits of a monitoring project. Chapter 5 of the *Alaska Quality Assurance Manual for Ambient Air Quality Monitoring* is devoted to this subject.

An audit is an independent assessment of the accuracy of data generated by an ambient air analyzer or a network of analyzers. Independence is achieved by having the SO₂ audit performed by an operator (trained and experienced in the SO₂ method he/she will be auditing) other than the operator conducting the routine field measurements and calibrations and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

The audit is an assessment of the measurement process under normal operations--that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not part of the auditing process.

Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

4.06.6 DATA ACQUISITION, PROCESSING, AND REPORTING

Sulfur Dioxide data is acquired from analyzers by data acquisition systems (DAS) or by strip chart recorders. **If a DAS is used, a strip chart recorder must also be employed to capture the same data.** In addition, 7% of reduced strip chart data must be compared against the corresponding DAS-acquired data, if the DAS is to be used as the primary data record. Processed raw data is forwarded to the agency program or project manager from their station manager(s).

Program and project managers are responsible for:

1. acquiring all processed raw data;
2. processing the data (and all other relevant SAROAD/AIRS site information) in SAROAD/AIRS report format;
3. certifying the integrity and validity of the reported data, including a report on reasons for missing or invalid data; and
4. reporting the data on a quarterly basis to the ADEC Air Program Data Base Manager. The data is to be provided on magnetic media to avoid additional data entry errors.

4.06.6.A DATA VALIDATION

Monitoring data of poor quality may be worse than no data. Data validation is one activity of a QA program to screen data for possible errors or anomalies. The following data validity checks should be applied to identify gross data anomalies:

4.06.6.A.1 SPAN DRIFT CHECK

The first level of data validation should be to accept or reject monitoring data based upon routine periodic analyzer checks. It is recommended that results from the Level 1 zero and span checks be used as the first level of data validation for accepting data. This means that up to two weeks of monitoring data may be invalidated if the span drift for a Level 1 zero and span check is equal to or greater than 25%. For this reason it is recommended that zero and span checks be conducted more frequently than the bi-weekly requirement.

4.06.6.A.2 HOURLY AVERAGE

Hourly Average--A minimum of 45 minutes of valid data is required to report an hourly average concentration.

4.06.6.A.3 EDIT OF STRIP CHART

The station operator has the primary responsibility for distinguishing valid measurements from indications caused by malfunctioning instruments or source interferences.

Data editing will be greatly enhanced if the station operator is conscious of several aids in chart review. These are listed below:

1. Familiarity with typical diurnal, daily, seasonal, or wind direction specific concentration variations (e.g., the times maximum concentrations occur);
2. Familiarity with the type of instrument malfunctions which cause characteristic trace irregularities;
3. Cyclical or repetitive variations (at the same time each day or at periodic intervals during the day) may be caused by excessive line voltage or temperature variations. Nearby source activity can also cause erroneous or non-representative measurements;
4. Traces showing little or no activity often indicate a loss of sensitivity, flow problems, or sample line leaks;
5. A wide, solid trace indicating excessive noise or spikes that are sharper than is possible with the normal instrument response time are indicative of erratic

behavior. Noisy outputs usually result when analyzers are exposed to vibration sources;

6. A long, steady increase or decrease in deflection;
7. A trace that drops below the zero baseline during certain periods; this may indicate a larger-than-normal drop in the ambient room temperature or the power line voltage. This may also indicate contaminant(s) in the zero air; and
8. Enter meaningful notes on the charts. **The more information that can be provided, the more valuable the strip charts will be.** Draw an arrow from each note to the area of the chart discussed. For example, notes should include:
 - a. the causes of, or comment on, irregularities in the trace, e.g., changes in zero from day to day, sudden changes in the trace, flow errors, or corrective actions;
 - b. checks and/or adjustments to the analyzer(s); and
 - c. span drift equal to or greater than 25% of the chart.

NOTE: Data must be flagged or voided for any time interval in which a malfunction of the sampling system is detected.

