



**South Coast
Air Quality Management District**

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**Source Test Protocol For
Determining Oxygen Corrected Pollutant Concentrations
From Combustion Sources With High Stack Oxygen Content
Based On Carbon Dioxide Emissions**

March 3, 2011

1.0 Overview and Applicability

Several South Coast Air Quality Management District (District) rule limits are expressed at a given oxygen concentration, which require that pollutant concentrations measured in the stack be adjusted or corrected to the appropriate oxygen level. For example, pollutant concentrations for boilers, heaters, and ovens are generally corrected to 3% oxygen, whereas engine and turbine pollutant concentrations are corrected to 15% oxygen. The formulae used to correct the measured pollutant concentration to either 3% or 15% oxygen, respectively, are displayed below:

$$\text{Pollutant Conc. @ 3\% O}_2 = (\text{Stack Pollutant Conc.}) \times \frac{20.9 - 3}{20.9 - \text{Stack O}_2 \text{ Conc.}}$$

$$\text{Pollutant Conc. @ 15\% O}_2 = (\text{Stack Pollutant Conc.}) \times \frac{20.9 - 15}{20.9 - \text{Stack O}_2 \text{ Conc.}}$$

In both these cases, the denominator of the second term will cause the pollutant concentration to increase exponentially as the stack oxygen levels approach the presumed ambient oxygen concentration of 20.9%. Moreover, at high ambient dilutions, slight errors in the oxygen measurement could vastly increase the uncertainty of compliance due to the compounding effect of the second term's denominator. For example, assuming a 20% stack oxygen content with a measurement error of $\pm 0.5\%$ oxygen (i.e., 2.5% relative error), the uncertainty in reporting a 10 ppm raw NO_x measurement corrected to 3% oxygen would range from 128 ppm to 448 ppm. This document provides an alternate means of calculating oxygen corrected pollutant concentrations when determining rule compliance for devices with high stack oxygen concentrations.

The underlying theory for this alternative calculation relies on the stoichiometric relationship between oxygen and carbon dioxide from combusting fuels of known composition. Established EPA Method 19 F-Factors may be used to convert measured emissions to an equivalent CO₂ concentration to compare against the emission standard. F-Factors for fuels not listed in EPA Method 19 may be determined based on an analysis of the fuel composition, and applying calculation procedures dictated by EPA Method 19.

This procedure is applicable for stack carbon dioxide concentrations greater than 1000 ppm, and stack oxygen concentrations greater than 19%. Additional samples and QA requirements are necessary for carbon dioxide concentrations less than 2000 ppm. Some assumptions regarding the stack emissions, fuel composition, and process operation should be confirmed before this procedure may be applied. First, it is presumed that the carbon monoxide concentration in the exhaust stack is less than two percent of the carbon dioxide concentration. If not, then the correction formula must account for carbon monoxide emissions. Secondly, the device is presumed to operate at steady state, so that emissions are not the result of non-stable fuel consumption, such as during a start-up operation. Lastly, it is presumed that oxygen used for

combustion is supplied solely from ambient air, and that the carbon dioxide produced is not scrubbed nor otherwise removed from the exhaust stream.

Modifications to this test procedure may be performed subject to written approval by the Executive Officer.

2.0 Combustion Equipment And Process Description

An assessment of the combustion equipment and process must be performed prior to application of this procedure. Some issues which must be addressed include the following:

- 1) Are the fuel or exhaust gas compositions modified by the process which would violate the assumptions made in Section 1.0 of this document? For example, is the fuel oxygen enriched, or is the carbon dioxide in the fuel removed? Furthermore, does the process emit significant concentrations of carbon dioxide due to non-fuel VOC combustion? The process must be carefully examined for fuel gas conditioning or other exhaust gas issues which would alter the expected stoichiometric ratio of oxygen and carbon in the exhaust stream.
- 2) A detailed review of the exhaust duct system shall be made to determine whether combustion flues from other sources are combined or manifolded upstream of the sampling point. If flue gas from various equipment are combined, either a sampling port may be installed upstream of the manifold, or the other combustion devices may be shut down during testing.

