

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 100.1

INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS  
EMISSION SAMPLING

OFFICE OF OPERATIONS  
TECHNICAL SERVICES DIVISION  
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## METHOD 100.1

# INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS EMISSION SAMPLING

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## METHOD 100.1

### INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS EMISSION SAMPLING

#### Section 1 of 3

## 1. Overview

### 1.1 Principle

A representative sample of an exhaust gas stream is continuously extracted, conditioned, and conveyed to instrumental analyzers for the determination of:

- Sulfur dioxide (SO<sub>2</sub>) gas concentrations using an ultraviolet (UV) or a non-dispersive ultraviolet (NDUV) analyzer.
- Oxides of nitrogen (NO<sub>x</sub>) gas concentrations using a chemiluminescent analyzer.
- Oxygen (O<sub>2</sub>) gas concentrations using an electrochemical (fuel cell) type analyzer.

- Carbon monoxide (CO) gas concentrations using a non-dispersive infrared (NDIR) analyzer.
- Carbon dioxide (CO<sub>2</sub>) gas concentrations using a non-dispersive infrared (NDIR) analyzer.

Other systems may be used to measure SO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub> if they meet the specifications of this method and have been subjected to a relative accuracy test to determine equivalence.

Performance specifications and test procedures are provided to ensure reliable data. Typical analyzer specifications are shown in Table 100.1-1.

## 1.2 Applicability

This method measures emissions of SO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub> from stationary source gas streams flowing in ducts, stacks, and flues. This procedure does not supersede the New Source Performance Standards (NSPS) requirement for permanently installed continuous monitoring instruments.

This test procedure is an alternative to SCAQMD reference methods, in particular SCAQMD Methods 3.1, 6.1, 7.1, and 10.1. It should be used only on sources where its equivalency to the reference methods has been established, or where specific regulations for the source specify this procedure.

### 1.3 Range and Sensitivity

#### 1.3.1 Analytical Range

The analytical range is selected so that the sample gas concentration for each run is between 20 and 95 percent of the range, for 95 percent of the test period. The run is considered invalid if the measured gas concentration exceeds the range during the test period. Data obtained below 20 percent of the range can be used only for qualitative purpose.

#### 1.3.2 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 shall be less than 2  
percent of the range.

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## 2. Field Procedures

### 2.1 Definitions

#### 2.1.1 Measurement System

Equipment required to determine sample gas concentration consists of three major sub-systems:

Sample Interface - The portion of the system used for sample acquisition, sample transport, sample conditioning, and protection of the analyzers from the effects of the stack effluent.

Gas Analyzer - The portion of the system that identifies the gas component and generates an output proportional to its concentration.

Data Acquisition - A strip chart recorder, analog computer and printer, or any combination thereof, for recording measurement data from the analyzer output.

#### 2.1.2 Range

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

#### 2.1.3 Calibration Gas

A gas of known concentration in an inert diluent gas.

#### 2.1.4 Analyzer Calibration Error

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



#### 2.1.5 Sampling System Bias

The difference between the gas concentrations exhibited by the measurement system when calibration gas is introduced at the sampling probe tip filter and when the same calibration gas is introduced directly to the analyzer.

#### 2.1.6 Zero Drift

The difference in the measurement system responses at a zero concentration level during the initial calibration, and final calibration check after a test. During this test there should be no unscheduled maintenance, repair, or adjustment of the measurement system.

#### 2.1.7 Calibration Drift

The difference in the measurement system responses at a mid-range concentration level during the initial calibration, and final calibration check after a test. During this test there should be no

unscheduled maintenance, repair, or adjustment of the measurement system.

#### 2.1.8 Response Time

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

#### 2.1.9 Interference Response

The output response of the measurement system to a component in the sample gas, other than the gas component being measured.

#### 2.1.10 Calibration Curve

A graph or other systematic method of establishing the relationship between the analyzer response and the actual calibration gas concentration introduced to the analyzer.

### 2.1.11 Linearity

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

## 2.2 Measurement System Performance Specifications

### 2.2.1 Analyzer Calibration Error

Less than  $\pm$  2 percent of the reading for calibration gases.

### 2.2.2 Sampling System Bias

Less than  $\pm$  5 percent of the range for the zero, and mid-or high range calibration gases.

### 2.2.3 Zero Drift

Less than  $\pm$  3 percent of the range over the period of each run.

#### 2.2.4 Calibration Drift

Less than  $\pm$  3 percent of the range over the period of each run.

#### 2.2.5 Interference Response

Each of the analyzers described shall have the following minimum interference response to the gases listed. For example, an SO<sub>2</sub> analyzer should respond no more than 30 ppm when the NO<sub>2</sub> concentration in the sample gas is 2000 ppm.

##### SO<sub>2</sub> Analyzer

NO<sub>2</sub> 2,000/30

NH<sub>3</sub> 10<sup>6</sup>/0

##### CO<sub>2</sub> Analyzer

H<sub>2</sub>O 10,000/1

CO 15,000/1

CH<sub>4</sub> 20,000/1

##### CO Analyzer

H<sub>2</sub>O 200,000/1

CO<sub>2</sub> 500,000/1

SO<sub>2</sub> 10<sup>6</sup>/1

NO 10<sup>6</sup>/1

NO<sub>2</sub> 10<sup>6</sup>/1

HC 10<sup>6</sup>/1

N<sub>2</sub>O 10<sup>3</sup>/1

#### 2.2.6 Linearity

Less than  $\pm$  1.0 percent of the range for the pretest and post test values.