4.06.6.B DATA REDUCTION

Data can be reduced either manually or automatically. Automatic data reduction is done by DAS that are programmed at the time of the analyzer's multi-point calibration.

4.06.6.B.1 WITH SIGNAL AVERAGER

Hourly average concentrations from a strip chart recorder with a signal averager may be obtained by the following procedure:

- a. Use of a signal averager is recommended to facilitate data reduction. The signal averager provides an average, for each hour, that is recorded by the chart recorder and data logger. The average shown by the signal averager always indicates the output of the analyzer, including any zero, span, or precision checks. The hourly average concentration may be obtained from the strip chart by reading/measuring the hourly averaged signal "tick" mark and computing the concentration using the current calibration equation.
- b. All hours in which a precision check was performed must be manually averaged to exclude the period precision gas was sampled through the ambient port of the analyzer.

NOTE: Use of the term "signal averager" refers solely to a stand-alone unit such as the Monitor Lab's 8640.

- c. The hours in which a zero-span was performed by the operator may have to be edited manually to exclude the zero span period from the sample average. There must be 45 minutes of sample time to form a valid hourly average.

NOTE: Complete data reduction documentation must be maintained on the strip chart recorder. The analyst's name and the date the data reduction took place must be included.

- d. Fill in the identification data called for at the top of, "Data Form for Recording Hourly Averages," Figure/Form 4.06-12.
- e. Read the hourly signal averaged deflection (% chart) for all of the hourly intervals for which data have not been marked invalid, and record all values on the hourly averaged data form in the column headed, "Reading--Original (Orig.)." Ignore the columns marked "Zero Baseline," "Difference," and "y, add + 5."
- f. Convert "Reading--Orig," values (% chart) to concentrations (ppm) by using the most recent SO₂ calibration curve, and record the concentrations in the last column of "Data Form for Recording Hourly Averages," Figure/Form 4.06-12.

4.06.6.B.2 WITHOUT USE OF SIGNAL AVERAGER

Hourly average concentrations from a strip chart record may be obtained by the following procedure:

- a. Make sure the strip chart record has a zero trace at the beginning and end of the sampling period;
- b. Fill in the identification data called for at the top of "Data Form for Recording Hourly Averages," Figure/Form 4.06-12;
- c. Draw a line from the zero baseline at the start of the sampling period to the zero baseline at the end of the sampling period by using a straight edge;
- d. Read the zero baseline (% chart) at the midpoint of each hourly interval, and record the value (y_z) on the data Figure/Form 4.06-12;
- e. Determine the hourly averages by placing a transparent straight edge parallel to the horizontal chart division lines. Adjust the straight edge between the lowest and highest points of the trace in the interval between two vertical hour lines of interest so that the area above the straight edge and bounded by the

trace and the hour lines is approximately equal to the area below the straight edge and bounded by the trace and hour lines.

Read the deflection (% chart) for all of the hourly intervals for which data have not been marked invalid, and record all values on Figure/Form 4.06-12;

- f. Subtract the zero baseline value from the reading value, and record the difference;
- g. Add the percentage of zero offset, if applicable, to each difference;
- h. Convert reading values (% chart) to concentrations (ppm) by using the most recent SO₂ calibration curve, and record the concentrations in the last column of the hourly data form; and
- i. An alternative method of converting % chart to ppm is to eliminate steps f and h and to use the following equation, Eqn. 4.06-6:

$$[\text{SO}_2]_{\text{STD}} = (y - y_z) / m \quad \text{Eqn. 4.06-6}$$

where: y = recorder reading in % scale (from step e)

y_z = zero baseline in % scale (from step d)

m = slope of the calibration relationship (from section 4.06.2.B)

4.06.6.C DATA QUALITY CONTROL

To ensure that only reliable, accurate, complete, representative, and comparable data is reported to the ADEC Air Program Data Base Manager, the following quality control (QC) activities will be performed on each set of reported data:

