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Preliminary Method 005- Determination of Nitrogen Oxide Emissions from Stationary Sources
(Ultraviolet Instrumental Analyzer Procedure)

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method is applicable to the determination of nitrogen oxide (NO_x) concentrations in controlled and uncontrolled emissions from stationary sources where analytical interferences are absent or when a specific ultraviolet detector design can be shown to adequately correct for these interferences. Typical compounds which may (depending on instrument design) be analytical interferents are SO_2, aromatic hydrocarbons and reduced sulfur compounds. Sulfur dioxide is typically compensated for within the instrument design. It should be noted that water vapor, while not an interferent, can present problems which could be addressed as described in Section 7.0.

1.2 Principle. A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of NO_x gas concentration using an ultraviolet (UV) analyzer. Performance specifications and test procedures are provided to ensure reliable data.

2. RANGE AND SENSITIVITY

2.1 Analytical Range. The analytical range is determined by the instrumental design. For this method, a portion of the analytical range is selected by choosing the span of the monitoring system. The span of the monitoring system shall be selected such that the pollutant gas concentration equivalent to the emission standard is not less than 30 percent of the span. If at any time during a run the measured gas concentration exceeds the span, the run shall be considered invalid.

2.2 Sensitivity. The minimum detectable limit depends on the analytical range, span, and signal-to-noise ratio of the measurement system. For a well designed system, the minimum detectable limit should be less than 2 percent of the span.

3. DEFINITIONS

3.1 Measurement System The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface. That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the analyzers from the effects of the stack effluent.

3.1.2 Gas Analyzer. That portion of the system that senses the gas to be measured and generates an output proportional to its concentration.

3.1.3 Data Recorder. A strip chart recorder, analog computer, or digital recorder for recording measurement data from the analyzer output.

3.2 Span. The upper limit of the gas concentration measurement range displayed on the data recorder.

3.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

3.4 Analyzer Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.5 Sampling System Bias. The difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the outlet of the sampling probe and when the same gas is introduced directly to the analyzer.

3.6 Zero Drift. The difference in the measurement system output reading from the initial calibration response at the zero concentration level after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.7 Calibration Drift. The difference in the measurement system output reading from the initial calibration response at a mid-range calibration value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.8 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.9 Interference Check. A method for detecting analytical interferences. Interferences are output responses of the measurement system to a component in the sample gas other than the component being measured.

3.10 Calibration Curve. A graph or other systematic method of

establishing the relationship between the analyzer response and the actual gas concentration introduced to the analyzer.

4.   MEASUREMENT SYSTEM PERFORMANCE SPECIFICATIONS

4.1   Analyzer Calibration Error.   Less than 2 percent of the span for the zero, mid-range, and high-range calibration gases.

4.2   Sampling System Bias.   Less than 5 percent of the span for the zero and mid-range calibration gases.

4.3   Zero Drift.   Less than 3 percent of the span over the period of each run.

4.4   Calibration Drift.   Less than 3 percent of the span over the period of each run.

5.   APPARATUS AND REAGENTS

5.1   Measurement System   Use any measurement system for NO_x that meets the specifications of this method.   Schematics of acceptable measurement systems are shown in Figures P-1A (Dry Basis System) and P-1B (Wet Basis System).   The essential components of the measurement system are described below:

5.1.1   Sample Probe.   Glass, stainless steel, or equivalent, of sufficient length to traverse the sample points.   The sampling probe shall be heated to prevent condensation.

5.1.2   Sample Line.   Heated (sufficient to prevent condensation) stainless steel or Teflon tubing, to transport the sample gas to the moisture removal system.

5.1.3   Sample Transport Lines.   Stainless steel or Teflon tubing, to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and sample gas manifold.

5.1.4   Calibration Valve Assembly.   A three-way valve assembly, or equivalent, for blocking the sample gas flow and introducing calibration gases to the measurement system at the outlet of the sampling probe when in the calibration mode.

5.1.5   Moisture Removal System   A refrigerator-type condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas.   The moisture removal system is not necessary for analyzers that can measure gas concentrations on a wet basis; for these analyzers, (1) heat the sample line and all

interface components up to the inlet of the analyzer sufficiently to prevent condensation, and (2) determine the moisture content and correct the measured gas concentrations to a dry basis using appropriate methods, subject to the approval of the Administrator. The determination of sample moisture content is not necessary for pollutant analyzers that measure concentrations on a wet basis when (1) a wet basis CO_2 analyzer operated according to Method 3A is used to obtain simultaneous measurements, and (2) the pollutant/CO_2 measurements are used to determine emissions in units of the standard.

5.1.6 Particulate Filter. An in-stack or heated (sufficient to prevent water condensation) out-of-stack filter. The filter shall be borosilicate or quartz glass wool, or glass fiber mat. Additional filters at the inlet or outlet of the moisture removal system and inlet of the analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of the components. All filters shall be fabricated of materials that are non-reactive to the gas being sampled.

5.1.7 Sample Pump. A leak-free pump, used to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled.

5.1.8 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. (<u>Note</u>: The tester may elect to install a back-pressure regulator to maintain the sample gas manifold at a constant pressure in order to protect the analyzer(s) from over pressurization, and to minimize the need for flow rate adjustments.)

5.1.9 Sample Gas Manifold. A sample gas manifold, to divert a portion of the sample gas stream to the analyzer and the remainder to the by-pass discharge vent. The sample gas manifold should include provisions for introducing calibration gases directly to the analyzer. The manifold may be constructed of any material that is non-reactive to the gas being sampled.

