

California Environmental Protection Agency



Method 100

Procedures for Continuous Gaseous Emission Stack Sampling

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Method 100

Table of Contents

	<u>Page</u>
1 OVERVIEW	1
1.1 PRINCIPLE	1
1.2 APPLICABILITY	1
1.3 SAFETY	1
1.4 ALTERNATIVE TEST PROCEDURES	1
1.5 DEFINITIONS	2
1.6 SOURCE TEST PERFORMANCE SPECIFICATIONS	3
2 EQUIPMENT	3
2.1 SAMPLE TRANSFER SYSTEM	3
2.2 GAS ANALYZERS AND DATA ACQUISITION	4
2.3 MEASUREMENT OF STACK FLOWRATE, MOISTURE, AND OTHER PARAMETERS	5
3 CALIBRATION GASES	6
3.1 CALIBRATION GASES	6
3.2 GAS DILUTION SYSTEM	7
4 ON-SITE PREPARATION FOR SAMPLING	7
4.1 CLEANING/ASSEMBLY OF SAMPLE TRAIN	7
4.2 CALIBRATION OF CONTINUOUS ANALYZERS	7
4.3 PRETEST LEAK CHECK	7
4.4 SAMPLE SYSTEM BIAS CHECK	8
4.5 DETERMINATION OF SAMPLING TRAVERSE POINTS	8

Table of Contents (con't)

5 SAMPLE COLLECTION 8

6 POST TEST PERFORMANCE CHECKS 8

6.1 ZERO AND CALIBRATION DRIFT 9

6.2 SAMPLING SYSTEM BIAS 9

7 CALCULATIONS 10

7.1 POLLUTANT CONCENTRATION 10

7.2 MASS EMISSION RATE 10

7.3 POLLUTANT CONCENTRATION FOR 12% CO₂ OR 3% O₂ 11

TABLE 100.1 GAS ANALYZER SPECIFICATIONS 12

FIGURE 100.1 METHOD 100 SAMPLE TRAIN ASSEMBLY 15

METHOD 100

Procedures for Continuous Gaseous Emission Stack Sampling

1 OVERVIEW

1.1 PRINCIPLE

A sample of an exhaust gas stream is extracted, conditioned and analyzed continuously by instruments. The measurements made by the continuous analyzers are used to determine average emission concentrations. By measuring the stack gas flowrate and moisture, and using this information with the average emission concentration, mass emission rates can be determined.

1.2 APPLICABILITY

This method is applicable for determining emissions of oxides of nitrogen, carbon monoxide, carbon dioxide, sulfur dioxide, total hydrocarbons, and oxygen from stationary source flowing gas streams in ducts, stacks and flues. This procedure does not supersede the New Source Performance Standards requirement for permanently installed continuous emissions monitoring instruments.

This test procedure is an alternative method to appropriate U.S. EPA reference methods, in particular, EPA methods 3A, 6C, 7E, 10, and 25A and B. This procedure should be used only on those sources where equivalency to the reference methods has been established or the specific regulations for the source specify this procedure.

1.3 SAFETY

This method does not address the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices including the safe handling of compressed gases, flammable gases and any hazardous compounds and to determine the applicability of regulatory limitations prior to use of this method.

1.4 ALTERNATIVE TEST PROCEDURES

Any modification of this method beyond those expressly permitted shall be subject to approval by the Executive Officer of the Air Resources Board or his or her authorized representative.

1.5 DEFINITIONS

1.5.1 Range

The upper limit of the gas concentration measurement range displayed on the data recorder. The range is selected so that the sample gas concentration is between 10 and 95 percent of the range for each pollutant of interest.

1.5.2 Calibration Gas

A known concentration of a gas in an inert diluent gas.

1.5.3 Analyzer Calibration Error

The difference between the known concentration of a calibration gas and the concentration measured by the gas analyzer when the calibration gas is introduced directly to the gas analyzer.

1.5.4 Sampling System Bias

The difference between the concentration measured by a gas analyzer when a known concentration calibration gas is introduced at the sampling probe and when the same gas is introduced directly to the analyzer.

1.5.5 Zero Drift

The difference between the concentration measured by the gas analyzer for zero gas before the sample run and the concentration measured by the analyzer for zero gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

1.5.6 Calibration Drift

The difference between the concentration measured by the gas analyzer for a calibration gas before the sample run and the concentration measured by the analyzer for that same calibration gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

1.5.7 Response Time

The time required for the data recorder to display 95% of the difference in gas concentration on the data recorder after a step change in gas concentration, such as a switch from zero gas to calibration gas.