1. Check 7% of the data for transcription error. If a transcription error is found, correct the problem. Recheck all data in the respective data batch for transcription correctness. Document the problem(s) and the appropriate corrective action(s) taken to report reliable data;
2. Randomly recalculate 7% of all data. Recalculations must agree within a round-off error of the original sample calculation. If not, recalculate all data in the respective data batch. Correct any error(s). Document the problem(s) and the appropriate corrective action(s) taken to report reliable data;
3. Conduct a level 1 zero/span SO₂ check at a minimum of once every two weeks (see section 4.06.3.B.1 for specifics on conducting a level 1 zero/span SO₂ check). The analyzer's response to the level 1 zero/span check concentration must be within $\pm 15\%$ of the SO₂ span check standard concentration and the zero must be within $\pm 3\%$ of the measurement range. If the level 1 zero/span check fails any of the above requirements:
 - a. identify the problem;
 - b. correct the problem;
 - c. recalibrate the SO₂ analyzer as soon as possible. If, however, the level 1 zero/span check result is outside $\pm 25.0\%$ of the SO₂ span checks or zero drift is $> \pm 5\%$ of the analyzer full scale range, then all data must be invalidated to the last acceptable span check or multi-point calibration. The SO₂ analyzer must also be recalibrated before being used to collect data; and
 - d. document the problem(s) and the corrective action(s) taken to return the SO₂ analyzer to acceptable routine operations;
4. Conduct a precision check at a minimum of once every two weeks. The analyzer's response to the precision check SO₂ concentration must be within $\pm 15\%$ of the SO₂ precision check standard concentration. If the precision check fails the above requirement, conduct a level 1 zero/span check to substantiate the problem and take the necessary corrective action(s) to return the SO₂ analyzer to acceptable routine operations; and
5. Visually inspect all sample information data/documentation sheets. Ensure all necessary information is recorded and complete.

4.06.6.D STATISTICAL TRACKING

All equipment must be maintained with current up-to-date maintenance log books. All repairs, maintenance, calibrations, etc., must be recorded, signed, and dated.

The program or project manager will ensure that the following X-S charts are maintained and up-to-date:

- Level 1 SO₂ zero/span checks;
- Level 2 SO₂ zero/span checks; and
- SO₂ precision checks.

NOTE: Please refer to *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems: Volume 1. Principles, Appendix H, Control Charts* for directions on establishing and maintaining control charts.

4.06.6.E DATA REPORTING

SO₂ information and hourly averages data is transcribed from the "Data Form for Recording Hourly Averages" (Figure/Form 4.06-12), to a SAROAD/AIRS hourly data form (See *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems: Volume 2.0.3* for details and basic instructions for filling out the SAROAD/AIRS forms).

SO₂ information and hourly averages from data acquisition systems may also be polled and processed into SAROAD/AIRS format by computer with the appropriate computer software. However, data reduced and reported in this manner must be verified against a 7% random strip chart data reduction check. Also, any SO₂ concentration anomalies reported by the DAS must be compared against the strip chart recorder reduced data. Differences between reported DAS collected/reduced data and strip chart recorder collected/reduced data must agree within 4% of the analyzer's calibrated full scale range (e.g., 0.02ppm for a 0-0.5ppm range). If obvious differences are noted between the two collection/reporting systems, all data back to the last acceptable Level 1 zero/span check must be examined by both systems. The reason(s) for the difference(s) must be investigated, corrected, and documented. The appropriate sections of collected data that do not meet data validation requirements must be invalidated. Other questionable data should be flagged and reported to the local agency data base manager. It is incumbent upon the local and/or ADEC data base manager to decide whether to include the flagged data in ADEC's air monitoring data base.

Quarterly data reports submitted to the Department must include (but not be limited to) the following QA documentation:

1. All valid or flagged one-hour, three-hour, and 24-hour averages;

2. Minimum and maximum one-, three-, and 24-hour averages and other summary statistics;
3. Data which has exceeded the full scale range of the analyzer shall be flagged and manually verified against strip chart recorder output. Copies of verified strip chart(s) shall be made available to the Department upon request;
4. Reasons for each hour of missing/invalid/flagged data shall be identified and explained;
5. Details of all maintenance activities and any changes to instrument and standard operating procedures;
6. Results of all pre-calibration checks and unadjusted zero/span checks;
7. Results of all analyzer calibrations;
8. Copies of calibration and equipment standards used for calibrations, calibration checks, and audits;
9. Results of all calibration flow checks; and
10. All final analyzer potentiometer (and other instrument) settings for all calibrations and zero/span checks.