### 2.3 Apparatus and Measurement System

A schematic of an acceptable measurement system is shown in Figures 100.1-1, 100.1-2, and 100.1-3. The essential components of the measurement system are described below.

#### 2.3.1 Probe

Use quartz, borosilicate glass, stainless steel, aluminum oxide, porcelain, Hastalloy, or Inconel tubing of approximately 1/4 inch diameter or larger. If stack temperatures are above 1200°F the probe should be designed to minimize the time the sample is kept at those high temperatures. Use a heated probe if condensation occurs.

### 2.3.2 Sample Line

Use Teflon or stainless steel tubing to transport the sample gas to the moisture removal system. The sampling line should be heated to prevent condensation. If the sample passes through a moisture knockout trap immediately after extraction from the stack, it is not necessary to heat the sample transport line downstream of the moisture removal trap. A sample line made from another material may be used if the material does not absorb, adsorb, evolve, or alter the pollutants being monitored.

### 2.3.3 Probe Calibration System

Calibration gases should be introduced into a baffled sample chamber around the probe tip filter when in the probe calibration mode.

#### 2.3.4 Sample Conditioning

- a. The sample conditioner should be capable of reducing moisture content to below a dewpoint of 35°F.
- b. All parts exposed to the sample should be glass, stainless steel, or Teflon.
- c. Remove water by using refrigeration or a permeation dryer designed to minimize contact between the condensate and sample gas.
- d. Provide for back flushing the probe filter with zero air to remove particulate buildup on the probe filter.

#### 2.3.5 Sample Transport Lines

Use Teflon or stainless steel lines to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and sample gas manifold.

### 2.3.6 Particulate Filter

Use an in-stack 5 micron stainless steel or Inconel 600 porous filter or a heated (sufficient to prevent water condensation) out-of-stack filter. The out-of-stack filter should 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 to extend the useful life of the components. All filters should be fabricated of materials that are nonreactive to the gas being sampled.

### 2.3.7 Sample Pump

Use a leak-free pump 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 nonreactive to the gas being sampled.



### 2.3.8 Sample Flow Rate Control

Use a control valve and rotameter to maintain a sampling rate constant within 10 percent.

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 analyzers from overpressurization or the need for flow rate adjustments.

### 2.3.9 Sample Gas Manifold

Use a sample gas manifold to divert a portion of the sample gas stream to the analyzer, and the remainder to the bypass discharge vent. The sample gas manifold also should include provisions for introducing calibration gases directly into the analyzer. The manifold may be constructed of any material that is nonreactive to the gas being sampled.

### 2.3.10 Gas Analyzer

Use a gas analyzer to continuously determine the SO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub>, CO<sub>2</sub>, or CO concentration in the sample gas stream. Each analyzer should meet the applicable performance specifications of Section 2.2. Each analyzer should be provided with a means of controlling its flow rate and a device for determining proper sample flow rate (e.g. precision rotameter, pressure gauge downstream of all flow controls).

An NO<sub>2</sub> to NO converter in an NO<sub>x</sub> analyzer is the portion of the system that converts nitrogen dioxide (NO<sub>2</sub>) in the sample gas to nitric oxide (NO). An NO<sub>2</sub> to NO converter is not necessary if data are presented to demonstrate that the NO<sub>2</sub> portion of the exhaust gas is less than 5 percent of the total NO<sub>x</sub> concentration. A high temperature (650°C) stainless steel converter should be used when no NH<sub>3</sub> is present and a low temperature (350°C) molybdenum converter should be used when NH<sub>3</sub> is present. Other converters may be used if equivalence is demonstrated.

Housing the analyzer in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.

#### 2.3.11 Data Recorder

Use a strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution, or readability should be 0.5 percent of range. Sampling measurements should be obtained at a minimum of 1 minute intervals.

#### 2.3.12 Interference Response Sampling System

Introduce an interference test gas to the analyzer. The analyzer zero should be given a positive offset prior to the test to allow measurement of a negative interference. As an alternative, offset chart paper may be used to avoid changing the analyzer zero.

#### 2.3.13 Pitot Tubes

Same as required by SCAQMD Methods 1.1 and 2.1.

#### 2.3.14 Differential Pressure Gauge

Same as required by SCAQMD Methods 1.1 and 2.1.

#### 2.3.15 Sample Gas Moisture Content Equipment

As specified by SCAQMD Method 4.1.

#### 2.3.16 Barometer

Use a mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 0.1 in. Hg.

#### 2.3.17 Vacuum Gauge

Use a 30 in. Hg gauge for leak checking the sampling system.

### 2.3.18 Thermocouple

Use a Type K thermocouple to measure the temperature of the stack gas.

## 2.4 Calibration Gases

Calibration gases shall be certified according to EPA Traceability Protocol Number 1 (see Table 100.1-2 for cylinder gas recertification schedule) or certified to an analytical accuracy of  $\pm 1$  percent and be traceable to applicable NIST\* Standard Reference Materials (SRM's). Traceability shall include identification of applicable SRM and its cylinder number.

Super blends, i.e. gas mixtures of nitric oxide, sulfur dioxide, carbon monoxide and carbon dioxide with nitrogen as the balance gas, may be used for simultaneous calibration of multiple analyzers. The average deviation of each component gas shall not exceed  $\pm 1$  percent of the tag value, and shall be confirmed using NIST traceable standards within the certification period of the lowest component in the mixture.