1.5.8 Interference Check

Determination of the concentration measured for a known concentration of a component in the sample gas other than the target gas component being measured by the gas analyzer.

1.6 SOURCE TEST PERFORMANCE SPECIFICATIONS

The following specifications must be met for data from a test run to be considered valid:

1.6.1 Analyzer Calibration Error

± 2 percent or less of the range when introducing zero or calibration gas.

1.6.2 Zero Drift

± 3 percent or less of the range during a test run.

1.6.3 Span Drift

± 3 percent or less of the range during a test run.

1.6.4 Sampling System Bias

± 5 percent or less of the range when introducing zero or calibration gas.

1.6.5 Interference Check

For each analyzer, ± 5 percent or less of the range.

2 EQUIPMENT

2.1 SAMPLE TRANSFER SYSTEM

A schematic of the sampling train is shown in Figure 100.1.

2.1.1 Probe Nozzle

Quartz, borosilicate glass, stainless steel, porcelain or aluminum oxide may be used for the probe nozzle.

2.1.2 Probe Filter

An internal or external probe filter may be used. As necessary, provisions should be made for back flushing the filter to remove particulate build-up.

2.1.3 Probe

The probe shall have an inside diameter of 6 mm or larger and shall be constructed of quartz, borosilicate glass, stainless steel, aluminum oxide or porcelain.

2.1.4 Sample Line

The sample line is constructed of teflon or other material which does not absorb or otherwise alter the sample gas.

2.1.5 Probe Calibration System

Calibration gases for a sampling system bias check are introduced at the probe. Depending on the configuration of the probe, calibration gas is injected at an internal probe filter, at the probe tip, or directly behind the probe outlet.

2.1.6 Sample Conditioner

The sample conditioner shall be capable of reducing the sample gas temperature to 15 °C (60 °F), or to 11 °C (20 °F) lower than the ambient temperature, whichever is lower. All parts of the conditioner exposed to the sample shall be glass, stainless steel or teflon. The sample gas shall not be bubbled or dispersed through the condensate such that minimum contact shall be maintained between any condensate and the sample gas. A temperature gauge shall be used to determine the temperature of the condenser outlet.

If needed, a glass filter is used at the inlet or the outlet of the conditioner to prevent the accumulation of particulate material.

2.1.7 Sample System Heaters

If needed to prevent condensation of water or hydrocarbons, or the reaction of other stack constituents, a probe heater may be used. If necessary, use a heated sample line, heated filters, and a heated analyzer. Heaters shall heat the sample to a minimum of 120°C (248°F) or to a temperature above the dewpoint of the target constituent, whichever is greater. Perform no sample conditioning that lowers the sample temperature.

2.2 GAS ANALYZERS AND DATA ACQUISITION

2.2.1 Specifications

Specifications for the acceptance of gas analyzers for use of Method 100 are listed in Table 100.1. The vendor must provide test data demonstrating that the following performance requirements are met: minimum detection limit, noise level, response time, repeatability, linearity, interference, sensitivity to temperature change, and 24-hour zero and calibration drift limits.

The analyzers shall be housed in a temperature-controlled, vibration-free environment.

2.2.2 Carbon Dioxide and Carbon Monoxide

Nondispersive infrared analyzers are acceptable.

2.2.3 Oxygen

A paramagnetic analyzer or an electrochemical (fuel cell) analyzer is acceptable.

2.2.4 Total Hydrocarbons

An analyzer using a flame ionization detector (FID) or a nondispersive infrared analyzer (NDIR) is acceptable. Propane or methane is usually used as a span gas. The hydrocarbon species should be characterized prior to the source test to determine that the detector will respond predictably to the organic compounds present. Compound-specific calibration curves must be determined for use of either the FID or the NDIR analyzer to measure specific organic compounds.

2.2.5 Oxides of Nitrogen

An analyzer using chemiluminescence is acceptable. The NO₂ to NO converter must have at least a 90% efficiency in converting nitrogen dioxide (NO₂) in the sample gas to nitric oxide (NO). An NO₂ to NO converter is not necessary if data are presented to demonstrate that the NO₂ portion of the exhaust gas is less than 5 percent of the total NO_x concentration. A low temperature (maximum 350°C) converter must be used when NH₃ is present. A high temperature (650°C) stainless steel converter may be used when no NH₃ is present.