4.06.7 ASSESSMENT OF MONITORING DATA FOR PRECISION AND ACCURACY

4.06.7.A PRECISION

For continuous analyzers, a periodic check is used to assess the data for precision. A one-point precision check must be conducted at least once every two weeks on each analyzer at a concentration between 16% and 20% of the analyzer's upper range limit (URL). The analyzer must be operated in its normal sampling mode. The precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The precision check gas standard must be traceable to a NIST-SRM, CRM, or NTRM. **The precision check standard should be independent from that used for calibration.**

The precision check procedure follows:

1. Connect the analyzer to a calibration system to generate an SO₂ precision gas that has a concentration between 16% and 20% of the analyzer's URL (between 0.08 and 0.10 ppm for a 0.5 ppm URL). Ensure that the precision gas is delivered to the analyzer at atmospheric pressure. The SO₂ precision gas may be generated by either Method A or Method B. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero or span adjustment(s);
2. Allow the analyzer to sample the precision gas until a stable response is obtained (at least 15 minutes); and
3. Record this value: a) on the precision check form (see figure/form 4.06-13 at the end of this section), b) on an X-S quality control chart, c) on the chart recorder paper, and d) in the station log book as "unadjusted precision check."

The difference between the concentration indicated by the analyzer and the actual concentration of the precision check gas is used to assess the precision of the monitoring data (see *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems; Volume 2.0.8 Calculations to Assess Monitoring Data for Precision and Accuracy for SLAMS and PSD Automated Analyzers and Manual Methods*).

Use the same control criteria to evaluate acceptable SO₂ precision checks as used to evaluate acceptable level 1 span checks (see figure 4.06-9).

4.06.7.A.1 SO₂ PRECISION CHECKS BY DYNAMIC DILUTION OF AN SO₂ CYLINDER GAS (METHOD A)

To conduct SO₂ precision checks by gas dilution, follow the procedures used in subsection 4.06.2.B.2 (SO₂ multi-point calibration by gas dilution). Instead of

generating multiple SO₂ gas concentrations for a multi-point calibration, generate one level of SO₂ between 16% and 20% of analyzer full range (e.g., 0.08 to 0.10ppm for a 0- 0.5ppm full scale range).

4.06.7.A.2 SO₂ PRECISION CHECKS BY DYNAMIC DILUTION OF AN SO₂ PERMEATION DEVICE (METHOD B)

To conduct SO₂ precision checks by SO₂ permeation device method, follow the procedures used in subsection 4.06.2.B.3 (SO₂ multi-point calibration by dynamic dilution of an SO₂ permeation device). Instead of generating multiple SO₂ gas concentrations for a multi-point calibration, generate one level of SO₂ between 16% and 20% of analyzer full range (e.g., 0.08 to 0.10ppm for a 0-0.5ppm full scale range).

4.06.7.B ACCURACY

The accuracy of the SO₂ analyzer is assessed by auditing the performance of the analyzer as described previously in section 4.06.5. The audit gas values and the corresponding analyzer-measured values are reported. The percentage differences between these values are used to calculate accuracy as described in 40 CFR 58, Appendices A and B.

4.06.8 DATA QUALIFICATION

Quarterly data reports must be ≥75% complete. Data reports <75% complete must be accompanied by a missing data report. The missing data reports will identify:

- specific and comprehensive reasons for missing data, and
- the appropriate corrective action(s) that were taken to return data reporting to acceptable levels of completeness.

NOTE: It is highly recommended that all data reports include a summary of missing data.