5.1.10 Gas Analyzer. A UV analyzer, to determine continuously the NO_x concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer. (<u>Note</u>: Housing the analyzer(s) in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.)

5.1.11 Data Recorder. A strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be 0.5 percent of span. Alternatively, a digital or analog meter having a resolution of 0.5 percent of span may be used to obtain the analyzer responses and the readings may be recorded manually. If this alternative is used, the readings shall be obtained at equally spaced intervals over the duration of the sampling run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be obtained. For sampling run durations greater than 1 hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be obtained.

5.2 NO$_x$ Calibration Gases. The calibration gases for the gas analyzer shall be NO in N$_2$.

5.2.1 High-Range Gas. Concentration equivalent to 80 to 100 percent of the span.

5.2.2 Mid-Range Gas. Concentration equivalent to 40 to 60 percent of the span.

5.2.3 Zero Gas. Concentration of less than 0.25 percent of the span. Ambient air may be used for the zero gas.

6.   MEASUREMENT SYSTEM PERFORMANCE TEST PROCEDURES

Perform the following procedures before measurement of emissions (Section 8).

6.1   Calibration Gas Concentration Verification.   There are two alternatives for establishing the concentrations of calibration gases. Alternative No. 1 is preferred.

6.1.1   Alternative No. 1--Use of calibration gases that are analyzed following the Environmental Protection Agency Traceability Protocol No. 1 (see Citation 1 in Bibliography). Obtain a certification from the gas manufacturer that Protocol No. 1 was followed.

6.1.2   Alternative No. 2--Use of calibration gases not prepared according to Protocol No. 1. If this alternative is chosen, obtain gas mixtures with a manufacturer's tolerance not to exceed 2 percent of the tag value. Within 6 months before the emission test, analyze each of the calibration gases in triplicate using Method 7. Citation 2 in the Bibliography describes procedures and techniques that may be used for this analysis. Record the results on a data sheet (example is shown in Figure P-2). Each of the individual NO$_x$ analytical results for each

calibration gas shall be within 10 percent (or 10 ppm, whichever is greater) of the triplicate set average; otherwise, discard the entire set and repeat the triplicate analyses. If the average of the triplicate analyses is within 10 percent of the calibration gas manufacturer's cylinder tag value, use the tag value; otherwise, conduct at least three additional analyses until the results of six consecutive runs agree within 10 percent (or 10 ppmv, whichever is greater) of the average. Then use this average for the cylinder value.

6.2 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and, as applicable, the other system components. Introduce the calibration gases in any sequence, and make all necessary adjustments to calibrate the analyzer and the data recorder. Adjust system components to achieve correct sampling rates.

6.3 Analyzer Calibration Error. Conduct the analyzer calibration error check by introducing calibration gases to the measurement system at any point upstream of the gas analyzer as follows:

6.3.1 After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas on a form similar to Figure P-3. Note: A calibration curve established prior to the analyzer calibration error check may be used to convert the analyzer response to the equivalent gas concentration introduced to the analyzer. However, the same correction procedure shall be used for all effluent and calibration measurements obtained during the test.

6.3.2 The analyzer calibration error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds 2 percent of the span for any of the calibration gases. If an invalid calibration is exhibited, take corrective action and repeat the analyzer calibration error check until acceptable performance is achieved.

6.4 Sampling System Bias Check. Perform the sampling system bias check by introducing calibration gases at the calibration valve installed at the outlet of the sampling probe. A zero gas and either the mid-range or high-range gas, whichever most closely approximates the effluent concentrations, shall be used for this check as follows:

6.4.1 Introduce the upscale calibration gas, and record the gas concentration displayed by the analyzer on a form similar to Figure P-4. Then introduce zero gas, and record the gas concentration displayed by the analyzer. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement

system other than those necessary to achieve proper calibration gas flow rates at the analyzer. Alternately introduce the zero and upscale gases until a stable response is achieved. The tester shall determine the measurement system response time by observing the times required to achieve a stable response for both the zero and upscale gases. Note the longer of the two times as the response time.

6.4.2 The sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for the analyzer calibration error check and for the sampling system bias check exceeds 5 percent of the span for either the zero or upscale calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

6.5 Interference Response. In combustion sources, SO_2 is commonly present along with NOx. Most UV NOx analyzers use an internal interference correction algorithm to remove the effects of SO_2 onto the NOx concentrations. An SO_2 interference check, consistent with the manufacturer's recommendations, must be conducted prior to the initial use of the monitor. Thereafter, recheck the measurement system if changes are made in the instrumentation which alter the interference response (e.g. changes to detector). The effectiveness of the interference rejection may be also observed during SO_2 linearity and span testing during which time the NOx response of the analyzer may be also monitored.

7. Quality Assurance / Quality Control Guidelines. In an effort to improve the reliability and accuracy of this method, the following set of QA/QC guidelines apply. These guidelines address specific issues both in the sampling and analytical systems which may affect the measurement results. The QA/QC guidelines are structured to provide:
1) A summary description of the problem encountered;
2) A description of the type of sample system which may be affected;
3) A brief description of the potential problem or concern which may arise;
4) An impact assessment;
5) Suggested QC methods to prevent the problem;
6) An assessment of the critical factors affecting the QC method suggested;
7) A methodology for QA testing to determine the effects of the problem; and
8) A statement on the EPA Methods affected.