If data are not available to demonstrate that the concentration of NO₂ in the sample gas is less than 5% of the total NO_x concentration, a test of the efficiency of the NO₂ converter must be conducted prior to each source test.

2.2.6 Sulfur Dioxide

An analyzer using infrared or ultraviolet absorption or fluorescence is acceptable.

2.2.7 Other Analyzers

An analyzer operating by measurement principles not listed in Table 100.1 may be used, if its performance meets the requirements of Table 100.1.

2.2.8 Data Acquisition System/Data Recorder

Provide a permanent record of gas analyzer data using a strip chart recorder. A data logger or other electronic data acquisition system may also be used. Any electronic data acquisition system must be capable of integration at a ten second interval. The strip chart, as well as the data acquisition system, must have a resolution of 0.5 percent of the analyzer range. Data reporting includes the following information: pollutant, source, analyzer range, date, time, zero offsets, person operating instruments, and any other pertinent data.

2.3 MEASUREMENT OF STACK FLOWRATE, MOISTURE, AND OTHER PARAMETERS

2.3.1 Stack Gas Flowrate and Moisture Measurement

Stack gas flowrate and moisture content can be determined using equipment specified by ARB Test Methods 1 through 4. Stack gas velocity can be determined from a pitot tube measurement as outlined by Methods 1 and 2. Two possible alternatives are:

- (1) A simultaneous traverse of stack gas concentration and velocity,

- (2) A pre and a post test velocity traverse. (Repeat the velocity traverse whenever aware of a change in process conditions which may affect emissions.)

Note: If the pitot tube and the sampling probe are used in combination in a testing assembly, care must be taken that any aerodynamic effects on the pitot tube are eliminated. Otherwise, the pitot tube must be calibrated with the other components of the test assembly in place. (See ARB Method 2, Section 4.1.1.)

Alternate methods of flowrate measurement, including consideration of fuel rate, combustion stoichiometry and oxygen concentration in the stack gas and applicable F-factors listed in 40 CFR Part 60 Appendix A, Method 19, must be approved by the Executive Officer of the Air Resources Board or his or her authorized representative.

2.3.2 Barometer

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg. shall be used.

2.3.3 Vacuum Gauge or Flowmeter

Use a vacuum gauge or a flowmeter for leak check of the sampling train.

3 CALIBRATION GASES

3.1 Calibration Gases

The calibration gases must be certified according to EPA Traceability Protocol¹. Alternately the calibration gases must be certified to an analytical accuracy of ± 2 percent, traceable to a reference material approved by the National Institute of Standards and Technology (NIST), and recertified annually.

Multi-component gas mixtures certified according to EPA Protocol are acceptable. Multi-component gas mixtures which meet the following requirements are also acceptable: the concentration of each component gas must be certified to an analytical accuracy of ± 2 percent, each component must be traceable to a NIST standard, and the mixture must be recertified semi-annually.

A permeation tube may be used as a calibration standard in place of the calibration gas, provided the following requirements of EPA Method 16 (CFR 60 Appendix A) are met for use of permeation tubes: Section 5.5 for the calibration system, Section 6.5 for the calibration gases, Sections 8.2 and 8.3 on pretest calibration, and Sections 10.2 and 10.3 on post test calibration.

For each pollutant to be measured, use the following three calibration gases:

1 "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, "EPA-600/R93/224, Revised September 1993.

3.1.1 High-Range Gas

The concentration should be between 80 and 100 percent of the analyzer range.

3.1.2 Mid-range Gas

The concentration should be between 40 and 60 percent of the analyzer range.

3.1.3 Zero Gas

Purified air or, if appropriate, nitrogen with a contaminant concentration less than 0.25% of the analyzer range for the appropriate pollutant gas may be used.

3.2 GAS DILUTION SYSTEM

A gas dilution system which meets the requirements of EPA Method 205, Verification of Gas Dilution Systems for Field Instrument Calibrations, CFR 40, Part 51, Appendix M, may be used to provide low-level calibration gases from a high-level calibration gas. The calibration gas used with a gas dilution system should be an EPA Protocol gas. A gas dilution system which meets the requirements of EPA Method 205 may be used for all analyzer calibrations and sampling system bias checks.

4 ON-SITE PREPARATION FOR SAMPLING

4.1 CLEANING/ASSEMBLY OF SAMPLE TRAIN

The sample train may be cleaned prior to being transported to the field. When at the testing site, assemble the cleaned sample train as shown in Figure 100.1.