EPA Traceability Protocol No. 1 is in the Appendix.

\*NIST - National Institute of Standards and Technology

Use three calibration gases as specified below:

#### 2.4.1 High-Range Gas

The concentration should be equivalent to 80 to 100 percent of the range.

#### 2.4.2 Mid-Range Gas

The concentration should be equivalent to 40 to 60 percent of the range.

#### 2.4.3 Zero Gas

The impurity concentration should be less than 0.25 of one percent of the range. Purified ambient air may be used for the zero gas by passing compressed air through a heatless dryer, a catalytic oxidizer, and a carbon dioxide scrubber.

Use ultra zero grade nitrogen gas for zeroing the O<sub>2</sub> analyzer.

## 2.5 Measurement System Performance Test Procedures

Perform the following procedures before measurement of emissions (Section 2.6).

### 2.5.1 Cleaning of Sample Train

As needed, thoroughly flush the probe, heat-trace line, and sample conditioner with distilled water, followed by acetone. Dry with filtered dry air.

### 2.5.2 Continuous Analyzers

Allow analyzers to warm up according to manufacturer's instructions.

### 2.5.3 Sampling System Preparation

A leak check of the sampling system is a good practice. However, it is optional.

Assemble the sample train as shown in Figures 100.1-1, 100.1-2 and 100.1-3.

Leak check the vacuum side of the assembly to a minimum of 20 inches of Hg (gauge). The sampling system should hold 20 inches of Hg vacuum for 5 minutes with less than 1 in. Hg loss. Correct any leaks found and repeat the leak check until a satisfactory result is obtained. Check the pressure side of the system with liquid soap solution and correct any leaks. Alternative leak check methods are acceptable if equivalent or better than the specified method.

The sample train assembly may be modified as follows to reflect actual stack conditions:

- If the stack is at or below ambient temperature and condensation is not observed upstream of the sample conditioner, the probe heating element and the heat trace line can be eliminated.
- If only concentration measurements are required, the Pitot tube can be eliminated.



Introduce zero and high range calibration gases directly to the instruments and make all necessary adjustments to calibrate the analyzer and the data recorder. Adjust system components to achieve individual analyzer sampling rates recommended by the instrument manufacturer.

#### 2.5.4 Analyzer Calibration Error

Conduct the analyzer calibration error check at the beginning and end of each test run by introducing calibration gases to the measurement system at any point upstream of the gas analyzer as follows:

- a. 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 100.1-4.

The calibration error check should be considered invalid if the gas concentration displayed by the analyzer exceeds  $\pm 2$  percent of the reading 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.

#### 2.5.5 Instrument Response Time

Establish during semi-annual certification.

#### 2.5.6 Sampling System Bias Check

A bias check of the sampling system is mandatory.

Backflush gas through the probe as necessary to prevent particulate buildup on the probe filter. Perform the sampling system bias check by introducing calibration gases into a baffled sample chamber around the probe tip filter.

A zero gas and either the mid-range or high-range gas, whichever most closely approximates the effluent concentrations, should be used for this check as follows:

- a. Introduce the upscale calibration gas and record the gas concentration displayed by the analyzer on a form similar to Figure 100.1-5. Introduce the 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 manufacturer recommended calibration gas flow rates at the analyzer.
- b. The sampling system bias check shall be considered invalid if the difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the sampling probe tip and when the same gas is introduced directly to the

analyzer, exceeds  $\pm 5$  percent of the analyzer range. 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.

#### 2.5.7 NO<sub>2</sub> to NO Conversion Efficiency

Conduct an NO<sub>2</sub> to NO conversion efficiency test in accordance with EPA Method 20 or by using an NBS traceable gas mixture of NO<sub>2</sub> in air.

### 2.6 Emission Test Procedure

Traverse the duct to determine if there is stratification (see Chapter X). Single point gas sampling is acceptable if the gas composition is homogeneous, i.e. < 10 percent variation between any two traverse points in the gas stream throughout the cross sectional diameter of the

stack. For multipoint gas sampling use every other point, as required by SCAQMD Method 5.1 for particulate matter. Determine moisture content and velocity pressures in the stack gas according to SCAQMD Methods 1.1, 2.1 and 4.1 if required for mass flow rate calculations. The probe inlet should never be closer than one inch to the stack wall. As an alternate method, the mass flow rate may be obtained by stoichiometric and gas composition relations.

#### 2.6.1 Chart Recorder Label

Turn on strip chart recorder and label the chart as to pollutant, source, range, calibration cylinder ID number, certified expiration date, zero and upper range calibration settings, chart speeds, date, time, person operating instruments, and other pertinent data.

#### 2.6.2 Sample Probe Traverse and Minimum Sampling Time

Insert the sample probe assembly into the stack and blank off the remainder of the opening. Conduct a gas sample traverse to

determine if single point sampling is acceptable and label the response obtained on the strip chart. If a traverse is required, leave the probe at each traverse point for at least the system response time plus one minute, allowing enough time for the system to be flushed and the instruments to respond fully. Move the probe to the next traverse point and repeat. Continue until the stack has been fully traversed.

A minimum sample time of 60 minutes is recommended. See District Rules and Regulations and permit conditions for applicable requirements. When the test duration exceeds one hour, conduct zero and span checks every 2 hours. Adjust settings as necessary, mark strip charts, and record in log books.

### 2.6.3 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. (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 100.1-5.

2.6.3.1 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 and the sampling system bias check procedure before repeating the run.