7.1 Condensate Forms in the Sampling System Absorbing NO_2 and Biasing the NO_x Results Negative.

7.1.1   If the sampling system is based on delivering a **sample to the detector:** By transferring the gas through heated sample lines to the analyzer system. Independent of whether the analyzer is based on a hot/wet or cold/dry measurement technique.

7.1.2   Then a **potential concern is**: Loss of NO_2 due to condensation of water in the sample line, and subsequent solvation of the gas. Also, a potential concern for acid mist condensation, or salt formation.

7.1.3   With potential bias effect: Results in negative bias to the species of interest. Also will result in slow response to zero gas, cal gas and changes in process gas composition due to absorption/desorption effects.

7.1.4   To minimize this problem, a **quality control surrogate is**: Use of a temperature controlled heated sample line at a minimum. Controlled lines are preferred over self-limiting lines, since the latter can exhibit large temperature variations as ambient conditions change. In cases where the effluent gas has been in contact with a wet scrubber, or other process situations where the stack gas is very near the water dewpoint temperature, a heated probe should also be used to minimize condensate formation.

7.1.5   With minimum QC performance criteria of: As a guideline, the sample system should be maintained at a temperature at least 20°C greater than the dewpoint temperature of the gas. The fairly large dewpoint margin is recommended to minimize the impact of cold spots in the sample line, and to ensure that excessively cold ambient conditions do not create additional problems. This dewpoint temperature may be calculated from the nominal water vapor pressure vs temperature data.

The following table may be used to determine a minimum sample line temperature to stay above the water dewpoint:

TABLE 1   WATER VAPOR DEWPOINT TEMPERATURE AS A FUNCTION OF WATER CONTENT

Water Vapor (abs) Pressure (mmHg)	Water Content (Mole %)	Dewpoint Temp. (°F/°C)	Recommended Sample Line Temp. (°F/°C)
17.5	2.3	(68/20)	(104/40)

31.8	4.2	(86/30)	(122/50)
55.3	7.3	(104/40)	(140/60)
92.5	12.3	(122/50)	(158/70)
149	19.7	(140/60)	(176/80)
234	30.8	(158/70)	(195/90)
355	49.7	(176/80)	(212/100)
525	69.1	(194/90)	(230/110)

In practice, there is little reason to ever use a sample line which operates at less than 100°C on an extractive analyzer system.

In the event that the stack gas to be analyzed contains ammonia, the sample system should be maintained above 150°C to prevent the formation of, and to expedite the decomposition of, ammonium sulfate or ammonium nitrate salts.

In the event that the stack contains significant quantities of SO_3, the sample system should be maintained above the SO_3/H_2SO_4 (acid mist) dewpoint temperature. This can be difficult, due to the high dewpoint temperature at even low concentrations of SO_3. The following table provides some guidelines:

TABLE 2   ACID DEWPOINT TEMPERATURE AS A FUNCTION OF SO_3 CONTENT
Note: Calculations based on a pressure of 14.7 (psia) and nominal water
content of 15 mole percent

SO_3 (acid mist) concentration (ppmv)	Acid Dewpoint (°C)
1	120.3
10	141.4
20	148.3
50	157.7

The condensation of acid mist in the sample system can lead to serious problems, including plugging and sluggish response speeds. An alternate method to minimize the transport of acid mist to the system is to include a sacrificial iron wool filter at the probe sample conditioning unit. SO_3 reacts with iron wool to form iron sulfate, which remains localized at the SCU and does not react with the other species.

7.1.6   And whose effectiveness may be confirmed by: A system

bias check must be performed by comparing the system response to calibration gas introduced directly to the analyzer and directly at the probe tip. First a probe tip calibration (as close to the probe tip as possible, and before any filtering elements in the system) must be performed, and the instrument response recorded. NO_2 calibration gas should then be introduced directly to the analyzer, and the NO_2 response from the device recorded, as well as the certified NO_2 concentration of the standard. The results of the two calibration checks must be reported on the documentation submitted with every test. A positive indication of sample system bias will be if:

$$\text{Absolute value} \left(100 * \frac{NO_2(\text{probe}) - NO_2(\text{Direct})}{NO_2(\text{Direct})} \right) > 4$$

This test determines that the sample line bias is less than 4 percent of the NO_2 test concentration.
Note that the test procedure must clearly state an order of events:

1)   System on stack gas for at least one hour;
2)   Direct to analyzer zero gas;
3)   Probe tip zero gas;
4)   Determine zero bias if any of sample system (occurs if degassing of condensate);
5)   System on stack gas for no less than one hour (allow any accumulation to occur);
6)   Probe tip calibration gas (this is to be done before direct to analyzer, since flow through sample   lines may stop while direct to analyzer calibration in progress); and
7)   Direct to analyzer calibration gas.

The sample system bias test should be performed immediately before the first test run on the facility, and after each subsequent test run.

Should the system fail the sample system bias test, the data collected since the last successful system bias check is presumed to have not met the method's stated DQO.

7.1.7   Methods Affected. Negative NOx bias in EPA Method 7E and this Method.

7.2 Absorption of NO_2 in Sample System Drier Condensate, Resulting in Negative NO_2 Bias.

7.2.1 If the sampling system is based on delivering a sample to the detector: On a dry basis system with a sample chiller/condenser.

7.2.2 Then a potential concern is: Loss of NO_2 due to contact water in the condenser, and subsequent solvation of the gas.