4.06.9 DATA SUBMISSION

SO₂ data will be reported on a quarterly basis. The data will be reported on magnetic media with a hard copy back-up. Quarterly reports will be submitted within a time period specified by the data base manager, but no later than one month following the end of the respective quarter. Independent projects performed in support of a permit application may not be required to submit quarterly reports.

SO₂ information and hourly averages from data acquisition systems may also be polled and processed into SAROAD/AIRS format by computer with the appropriate computer software. However, data reduced and reported in this manner must be verified against a 7% random strip chart data reduction check. Also, any SO₂ concentration anomalies reported by the DAS must be compared against the strip chart recorder reduced data. Differences between reported DAS collected/reduced data and strip chart recorder collected/reduced data must agree within 4% of the analyzer's calibrated full scale range (e.g., 0.02ppm for a 0-0.5ppm range). If obvious differences are noted between the two collection/reporting systems, all data back to the last acceptable Level 1 zero/span check must be examined by both systems. The reason(s) for the difference(s) must be investigated, corrected, and documented. The appropriate sections of collected data that do not meet data validation requirements must be invalidated. Other questionable data should be flagged and reported to the local agency data base manager. It is incumbent upon the local and/or ADEC data base manager to decide whether to include the flagged data in ADEC's air monitoring data base.

Quarterly data reports submitted to the Department must include (but not be limited to) the following QA documentation:

1. All valid or flagged one-hour averages (from all channels used to calculate and report SO₂ data);
2. Minimum and maximum one-hour averages and other summary statistics for all reported parameters;
3. Data which has exceeded the full scale range of the analyzer shall be flagged and manually verified against strip chart recorder output. Copies of verified strip chart(s) shall be made available to the Department upon request;
4. Reasons for each hour of missing/invalid/flagged data shall be identified and explained;
5. Details of all maintenance activities and any changes to instrument and standard operating procedures;
6. Results of all pre-calibration checks and unadjusted zero/span checks;

7. Results of all analyzer calibrations;
8. Copies of calibration and equipment standards used for calibrations, calibration checks, and audits;
9. Results of all calibration flow checks; and
10. All final analyzer potentiometer (and other instrument) settings for all calibrations and zero/span checks.

4.06.10 EQUIPMENT DE-INSTALLATION

When an SO₂ monitoring site is to be shut down, the actions listed below are highly recommended. If the site is to be permanently shut down, a final performance and systems audit is to be performed. If the site is to be a seasonal shutdown only, a performance audit should be performed prior to the shutdown, but certainly within the final calendar quarter of instrument operation.

1. Conduct a final Level 1 zero/span check and precision check to validate the last portion of collected data;
2. Log the date, time, zero/span values, zero and span potentiometer values, and any other pertinent information, on the operator logsheet;
3. Turn off and unplug the SO₂ analyzer (consult the respective manufacturer's operating manual);
4. Turn off and shut down the gas calibrator/permeation device calibrator (consult the respective manufacturer's operating manual);
5. Turn off and shut down the data logger (consult the respective manufacturer's operating manual);
6. Turn off and shut down the signal averager and chart recorder (consult the respective manufacturer's operating manuals);
7. Turn off and shut down the zero air system (consult the respective manufacturer's operating manual);
8. Turn off and shut down the power conditioning system (consult the respective manufacturer's operating manual); and
9. Close gas tank valves for precision gas tank, span gas tank, zero air tank (if applicable), and calibration gas tank. Remove pressure regulators and replace with twist caps for safety transportation.

4.06.11 SAFETY PROCEDURES

The following basic precautions should be taken while working with SO₂ instrumentation:

1. Operate all monitoring instruments with the available grounding plug (3-wire plug);
2. Exhaust the analyzer safely, especially when calibrating the unit with high SO₂ concentrations;
3. When working/troubleshooting/repairing any electrical instrument, the power should usually be turned off and the power line disconnected;
4. Take normal precautions for shock protection/prevention when working inside of any electrical instrument with the power connected; and
5. Ensure that all high-pressure gas tanks are securely chained or otherwise attached to something solid so that the tanks remain in an upright and secure position at all times.