2.6.3.2 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 and the sampling system bias check procedure before conducting additional runs.

#### 2.6.4 Post Run Leak Check

If a prerun leak check is conducted, proceed as follows:

See Section 2.5.3. If the leak rate is 2 percent or more of the total sample flow rate (approximately 0.4 SCFH) discard the test.

#### 2.7 Emission Calculation

Determine the average gas effluent concentration from the average gas concentration displayed by the gas analyzer and adjust for zero and high range calibration drift. The average gas concentration displayed by the analyzer may be determined by integration of the area under the curve for chart recorders, or by averaging all of



the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. Sampling measurements should be obtained at a minimum of 1 minute intervals. Calculate the effluent gas concentration using the following equation:

$$C_{\text{gas}} = (\bar{C} - C_0) \frac{C_{\text{ma}}}{C_{\text{m}} - C_0}$$

where:

$C_{\text{gas}}$  = Effluent gas concentration, dry basis, ppm

$\bar{C}$  = Average gas concentration indicated by gas analyzer, dry basis, ppm

$C_{\text{ma}}$  = Actual concentration of the upscale calibration gas, ppm

$C_{\text{m}}$  = Average of initial and final system calibration bias check responses for the upscale calibration gas, ppm

C<sub>0</sub> = Average of initial and final system  
calibration bias check responses for the  
zero gas, ppm

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### 3. Calculations and Reporting

#### 3.1 Emission Rate of Gas

$$E = \frac{(C_g)(M)}{379 \times 10^6} (Q) (60)$$

where:

E = Emission rate, lb/hr

C<sub>g</sub> = Concentration of gas, ppm

M = Molecular weight of gas\*, lb/lb-  
mole

Q = Stack Effluent, dscfm

60 = Conversion factor, min/hr

379 x 10<sup>6</sup> = Conversion factor, scf/lb-mole

\*NO<sub>x</sub> is often expressed as NO<sub>2</sub>

### 3.2 Percent Excess Air

$$EA = \frac{[O_2 - 0.5 CO]}{[0.264 N_2 - (O_2 - 0.5 CO)]} \times 100$$

where:

EA = Percent excess air

O<sub>2</sub> = Percent O<sub>2</sub> by volume, dry basis  
(measured)

CO = Percent CO by volume, dry basis  
(measured)

N<sub>2</sub> = Percent N<sub>2</sub> by volume, dry basis  
(calculated)

0.264 = Ratio of O<sub>2</sub> in air, v/v

### 3.3 Pollutant Concentration Calculated to 12 Percent CO<sub>2</sub>, 3 Percent O<sub>2</sub>, and 15 Percent O<sub>2</sub>

Concentration(12 Percent O<sub>2</sub>) =

$$\text{Concentration(std)} \times \frac{12}{CO_2 \text{ (measured)}}$$

CO<sub>2</sub> = Percent CO<sub>2</sub> by volume, dry basis

Concentration(3 Percent O<sub>2</sub>) = Concentration(std)

$$\text{Concentration(std)} \times \frac{20.9 - 3.0}{20.9 - O_2 \text{ (measured)}}$$

Concentration(15 Percent O<sub>2</sub>) = Concentration(std)

$$\text{Concentration(std)} \times \frac{20.9 - 15.0}{20.9 - \text{O}_2 \text{ (measured)}}$$

Based on O<sub>2</sub> in air as 20.9 percent.

TABLE 100.1-1

ANALYZER SPECIFICATIONS FOR CONTINUOUS GASEOUS EMISSION STACK SAMPLING

	Sulfur Dioxide	Oxides of Nitrogen	Carbon Monoxide	Carbon Dioxide	Oxygen
Typical Principle of Operation (1)	Ultra-Violet or Non-Dispersive Ultra-Violet Absorption Photometry	Chemiluminescence	Non-Dispersive Infrared Absorption	Non-Dispersive Infrared Absorption	Electrochemical
Typical Range of Conc.	50, 250, 1000 ppm	10, 25, 100, 250, 1000, 10,000 ppm	5, 10, 50, 500, 2500, 5000 ppm	2, 10, 20 Percent	5, 10, 25 Percent
Noise Level, Percent of Full Scale	< ± 1.0	< ± 1.0	< ± 1.0	< ± 1.0	< ± 1.0
Response Time, Time Interval from a Step Change in Input Conc. at Inlet to Instrument to Output Reading of 95 Percent of Steady State	10 Seconds	3 Seconds	10 Seconds	10 Seconds	10 Seconds
Analyzer Calibration Error, Percent of Range for the Zero, Mid-Range Calibration Gases	< ± 2.0	< ± 2.0	< ± 2.0	< ± 2.0	< ± 2.0
Zero Drift, Percent of Range Over the Period of Each Run	< ± 3.0	< ± 3.0	< ± 3.0	< ± 3.0	< ± 3.0

TABLE 100.1-1 CONT.