7.2.3 With potential bias effect: Results in negative bias to the species of interest. The presence of NO_x will also result in slow response at the analyzer due to absorption/desorption effects.

7.2.4 To minimize this problem, a quality control surrogate is: Use of a sample drier which minimizes gas contact with the condensate.

7.2.5 With minimum QC performance criteria of: As a guideline, the sample system should use a drier automatically removes condensate from the condenser region. Also, it should be designed to minimize contact time in the condenser region.

7.2.6 And whose effectiveness may be confirmed by: The system bias check (described previously) will provide some indication of the reliability of the sample drier. A more direct test for drier bias is as follows:

A condenser bias check may be performed by comparing the system response to calibration gas introduced directly to the analyzer and directly at the condenser inlet. First a condenser inlet calibration must be performed, and the instrument response recorded. NO_2 calibration gas should then be introduced directly to the analyzer, and the NO_2 response from the device recorded, as well as the certified NO_2 concentration of the standard. The results of the two calibration checks must be reported on the documentation submitted with the every test. A positive indication of sample system bias will be if:

$$\text{Absolute value} \left(100 * \left(\frac{NO_2(\text{inlet}) - NO_2(\text{Direct})}{NO_2(\text{Direct})}\right)\right) > 6$$

This test determines that the sample line bias is less than 6 % of the NO_2 test concentration which represents one half of the converter efficiency. Note that the test procedure must clearly state an order of events:

1)   System on stack gas for at least one hour;
2)   Direct to analyzer zero gas;
3)   Probe tip zero gas;
4)   Determine zero bias if any of sample system (occurs if degassing of condensate);
5)   System on stack gas for no less than one hour (allow any accumulation to occur);
6)   Probe tip calibration gas (this is to be done before direct to analyzer cal, since flow through sample lines may stop while direct to analyzer cal is in progress); and
7)   Direct to analyzer calibration gas.

Should the system fail the condenser bias test, the data collected since the last successful condenser
bias check is presumed to have not met the methods stated DQO.

7.2.7   Methods Affected.   No effect on EPA Method 7E and this Method. Negative NO_x bias on EPA
Method 7E if being used simultaneously with this Method.

7.3 Loss of Converter Efficiency, Resulting in Negative NO_2 Bias.

7.3.1   If the sampling system is based on delivering a sample to the detector: Any Sample System.

7.3.2   Then a potential concern is: Loss of NO_2 to NO conversion efficiency, if such a converter is used in the analyzer system.

7.3.3   With potential bias effect: Results in negative bias to the NO_x measurement.

7.3.4   To minimize this problem, a quality control surrogate is: Use of a proven NO_2 to NO converter system.

7.3.5   With minimum QC performance criteria of: Hours of online usage are to be recorded. Manufacturer data regarding anticipated lifetime (usually expressed in terms of hours of continuous use at a given NO_2 concentration) must also be reported on the data sheet. The NO_2 converter should be regenerated periodically, as advised from the manufacturers data.

7.3.6   And whose effectiveness may be confirmed by: Follow converter efficiency test method in Method 20.

Alternatively, the use of a certified NO_2 standard may be used to

test converter efficiency. Note also that the results obtained during the sample system bias check may be used to determine the NO_2 to NO converter efficiency. Performance criteria requires that a minimum 90 percent conversion efficiency be achieved. Thus, the analyzer will be deemed to pass the converter efficiency test if:

Absolute value (100 * ($\underline{NO_2(Cylinder) - NO_2(Direct)}$)) < 10
$NO_2(Cylinder)$

Converter efficiency tests must be performed immediately before beginning any test runs, and at the end of the test runs.

Should the system fail the sample system bias test, the data collected since the last successful converter efficiency check is presumed to have not met the methods stated DQO.

7.3.7 Methods Affected. EPA Method 7E and this Method. If the analyzer manufacturer employs an NO_2 to NO converter.

7.4 Adsorption/Permeation of NO Into Sample Lines, Resulting in Slow Response and Bias.

7.4.1 If the sampling system is based on delivering a sample to the detector: Any sample system employing Teflon® or other polymeric materials in the sample lines.

7.4.1 Then a potential concern is: Adsorption/Permeation of NO into sample lines, or permeation of NO out of sample lines during zero gas operations.(may also apply to varying extent to SO_2, NO_2 and CO)

7.4.2 With potential bias effect:

The potential bias effects will be:

Sampling Condition	Effect
With Zero gas flow thru sample system	Back-Permeation of NO – causes NO to be present in zero gas delivered to analyzer – bias effect is that Zero is set to correspond to positive NO concentration which causes negative bias of NO
With NO cal gas flow thru sample system	Permeation of NO into sample line – results in slow

(NO calibration gas concentration greater than typical stack gas NO concentration)	response and possible negative bias to NO
With NO cal gas flow thru sample system (NO cal gas concentration less than typical stack gas NO concentration)	Back-Permeation of NO out of sample line – results in slow response and possible positive bias to NO
With stack gas flowing through the sample system	Initial NO bias negative when flow first started, may introduce process lag as system becomes slow to respond to changes in NO concentration due to requirement for equilibrium to be achieved

7.4.3 To minimize this problem, a Quality Control surrogate is: Use a high quality, thick wall PFA sample line, and do not operate the sample line at higher temperatures than required (as defined in 7.1 and 7.2). Note that temperature controlled lines provide more stable temperatures than self limited lines.