4.2 CALIBRATION OF CONTINUOUS ANALYZERS

Allow analyzers to warm up according to manufacturer's instructions. Adjust system components to achieve the individual analyzer sampling rates recommended by the instrument manufacturer. Alternately introduce zero and calibration gases to the instruments and make all necessary adjustments to calibrate the analyzer and the data recorder.

Conduct the analyzer calibration error check by sequentially introducing the three calibration gases (high-range, mid-range and zero gas) and recording the analyzer response to each calibration gas. Make no adjustments to the sampling/analysis system except those necessary to achieve the proper calibration gas flowrate. The test run will be considered invalid if the analyzer calibration error for any calibration gas exceeds ± 2 percent of the range. If needed, take corrective action until acceptable performance is achieved.

4.3 PRETEST LEAK CHECK

Perform a leak check on the vacuum side of the assembly at the maximum pump vacuum. Correct any leaks found and repeat the leak check and correction procedure until no leak is detected.

4.4 SAMPLE SYSTEM BIAS CHECK

A pretest sampling system bias check is required for each gas analyzer.

Perform the sampling system bias check by alternately introducing at the probe the zero gas and either the high-range or mid-range calibration gas, whichever calibration gas is closest in concentration to the sample gas. Record the gas concentrations 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 rate. Determine the sampling system response time.

If the difference between the gas concentrations for the analyzer calibration error check and the sample system bias check exceeds $\pm 5\%$ of the range for either the zero or upscale calibration gas, the bias check is invalid. If needed, take corrective action before repeating the sample system bias check. If the analyzer is adjusted, repeat the analyzer calibration error check before repeating the bias check.

4.5 DETERMINATION OF SAMPLING TRAVERSE POINTS

Select gas sampling traverse points according to the guidelines given in ARB Methods 1 and 2 for velocity traverses. Multipoint gas sampling must be performed unless data are available to demonstrate that the mean pollutant concentration is less than 10% different from that at any single point.

5 SAMPLE COLLECTION

Insert the sample probe assembly into the stack and block off the remainder of the sample port opening. Set the probe at the predetermined position and begin data acquisition. If a traverse is required, the sampling time at each traverse point is constant. Sample for at least the sampling system response time plus one minute, allowing enough time for the system to be flushed and the instruments to respond fully. Move probe to next position and repeat. Continue until the stack has been fully traversed.

A test shall include at least three sample runs. Each sample run shall be the length of time specified in the applicable emission limit regulation. As a minimum, the sampling time must be such that the emission test is conducted during representative operating conditions of the source. For a sample run exceeding two hours, conduct sampling system bias checks every two hours. Record performance check data. As necessary, back flush through the probe to prevent particulate build-up on the probe filter. Periodically check the sample conditioner and remove condensate as needed.

If adjustments to the sampling train are necessary during the sample run, conduct a system bias check before any adjustments are made. After any adjustments are made to the analyzer, the analyzer calibration error check shall be conducted. After all adjustments are made to the sampling system, the sampling system bias check shall be performed prior to continuation of the test run.

6 POST TEST PERFORMANCE CHECKS

At the end of the sample run, conduct a sampling system bias check for all analyzers. Perform the sampling system bias check by alternately introducing the zero gas and the calibration gas at the probe. During the sampling system 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 through the sampling system to the gas analyzer.

6.1 ZERO AND CALIBRATION DRIFT

The test run shall be considered invalid if the difference of zero or calibration gas measured for the post run sampling system bias check and zero or calibration gas measured for the initial sampling system bias check of the first test run (Section 4.5) exceeds ± 3 percent of the range. Use Equation 100-1, below:

$$\text{Drift} = \frac{(c_{ib} - c_{fb})}{r} \times 100$$

Eq. 100 - 1

Where:

c_{fb} = analyzer response for the zero or upscale calibration gas for post run sampling system bias check

c_{ib} = analyzer response for the zero or upscale calibration gas for initial sampling system bias check

r = analyzer range

6.2 SAMPLING SYSTEM BIAS

The test run shall be considered invalid if the difference of zero or calibration gas measured for the post run sampling system bias check and zero or calibration gas measured for the initial analyzer calibration (Section 4.2) exceeds ± 5 percent of the range. Calculate bias using Equation 100-2:

$$\text{Bias} = \frac{(c_a - c_{fb})}{r} \times 100$$

Eq. 100 - 2

Where:

c_{fb} = analyzer response for the zero or upscale calibration gas for post run sampling system bias check

c_a = analyzer response for the zero or upscale calibration gas for initial analyzer calibration

r = analyzer range

7 CALCULATION OF POLLUTANT CONCENTRATION AND MASS EMISSION RATE

7.1 POLLUTANT CONCENTRATION

Determine the average concentration, C_{gas} , of each stack gas constituent using Equation 100-3:

$$C_{\text{gas}} = (C_{\text{avg}} - C_o) \times \frac{C_{\text{cal}}}{(C_{\text{bcal}} - C_o)}$$