	Sulfur Dioxide	Oxides of Nitrogen	Carbon Monoxide	Carbon Dioxide	Oxygen
Calibration or Span Drift, Percent of Range Over the Period of Each Run	< ± 3.0	< ± 3.0	< ± 3.0	< ± 3.0	< ± 3.0
Precision, Maximum Avg. Deviation from Mean Change as Percent of Range	< ± 1.0	< ± 1.0	< ± 1.0	< ± 1.0	< ± 1.0
Linearity (2)	< ± 1.0	< ± 1.0	< ± 1.0	< ± 1.0	< ± 1.0
Interference Response	NO <sub>2</sub> 2000/30 NH <sub>3</sub> 10 <sup>6</sup> /0	-	H <sub>2</sub> O 200,000/1 CO <sub>2</sub> 500,000/1 SO <sub>2</sub> 10 <sup>6</sup> /1 NO 10 <sup>6</sup> /1 NO <sub>2</sub> 10 <sup>6</sup> /1 HC 10 <sup>6</sup> /1 N <sub>2</sub> O 10 <sup>3</sup> /1	H <sub>2</sub> O 10,000/1 CO 15,000/1 CH <sub>4</sub> 20,000/1	-

(1) Other types may also be acceptable.

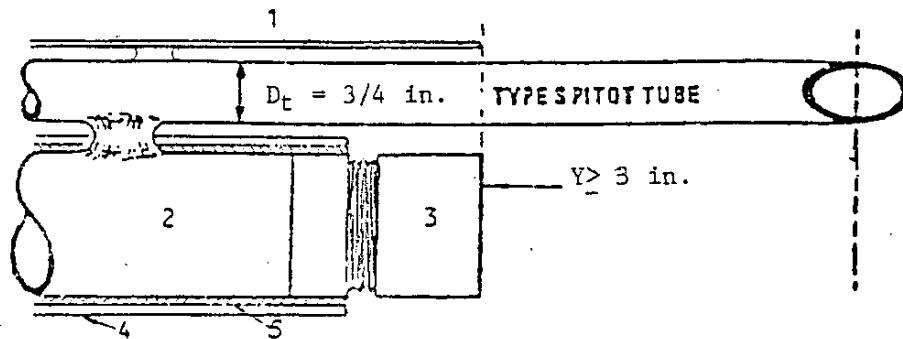
(2) Maximum deviation between a mid-range calibration reading and the reading predicted by a straight line drawn between high-range and zero gas calibration points, as a percent of range.

TABLE 100.1-2

Cylinder Gas Recertification Schedule for EPA  
Protocol 1 Traceable Standards

Pollutant	Balance Gas	Concentration Range	Maximum Months Until Recertification for Passivated Aluminum Cylinders: Al
Carbon Monoxide	N <sub>2</sub> Air	≥ 10 ppm	36
Carbon Dioxide	N <sub>2</sub>	> 0.5%	36
Nitric Oxide	N <sub>2</sub>	≥ 5 ppm	24
Nitrogen Dioxide	N <sub>2</sub> or Air	≥ 1000 ppm	24
Oxygen	N <sub>2</sub>	≥ 2%	36
Propane	Air	≥ 3 ppm	36
Sulfur Dioxide	N <sub>2</sub> or Air	50-499 ppm	24
Others not Specifically Listed			6