Ensure that sample gas flow rates are large enough to minimize contact time with the sample line (rule of thumb is minimum 2 liters/min for every 50 feet of sample line length).

As a last resort, inject calibration gases direct to the analyzer

7.4.4 With minimum QC performance criteria of: For all sample lines, identify material of construction, internal diameter and wall thickness. Maintenance of sample lines is also important. Corroded surfaces, abraded surfaces, particulate deposits, or condensed organic materials will all lead to greater adsorption and/or permeation. Sample lines can be cleaned through acid washing, or by steaming out the sample line. After cleaning lines, condition the line with either sample gas or a calibration gas whose concentration(s) are similar to the stream composition of the stack gas in the intended use.

An important consideration is to prevent flow/diffusion of sample gas into the line when the line is cold. The occurrence of condensation in the line will lead to increased adsorption effects, and may result in acid formation which will damage the line and

promote permeation.

7.4.5 And whose effectiveness may be confirmed by: The influence of the sample line may be determined by a number of methods. The simplest is to allow sample gas to flow through the lines and analyzer for a period of time (minimum 2 hours). This allows for any adsorption or permeation of species into the line to occur. During this time, zero the analyzer by direct injection of the zero gas. Immediately after the direct zero, inject zero gas at the probe tip. If the zero achieved after injection of the sample gas at the probe tip is within 1% of the span concentration for the species of interest after three minutes, it is assumed that no adsorption or permeation is occurring.

If a positive deflection from zero is observed after three minutes of zero gas flow through the line, it may be assumed that Analyte gas is desorbing or back-permeating from the line. Record the data from analyzer as a function of time, at 30-second time intervals, during which time it is expected that the Analyte concentration will slowly decrease to a stable value. Determine the time it takes for the analyzer to achieve a stable zero reading. Stability is defined here as meaning that the change over a 2-minute time interval is less than 1 % of the span value for the analyzer, and that this level of stability is achieved over a time period of three consecutive readings.

In the event that it is determined that adsorption/desorption effects are experienced, the amount of time required to achieve a stable zero should be recorded on the test report, and all calibration gases (zero, span) must be run for a period of time equal to twice the stabilization period to allow for variations in the adsorption/permeation rates and to ensure that stability was achieved.

7.4.7 **Methods Affected.** EPA Method 6C, EPA Method 7E and this Method.

7.5 **Ambient Temperature and Pressure Effects on Analytical Results.**

7.5.1 If the sampling system is based on delivering a sample to the detector: Any sampling system.

7.5.2 Then a potential concern is: Effect of ambient pressure or temperature changes.

7.5.3   With potential bias effect: Results in sensitivity changes which is seen as span drift.

7.5.4   To minimize this problem, a quality control surrogate is: Use analyzers in a temperature controlled environment if possible. Vent analyzers to atmosphere or a vent header with minimal pressure fluctuations. Employ analyzers with automatic temperature and pressure compensation.

7.5.5   With minimum QC performance criteria of: Temperature variations during a test run should be not be greater than $5°C$, while pressure variations should be less than 10 mmHg. Should the ambient conditions around the analyzer change by greater amounts than this, a correction factor may be applied to compensate for these changes. The correction factor will be determined by the type and manufacturer of the analyzer in use, and should be provided by the vendor.

7.5.6   And whose effectiveness may be confirmed by: The effects of ambient temperature and pressure changes should be observed on the zero and span values recorded during the course of the test runs. Thus, the effectiveness of the temperature and pressure compensations, or the significance of temperature and pressure related drift, will be seen by the reproducibility of the zero and span gas data sets. The reproducibility of the zero and span should be better than 2 percent of the full scale range for the analyzer.

7.5.7   **Methods Affected.** EPA Method 6C, 7E and this Method.

7.6 CO_2 Quenching / O_2 Quenching.

7.6.1   If the Sampling System is Based on Delivering a Sample to the Detector: Direct extractive sample systems.

7.6.2   Then a potential concern is: If a chemiluminescent system used for NO_x (or pulsed fluorescence for SO_2), differences between the calibration gas background composition and the sample gas background composition may bias the results.

7.6.3   With potential bias effect: Results in negative bias to the NO_x measurement, positive or negative bias in the SO_2 measurement.

7.6.4   To minimize this problem, a quality control surrogate is:

Use of calibration gas blends which simulate the composition of the stack gas.

7.6.5   With minimum QC performance criteria of: In the case of chemiluminescent NO_x analyzers, the NO_x calibration cylinder should be a three component blend of NO, CO_2 and Nitrogen, with the CO_2 content being similar (+/- 2 mole percent) to the CO_2 content of the stack gas. In the absence of a suitable calibration blend, a correction factor may be applied based on test data or vendor data which demonstrates the degree of CO_2 quenching as a relative error per mole percent of CO_2 content.

In the case of pulsed flourescent SO_2 analyzers, the calibration gas should be a three component blend of SO_2, oxygen and nitrogen, with the oxygen content being similar (1 mole percent) to the oxygen content of the stack gas. In the absence of a suitable calibration blend, a correction factor may be applied based on test data or vendor data which demonstrates the degree of O_2 quenching as a relative error per mole percent of O_2 content.

In the event that correction factors are applied, the correction factor must be clearly indicated on the test data sheets.

7.6.6   And whose effectiveness may be confirmed by: There are no reliable field methods to confirm that quenching effects did not occur when sampling stack gas. The degree to which said effects occur depend largely on the properties of the individual analyzers.