Eq. 100 - 3

Where:

- C_{gas} = Effluent gas concentration, ppm or % by volume
- C_{avg} = Average gas concentration indicated by gas analyzer, ppm or % by volume
- C_o = Average of initial (c_{ib}) and final (c_{fb}) system bias responses for zero gas, ppm or % by volume
- C_{cal} = Actual concentration of the calibration gas used for the bias check, ppm or % by volume
- C_{bcal} = Average of initial (c_{ib}) and final (c_{fb}) sampling system bias responses for the calibration gas, ppm or % by volume

7.2 MASS EMISSION RATE

The emission rate in pounds per hour of pollutant is E in Equation 100-4:

$$E = C_{\text{dgas}} \times \frac{M}{385 \times 10^6} \times Q \times 60$$

Eq. 100 - 4

Where:

- C_{dgas} = effluent gas concentration corrected to dry basis, ppm
- M = molecular weight in lb/lb-mole
- 385 = standard volume in cubic feet of one lb-mole (at 528° R and 1 atmosphere)
- Q = Stack flowrate in standard dry cubic feet per minute of stack effluents, determined from ARB Methods 2 and 4, or alternative determinations of flow rate and moisture content

7.3 POLLUTANT CONCENTRATION FOR 12% CO₂ OR 3% O₂

The pollutant concentration C_{dgas} is adjusted for 12% CO₂ in Equation 100-5:

$$C_{12\% \text{ CO}_2} = C_{\text{dgas}} \times \frac{12\%}{\% \text{ CO}_2 \text{ during test}}$$

Eq. 100 - 5

For correction to 3% O₂ (using O₂ in air as 20.9%), use Equation 100-6:

$$C_{3\% \text{ O}_2} = C_{\text{dgas}} \times \frac{20.9 - 3.0}{20.9 - \% \text{ O}_2 \text{ during test}}$$

Eq. 100 - 6

**Table 100.1 (page 1 of 3)
Gas Analyzer Specifications**

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
Typical Principle of Operation ²	Ultraviolet or infrared absorption or fluorescence	Chemiluminescence	Infrared absorption	Infrared absorption	Flame ionization or infrared absorption	Paramagnetic or electrochemical cell
Typical Concentration Ranges PPM or % by volume	10 - 2500 ppm	10 - 1000 ppm	10 - 1000 ppm	5 - 20 %	50 ppm - 50%	5 - 25 %
Minimum detection limit, % of full scale for lowest range.	2%	2%	2%	2%	2% as Propane	2%
Noise Level % of range	< ±1%	< ±1%	< ±1%	< ±1%	< ±1%	< ±1%
Response Time to 95% of steady state after a step change in concentration	< 30 secs.	<30 secs.	< 60 secs.	< 60 secs.	< 30 secs.	< 60 secs.
Repeatability, % of range ³	1%	1%	1%	1%	1%	1%
Zero Drift after 24 hours of unadjusted continuous operation, % range	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%

² Other types will also be acceptable provided that the criteria listed below are met.

³ 1% of the analyzer range is the maximum absolute difference between replicate results which may be expected with a probability of 95%.