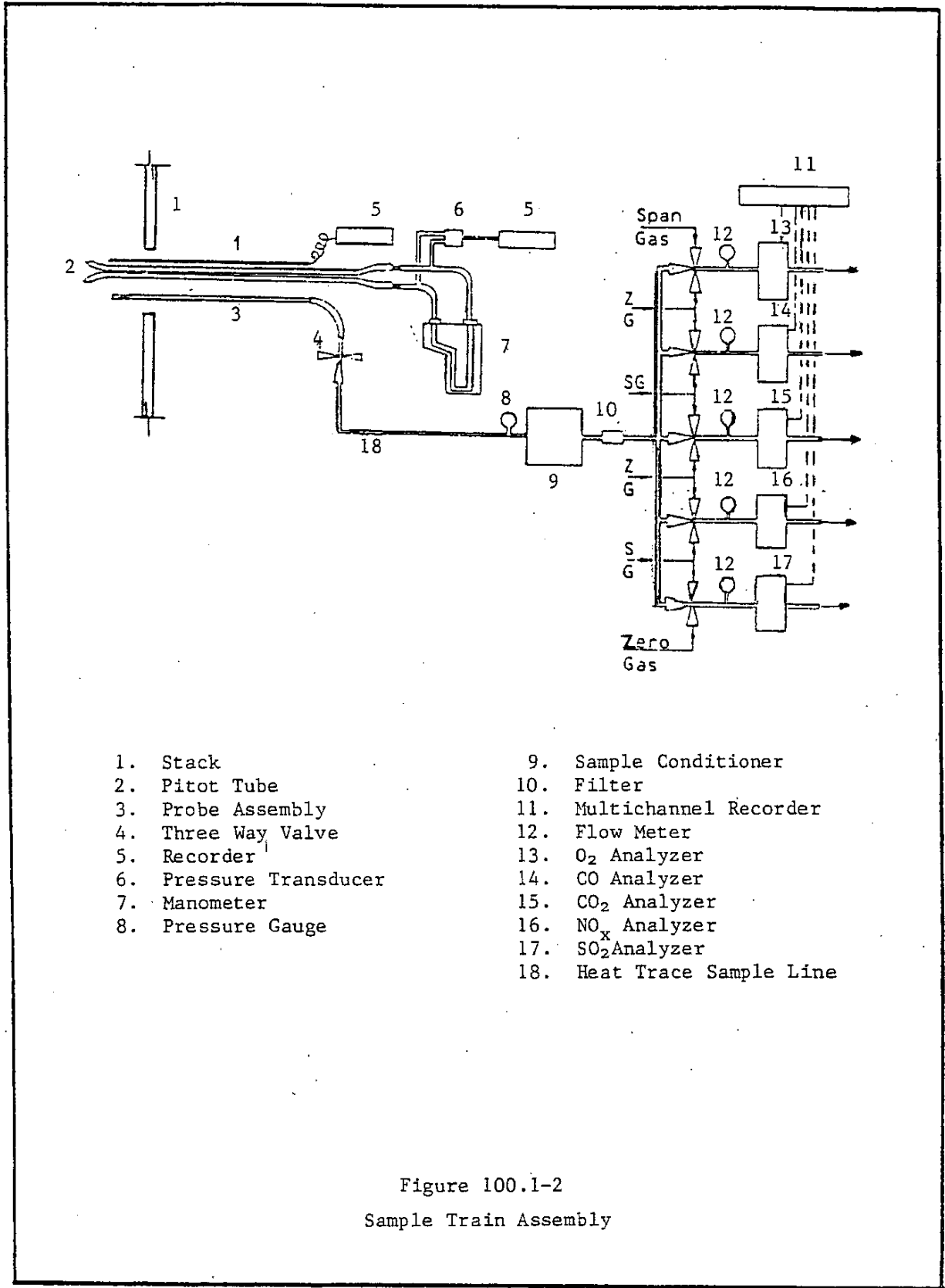




1. Thermocouple
2. Sample Probe
3. Probe Filter
4. Probe Shield
5. Heating Element

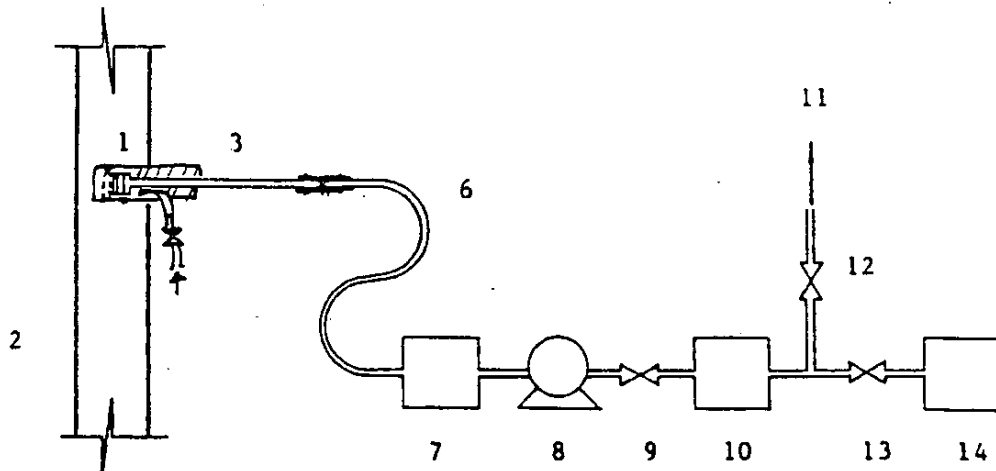
Figure 100.1-1

Sample Probe Assembly



- |                        |                              |
|------------------------|------------------------------|
| 1. Stack               | 9. Sample Conditioner        |
| 2. Pitot Tube          | 10. Filter                   |
| 3. Probe Assembly      | 11. Multichannel Recorder    |
| 4. Three Way Valve     | 12. Flow Meter               |
| 5. Recorder            | 13. O <sub>2</sub> Analyzer  |
| 6. Pressure Transducer | 14. CO Analyzer              |
| 7. Manometer           | 15. CO <sub>2</sub> Analyzer |
| 8. Pressure Gauge      | 16. NO <sub>x</sub> Analyzer |
|                        | 17. SO <sub>2</sub> Analyzer |
|                        | 18. Heat Trace Sample Line   |

Figure 100.1-2  
Sample Train Assembly



- |                            |                             |
|----------------------------|-----------------------------|
| 1. Filter                  | 8. Pump                     |
| 2. Stack                   | 9. Flow Control Valve       |
| 3. Probe                   | 10. Sample Gas Manifold     |
| 4. Calibration Valve       | 11. Sample Bypass Discharge |
| 5. Calibration Gas Inlet   | 12. By pass Flow Control    |
| 6. Heated Sample Line      | 13. Analyzer Flow Control   |
| 7. Moisture Removal System | 14. Gas Analyzer            |

Figure 100.1-3  
Measurement System Schematic

Date \_\_\_\_\_

Analyzer \_\_\_\_\_

Range \_\_\_\_\_

	Cylinder Value (Indicate Units)	Analyzer Calibration Response (Indicate Units)	Absolute Difference (Indicate Units)	Difference (Percent of Range)
Zero Gas				
Mid-Range Gas				
High-range Gas				

Pretest Linearity Error \_\_\_\_\_ Percent Range

Post Test Linearity Error \_\_\_\_\_ Percent Range

Figure 100.1-4  
Analyzer Calibration Data Form

Date \_\_\_\_\_

Analyzer \_\_\_\_\_

Range \_\_\_\_\_

	Analyzer calibration response	Initial Values		Final Values		Drift
		System calibration response	System calibration bias (percent of range)	System calibration response	System calibration bias (percent of range)	(percent of range)
Zero gas						
High-range gas						

System Calibration Bias =

$$\frac{\text{System Calibration Response} - \text{Analyzer Calibration Response}}{\text{Range}} \times 100$$

Drift =

$$\frac{\text{Final System Calibration Response} - \text{Initial System Calibration Response}}{\text{Range}} \times 100$$