7.6.7   **Methods Affected.**   EPA Method 7E and EPA Method 6C.

7.7 SO_2 Cross Interference Onto NO.

7.7.1   If the sampling system is based on delivering a sample to the detector: Any Sample System.

7.7.2   Then a potential concern is: Improper calibration of the system results in cross-interference of SO_2 onto the NO channel, which biases the NO concentration accuracy.

7.7.3   With potential bias effect: Results in positive or negative bias to the NOx measurement.

7.7.4   To minimize this problem, a quality control surrogate is: When calibrating the analyzer, use an SO_2 cylinder whose

concentration is within 25 percent of the actual stack gas concentration. When the calibration is performed, perform any adjustments to the analyzer to minimize the cross-interference.

When using the UV method for NO_x on streams which contain SO_2, ensure that the predicted stack gas composition falls within the manufacturers specifications for maximum SO_2/NO_x ratio.

7.7.5   With minimum QC performance criteria of: When performing the SO_2 calibration, record both the SO_2 concentration results and the NO_x concentration results. During the SO_2 calibration, the maximum allowed NO_x is the greater of:

A) 2 percent of the SO_2 concentration, or
B) 2 percent of the minimum full scale range for NO_x as specified by the manufacturer.

7.7.6   And whose effectiveness may be confirmed by: In the event that the efficacy of the SO_2 correction procedure is in question, a three point calibration should be performed under laboratory conditions to determine if the correction factor works across the concentration range of interest. The three point calibration would include a 10 percent of full scale, midpoint and 90percent of full scale gas run with SO_2. The results will be analyzed in accordance with the minimum QC performance criteria stated in 7.9.5.

7.7.7   Methods Affected.   This Method.

7.8   **Interference on NO Channel, Bias NO Positive.**

7.8.1   If the sampling system is based on delivering a sample to the detector: Any Sample System.

7.8.2   Then a potential concern is: The presence of another UV absorbing gas, other than SO_2 or NO_2, which interferes with the measurement of NO is present in the stack gas.

7.8.3   With potential bias effect: Results in positive bias to the NO_x measurement.

7.8.4   To minimize this problem, a quality control surrogate is: The UV method for NO_x should only be used on source categories as specified in the method, and in which there is no process data or past experience to predict the presence of interferences. Common interfering gases are reduced sulfur compounds and aromatic

hydrocarbons.

In addition, some UV NO_x analyzers may employ an additional analytical wavelength which is used as an internal QA check. This additional wavelength is used to perform measurements in a wavelength region where typical NO interferents absorb. The internal QA check provides information as to whether the analyzer can readily determine the fact that another UV absorbing species is present in the sample gas.

7.8.5   With minimum QC performance criteria of: Identification of Manufacturer dependant interfering species and method dependant allowed source categories.

7.8.6   And whose effectiveness may be confirmed by: When used on source categories other than those specified in the method, or when the results are questioned, good engineering judgement should be applied to determine if the combustion source is likely to produce interfering gases. In addition, the source or source category results may be corroborated by any other of the reference methods for NO_x.

7.8.7   **Methods Affected.** This Method.

7.9   Dilution Extractive System, Flow Through Dilution Probe
     Stream Dependant (positive or negative bias
on all species).

7.9.1   If the sampling system is based on delivering a sample to the detector: Dilution extractive system.

7.9.2   Then a potential concern is: Flow through the dilution system is affected by changes in sample gas molecular weight, as well as absolute stack pressure and stack temperature.

7.9.3   With potential bias effect: Results in positive or negative bias to the NO_x measurement.

7.9.4   To minimize this problem, a quality control surrogate is: Use of multi-component gas mixtures for calibration of the dilution probe system. The addition of CO_2 (to emulate stack composition) will minimize molecular weight differences between stack gas and calibration gas, and provide a more accurate match to the sampling conditions.

7.9.5   With minimum QC performance criteria of: None

7.9.6   And whose effectiveness may be confirmed by: EPA Report "Eliminating Bias …." By James Jahnke.

7.9.7   Methods Affected. EPA Method 7E, 6C and this Method if dilution extractive system is used.

8.   EMISSION TEST PROCEDURE

8.1   Selection of Sampling Site and Sampling Points.   Select a measurement site and sampling points using the same criteria that are applicable to Method 7.

8.2   Sample Collection.   Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check.   Maintain constant rate sampling (i.e., 10 percent) during the entire run.   The sampling time per run shall be the same as for Method 7 plus twice the average system response time.   For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed to determine the average effluent concentration.

8.4   Zero and Calibration Drift Tests.   Immediately preceding and following each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in Section 6.4.   (Make no adjustments to the measurement system until after the drift checks are completed.) Record the analyzer's responses on a form similar to Figure P–4.

8.4.1 If either the zero or upscale calibration value exceeds the sampling system bias specification, then the run is considered invalid.   Repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before repeating the run.

8.4.2 If both the zero and upscale calibration values are within the sampling system bias specification, then use the average of the initial and final bias check values to calculate the gas concentration for the run. If the zero or upscale calibration drift value exceeds the drift limits, based on the difference between the sampling system bias check responses immediately before and after the run, repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section

6.4) before conducting additional runs.

9. EMISSION CALCULATION

Follow Section 8 of Method 6C.