**Table 100.1 (page 2 of 3)
Gas Analyzer Specifications**

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
Span Drift after 24 hours of unadjusted continuous operation, % range	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%
Interference of a component other than the target component measured by the gas analyzer, % of range	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %
Analyzer response to temperature variation ⁴	✓	✓	✓	✓	✓	✓
A change in ambient temperature of ± 20° C from 25°C shall not cause a permanent change to the zero or span response of analyzer	✓	✓	✓	✓	✓	✓

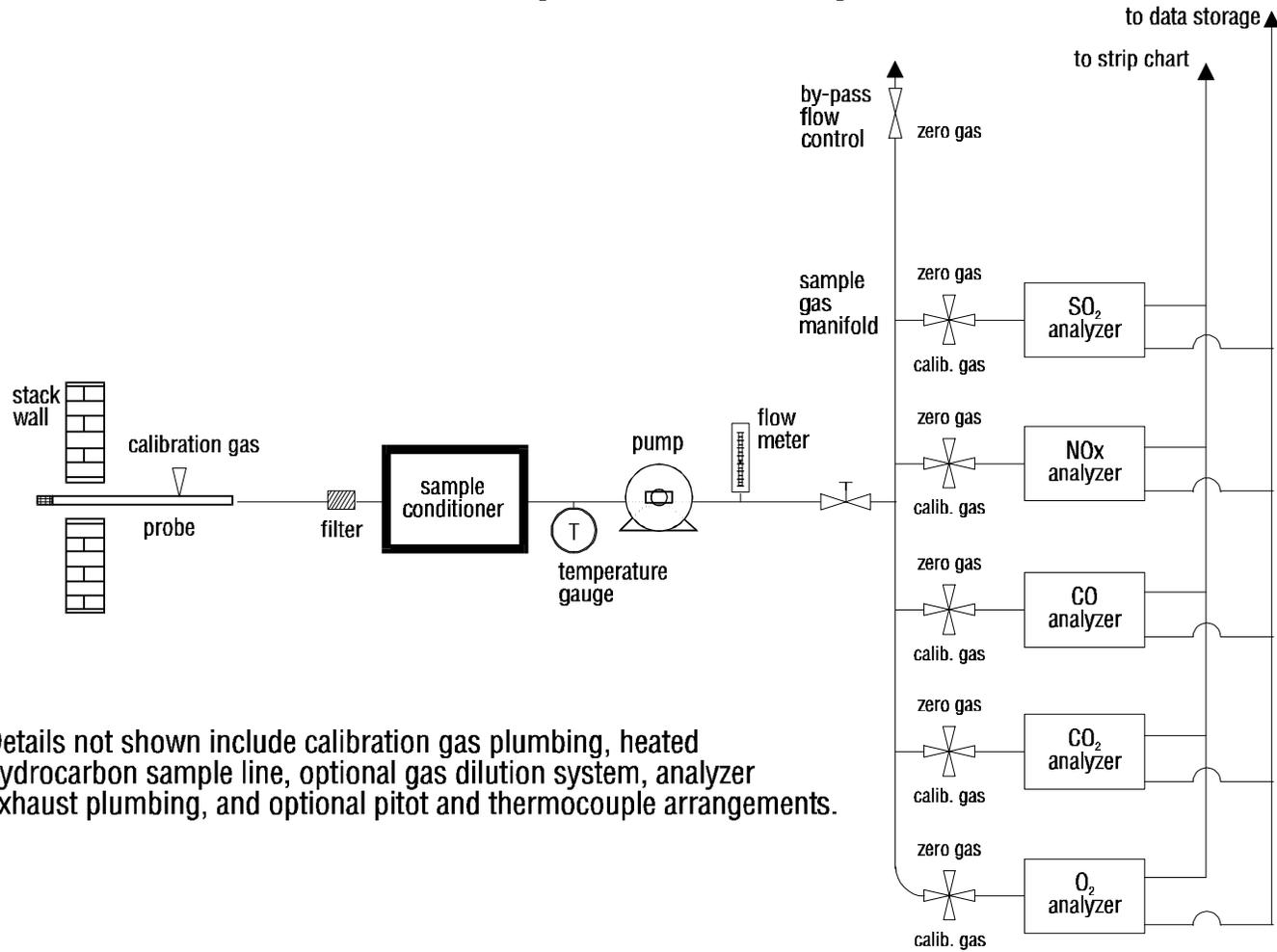
⁴ When sampling zero or span gas, the analyzer response shall not change more than ± 2% of range when the ambient temperature changes ± 10 °C from 25 °C.

**Table 100.1 (page 3 of 3)
Gas Analyzer Specifications**

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
Linearity ⁵	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%

⁵ Maximum deviation between a mid-range calibration reading and the reading predicted by a straight line drawn between high-range and zero gas calibration points, as a percent of the range.

FIGURE 100.1
Method 100 Sample Train Assembly



* Details not shown include calibration gas plumbing, heated hydrocarbon sample line, optional gas dilution system, analyzer exhaust plumbing, and optional pitot and thermocouple arrangements.