Figure 100.1-5  
System Calibration Bias and Drift Data

## GENERAL CONTINUOUS GAS MONITORING REQUIREMENTS

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The District requires continuous gas monitoring equipment employing sample extraction and conditioning, and electronic detection, to be conducted strictly according to District Method 100.1, with the emphasis upon representativeness, documentation, and quality assurance. This includes, in part:

1. Gas analyzers must meet minimum acceptable standards for method of detection, sensitivity, noise, precision, linearity, and interference (see TABLE 100.1-1 for details). Also, the gas sample extraction and conditioning equipment (probe, filter, pump, conditioner, connective plumbing, etc., and data acquisition and logging equipment shall meet minimum acceptable specifications, as described in Method 100.1.
2. It is recommended that the entire sampling system for continuous gas monitoring instruments should be leak checked before and after each test run by evacuating the system to a minimum of 20 in. Hg vacuum, and plugging for a period of 5 minutes. The resultant loss of vacuum can not exceed 1 in. Hg during this period.
3. Calibration of all analyzers must be accomplished at zero, mid span (40-60% of full scale range), and high span (80-95% of full scale range). The lowest practicable range should be selected for monitoring, so that the measured emission values are within 20-95% of the range. If a significant amount of the data are outside of this range, the data may be rejected, depending upon the application.
4. The calibration gases must be certified according to EPA Protocol Number 1, or certified to an analytical accuracy of  $\pm 1\%$  and be NIST traceable (except cal gases used for system bias check), following EPA-600/R93/224, "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards", TABLE 2-2. Superblend or multi-component blend gas recertifications are based upon the individual component(s) with the shortest recertification date.
5. Field calibrations employing gas dilution systems (mass flow or critical orifice) must be performed in accordance with EPA Method 205, "Gas Dilution Verification Protocol", or available "Draft" SCAQMD Method, and supported with appropriate documentation. A 5-point check is required.
6. A calibration error check, and zero/span drift check must be performed before and after each test run.

Calibration error must be less than  $\pm 2\%$  of the range of measurement for zero, mid, and high range calibration gases. Zero/span drift must be less than  $\pm 3\%$  of the range of measurement.

7. A system bias check must be performed before and after each test run by alternately introducing cal gases to the entire sampling system, then to the gas analyzer(s), for comparison. The difference can not exceed  $\pm 5\%$  of the analyzer range.
8. Semi-annual analyzer certifications consisting of linearity plot, calibration curve, response time, and interference response must be furnished with the other calibrations to satisfy Q/A documentary requirements.
9.  $\text{NO}_x$  measurement must be performed in the  $\text{NO}_x$  mode of the analyzer. An  $\text{NO}_2$  to  $\text{NO}$  converter is required if  $\text{NO}_2$  constitutes 5% or more of the total  $\text{NO}_x$  in the sample stream, or the rule or permit condition requires " $\text{NO}_x$ " monitoring. The  $\text{NO}_2$  to  $\text{NO}$  converter must be at least 90% efficient (use the  $\text{NO}_2$  to  $\text{NO}$  converter efficiency procedure). The converter should be high temperature ( $650^\circ\text{C}$ ) stainless steel, if no  $\text{NH}_3$  is present. If  $\text{NH}_3$  is present in the sample stream, then a low temperature ( $350^\circ\text{C}$ ) molybdenum catalyst must be used in the converter. This check must be done at the beginning of the test.
10. The connective tubing from the probe to the sample conditioner must be heated above the dewpoint and the dewpoint reported. The sample conditioner must be able to maintain a dewpoint temperature of  $37^\circ\text{F}$  or less. (Refer to the "Sample Conditioning Requirements for Method 100.1" Addendum, for details)
11. Data recorder resolution must be at least 0.5% of the range of measurement. A data point for each contaminant/diluent monitored must be recorded at least once/minute. Analog chart recorders must have a minimum 10-inch chart width, with 100 minor divisions.
12. All facets of testing must be continuously recorded. This includes the 3-point calibration, system bias, calibration error, and zero/span drift checks, which must precede and conclude each test run.

13. All chart traces, or digital printouts, must be included in the final report and must be clearly identified as to:

- location/source
- operator initials
- date/running times
- actual test interval
- contaminant/diluent
- range changes
- range of measurement
- calibrations
- calibration gas conc./cylinder number
- range of calibration

14. When more than one gas trace is shown on a chart, the individual traces must be distinguishable by color coding or some other means (original charts may be submitted, and returned following evaluation). If a gas measurement range has been "offset" from zero, or zero has been "transposed to the right side of the recorder chart, it must be clearly identified. This offset should not be more than 5-small divisions of the chart. This data must be corrected using the ratio of the offset.

15. Gaseous measurements must be conducted a minimum of 15 continuous minutes at each load or specified condition, after the readings have stabilized (RECLAIM reference method sampling requires a minimum of 30 continuous minutes at each load for RATAs). Processes having multiple exhausts exhibiting non-cyclic (i.e. steady-state) characteristics may alternatively be monitored using the above criteria. Otherwise, simultaneous sampling may be required.

16. Sampling locations not meeting the minimum site selection standards for District Method 1 must be tested for absence of stratification. (A gaseous constituent concentration profile differing more than 10% between any two monitoring points within the same cross-sectional plane of a stack or duct indicates stratification.) If stratification is present, and alternate approved site selection or modification is not possible, then special monitoring (see Chapter X of the District Source Testing Manual) will be required.