10. BIBLIOGRAPHY
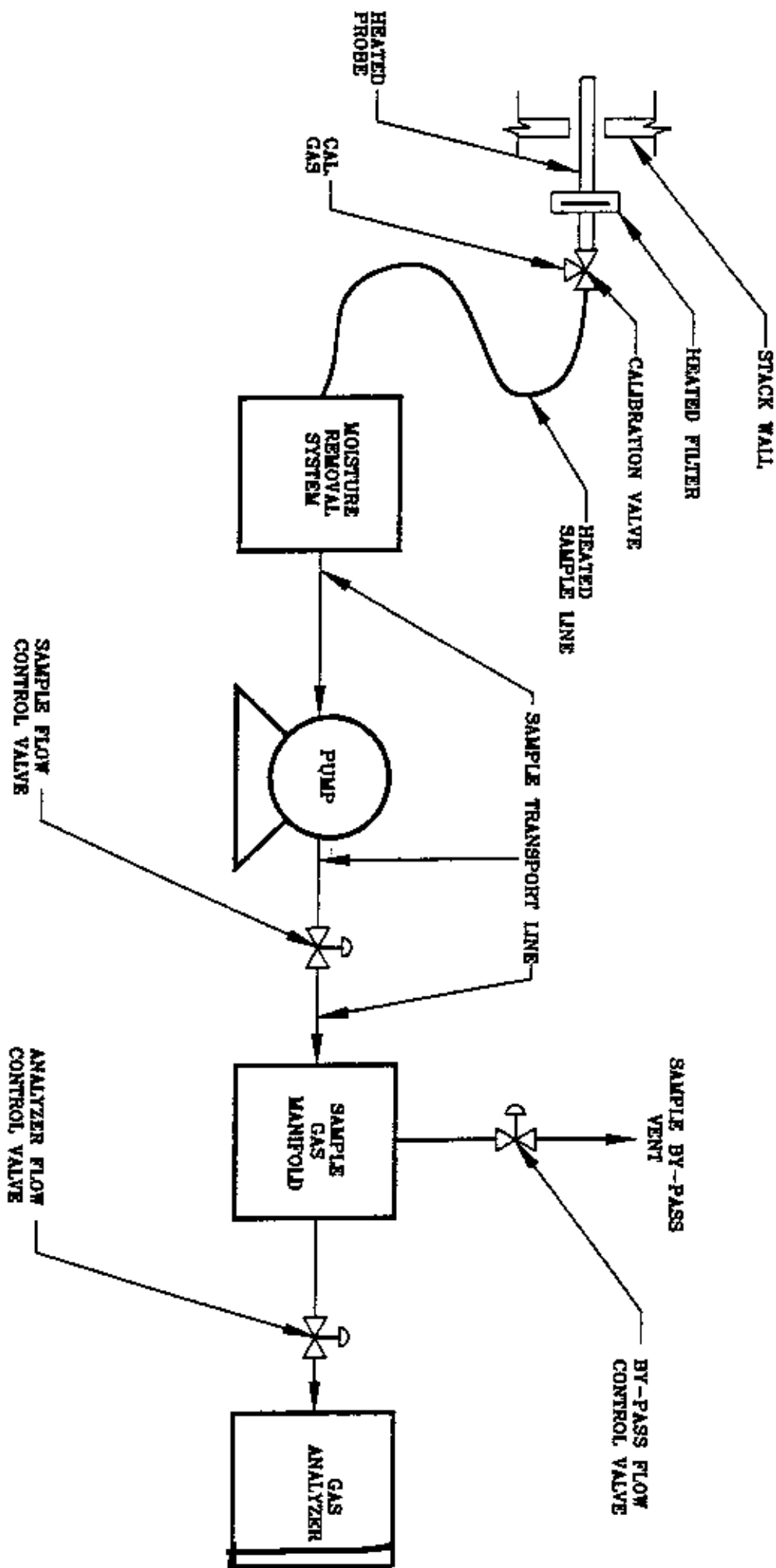
Same as bibliography of Method 6C.

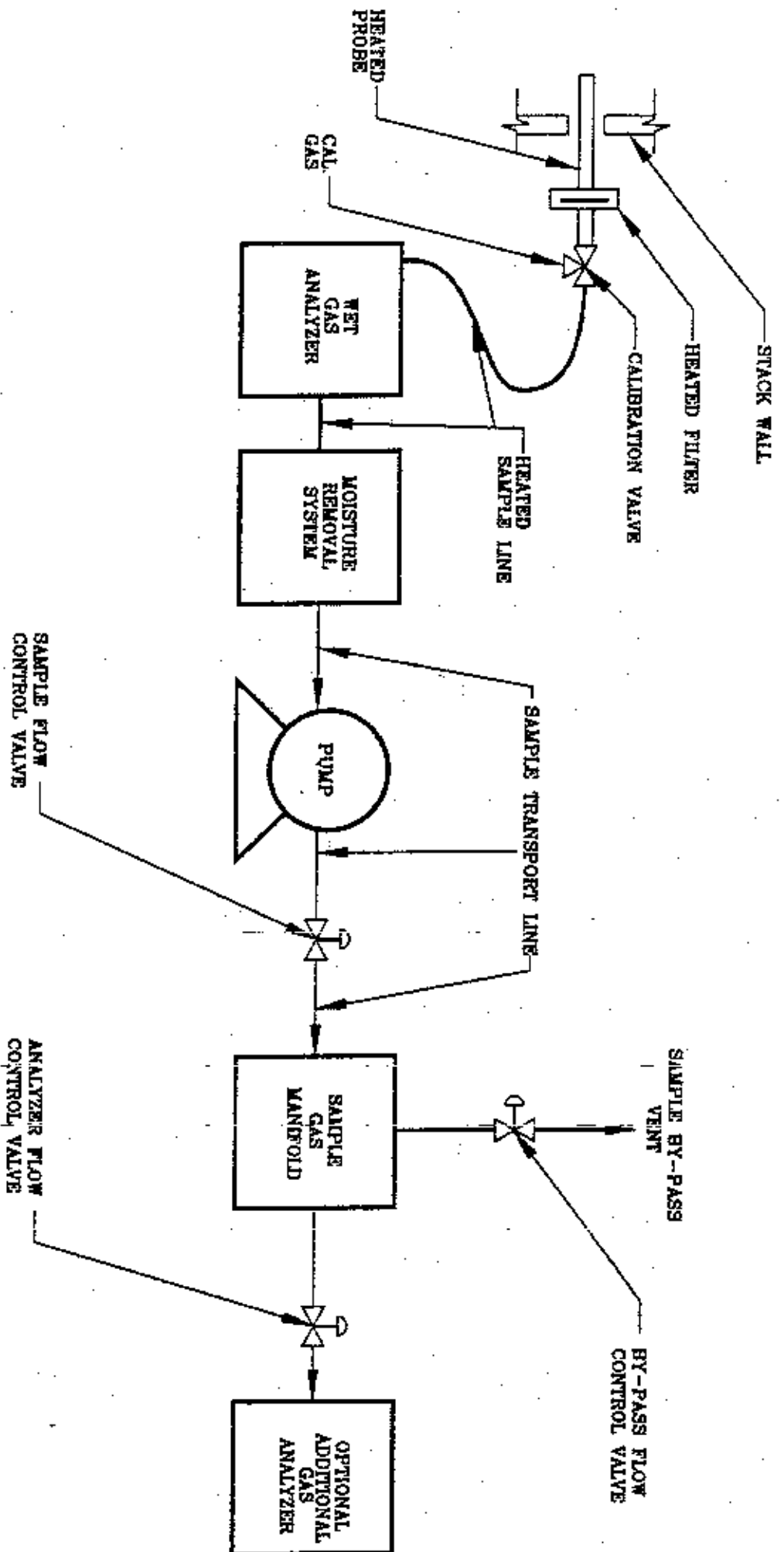Figure P–1A   DRY MONITOR MEASUREMENT SYSTEM SCHEMATIC.

Figure P–1B – WET MONITOR MEASUREMENT SYSTEM SCHEMATIC.

NOTE:
ALL EQUIPMENT AFTER THE WET GAS ANALYZER IS OPTIONAL. WET ANALYZERS MAY BE
PROVIDED WITH THEIR OWN INTERNAL SAMPLE PUMP OR ASPIRATOR SYSTEM TO PROVIDE
SAMPLE GAS FLOW THROUGH THE ANALYZER.

HEATED
PROBE

CAL.
GAS

STACK WALL

HEATED FILTER

CALIBRATION VALVE

WET
GAS
ANALYZER

HEATED
SAMPLE LINE

MOISTURE
REMOVAL
SYSTEM

SAMPLE FLOW
CONTROL VALVE

SAMPLE TRANSPORT LINE

PUMP

SAMPLE GAS
MANIFOLD

SAMPLE BY-PASS
VENT

BY-PASS FLOW
CONTROL VALVE

ANALYZER FLOW
CONTROL VALVE

OPTIONAL
ADDITIONAL
GAS
ANALYZER

FIGURE P-2—ANALYSIS OF CALIBRATION GASES

Date _____
Analytic method used _____

| | Gas concentration (indicate units) | | |
	Zero [a]	Mid-range [b]	High-range [c]
Sample run:			
1 _____	____	____	____
2 _____	____	____	____

| | Gas concentration (indicate units) | | |
	Zero [a]	Mid-range [b]	High-range [c]
3 _____	____	____	____
Average _____	____	____	____
Maximum percent deviation _____			

[a] Average must be less than 0.25 percent of span.