ADDENDUM TO "General Continuous Gas Monitoring Requirements"

**SAMPLE CONDITIONING REQUIREMENTS FOR METHOD 100.1**

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For Method 100.1 tests, proper sample conditioning is essential for representative sampling. Sample conditioning includes removal of particulate matter and moisture present in the sample gas stream. The design of the sample conditioning system must be such that during the process of particulate and moisture removal, the pollutants of interest are not also removed from the gas stream. Method 100.1 requires that the tester select a system which will have a minimum "scrubbing" effect. In particular, NO<sub>2</sub> and SO<sub>2</sub> are more susceptible to scrubbing than, for example NO or CO, because of their high solubility in water. Since Method 100.1 is a reference method, it is required that a sample conditioning system cause only minimum loss of these pollutants.

The District recommends a gas sampling system which can be used universally<sup>1</sup> (i.e. under all testing conditions). The set-up includes a heated 1/4-inch stainless steel probe with a 50-80 micron size, sintered 316 stainless steel or ceramic filter at the tip; and a short (not more than 6 feet) heated Teflon line to the sample conditioning system. The temperature of the probe and the Teflon line should be maintained at about 250°F. The conditioning system consists of a pair of standard Greenburg-Smith impingers with the stems cut to about 1-inch length from the top, immersed in a bath containing water and dry ice pellets, and immediately followed by a thermo-electric cooler or permeation drier. The gas temperature at the outlet of the impinger shall be less than 60°F and the gas at the drier outlet shall be maintained at a dew point less than 37°F. If the drier can not be directly connected to the impinger outlet, then a Teflon line heated to 10°F above the impinger outlet gas temperature can be used for connection. Another particulate filter (about 5 microns) should be in the line right after the cooler/drier. All the temperatures should be measured and recorded, preferably on a strip chart recorder. If the moisture content of the exhaust gas is below 5% and the sample gas flow rate is less than 10 liters/minute, the impinger set-up need not be used, as long as no moisture condensation occurs in the system and the conditioned sample is maintained at the required dew point.

**PRECAUTIONS:** Never allow the water in the impingers to accumulate more than 1/4 of the impinger height. Don't allow the water bath to become frozen around the impingers, or cracking of the glassware may result. Assure that the thermo-electric cooler/permeation drier has adequate design capacity. Follow a good maintenance schedule for the cooler/drier gas conditioning system.

**ATTACHMENT B**

Other systems may be used, upon District approval, emphasizing the requirements that water is removed immediately after separation from the gas stream, and minimal water contact with the gas stream is assured.

1. An example of a non-universally applicable water removal system is based on the refrigerated cooling coil principle. A refrigerated cooling coil system can scrub out a high percentage of water soluble pollutants due to a comparatively long residence time, and intimate contact between the sample gases and the water droplets collected on the inside of the coil. Consequently, it will show a high bias for the CEMS being tested if the sample gas contains a significant amount of NO<sub>2</sub>, compared to NO<sub>x</sub> or SO<sub>2</sub>, and therefore it may not be suitable in all cases.

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**NO<sub>2</sub> TO NO CONVERSION TEST PROCEDURE**

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(Alternative to O<sub>3</sub> Titration Method-40 CFR 50.1, Appendix F)

**1. NO<sub>x</sub> Analyzer Requirements**

- a. Full span range 0-20 ppm or 0-25 ppm
- b. Equipped with NO and NO<sub>x</sub> modes

**2. Auditing Gas Requirements**

- a. NO<sub>2</sub> in air (or N<sub>2</sub>): Use NO<sub>2</sub> in air for a stainless steel converter.
- b. Concentration of NO<sub>2</sub>: 15 to 18 ppm (C<sub>0</sub>, ppm)
- c. Recertification: An audit gas should be recertified after six months.

**3. Calibration Gas Requirements**

- a. Concentration:
  - NO (17 to 19 ppm) with less than 0.1 ppm NO<sub>2</sub> - High Span
  - NO (10 to 13 ppm) with less than 0.1 ppm NO<sub>2</sub> - Mid Span
- b. Zero Gas: High purity N<sub>2</sub>

**4. Calibration of Analyzer:**

- a. Calibrate NO mode with the NO calibration gases.
- b. Calibrate NO<sub>x</sub> mode with the same gases without any gain adjustment.
- bl. If the analyzer is equipped with two independent gain adjusting circuits, skip 4.b., then repeat 4.a. for the NO<sub>x</sub> mode.

**5. Conversion Efficiency (CE) Test**

- a. Analyze the audit gas with NO mode. Read and standardize concentration. (C<sub>1</sub>, ppm)
- b. Analyze the audit gas with NO<sub>x</sub> mode. Read and standardize concentration. (C<sub>2</sub>, ppm)

**6. Calculation for Conversion Efficiency:**

$$\%CE = \frac{|C_2 - C_1|}{C_0} \times 100$$

**7. Criteria for Acceptability of CE**

- a. %CE must be larger than 90%.
- b. C<sub>1</sub> must be less than 5% of total NO<sub>x</sub> (NO + NO<sub>2</sub>) in the NO<sub>2</sub> audit gas (Section 2b).

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**NOTE:** NO<sub>2</sub> audit gas concentration of higher value than what is specified in Section 2. may be required where NO<sub>2</sub> present in the exhaust gas being measured is greater than 30 ppm. Select the NO<sub>2</sub> gas within 10% of the expected NO<sub>2</sub> concentration in the exhaust.

## Appendix

The EPA Traceability Protocol can be downloaded here:  
<http://www.epa.gov/oamcinc1/0410474/protocol.pdf>