[b] Average must be 50 to 60 percent of span.
[c] Average must be 80 to 90 percent of span.

FIGURE P-3 —ANALYZER CALIBRATION DATA

Source Identification: _____ Analyzer calibration data for sampling
Test personnel: _____ runs: _____
Date: _____ Span: _____

	Cylinder value (indicate units)	Analyzer calibration response (indicate units)	Absolute difference (indicate units)	Difference (percent of span)
Zero gas _____	____	____	____	____
Mid-range gas _____	____	____	____	____
High-range gas _____	____	____	____	____

FIGURE P-4 —SYSTEM CALIBRATION BIAS AND DRIFT DATA

Source Identification: _____ Date: _____
Test personnel: _____ Run number: _____
Span: _____

| | Analyzer calibration response | Initial values | | Final values | | Drift (percent of span) |
		System calibration response	System cal. bias (percent of span)	System calibration response	System cal. bias (percent of span)	
Zero gas _____	____	____	____	____	____	____
Upscale gas _____	____	____	____	____	____	____

$$\text{System Calibration Bias} = \frac{\text{System Cal. Response} - \text{Analyzer Cal. Response}}{\text{Span}} \times 100$$

$$\text{Drift} = \frac{\text{Final Cal. Response} - \text{Analyzer Cal. Response}}{\text{Span}} \times 100$$