As a special case of this scenario, some equipment combine two devices, such as an oven attached to an afterburner unit. These two devices may have different emission limits, which need to be evaluated separately. The equipment manufacturer should be contacted to determine whether the two devices may be operated independently.

During testing, the equipment shall be monitored for steady operating conditions. If the equipment modulated during sampling, the extent of modulation (with respect to the firing rate) shall be noted. Surges in the unit operation, such as additional batches of process materials or sudden increases in the amount of VOC combusted, must be fully documented. Possible biases from any process change during sampling shall be addressed in the Test Critique section of the final report.

3.0 Analytical Requirements And Sampling Procedures

3.1 Applicability

Two options are available for conducting this procedure. The first alternative employs District Method 100.1 to monitor stack CO₂ emissions. The applicability of this method is dependent on the CO₂ instruments available to the tester, since Method 100.1 and District policy allows quantitative measurements to 20 percent of the range. The second alternative uses District Method 25.3 sampling equipment to collect stack emissions. Some restrictions on the use of this second alternate include the availability of an appropriate orifice to sample for the allotted time, or perhaps a strongly negative static pressures in the stack, which could prohibit the collection of a sufficient sample. It should be noted that the use of portable analyzers for this procedure is currently not acceptable.

3.2 District Method 100.1 Procedure

Sampling and analysis of the exhaust gases must be performed in accordance with District Method 100.1. Simultaneous and concurrent stack gas measurements of CO₂ and CO, as well as the pollutant of interest, must be performed using the principles of operation, sensitivity, and other specifications required by Method 100.1. Other types of analyzer principles may be employed upon written approval by the District. As per District Method 100.1, the sample concentration must fall within 20 to 95% of the analyzer range for at least 95% of the time. However, measurements of CO₂ concentrations down to 10% of the analyzer range may be conducted if an additional calibration injection directly into the analyzer, as well as the probe tip are conducted. The performance specifications for analyzer calibration error, system bias, and drift must be satisfied at this 10% calibration range.

Emissions must be recorded by both the data acquisition system (DAS) and stripchart output. DAS output must be recorded at a minimum of one-minute intervals, and shall be used for all performance criteria and emission calculations. Both the stripchart and DAS output shall be annotated when injections commence for each type of calibration, and the value used in the Method 100.1 performance calculations shall be highlighted. The concentrations shall be recorded to two significant figures, although reporting to three significant figures is preferred.

When addressing gaseous stratification in the stack, the NO_x and CO₂ measurements must be taken simultaneously at the same traverse location. If the probe is traversed through the stack, the tester must annotate both the DAS and stripchart output at each probe location. Furthermore, a schematic of the stack diameter depicting the traverse point locations (with dimensions from the stack side walls) must be included in the final report.

3.3 Canister Sample Alternative Procedure

As an alternative to District Method 100.1, duplicate stack gas measurements may be sampled and analyzed using canister samples similar to those used for District Methods 25.1 and 25.3. However, for the purpose of this alternative procedure, trap samples are not necessary. Note this

procedure is required for all cases where the stack CO₂ concentration is below the quantifiable range of the Method 100.1 analyzer. Sampling of stack gases using canister samples must be concurrent with the sampling for the pollutant of interest. The field sampling procedures must comply with the sampling requirements in Section 3 of Method 25.3, except that data recording shall be at 5 minute intervals.

Analysis of the canister samples for CO₂ and CO must be performed in accordance with the Sections 4.8 and 4.9 of Method 25.3. Note that all the raw data package of the analysis must be submitted with the final report for review. The CO₂ and CO results between duplicate samples shall be within the data quality tolerance specified in Section 5.1 of Method 25.3.

For stack CO₂ concentrations less than 2000 ppm, but greater than 1000 ppm, two paired samples must be collected both at the exhaust stack, and at the ambient locations. The CO₂ and CO results must not deviate more than 20% from the average of the four samples. Other sampling and analytical procedures which have a 50 ppm detection limit for CO₂ and CO, and have a $\pm 20\%$ precision, is acceptable if approved in writing by the AQMD.

3.4 Background/ Ambient Monitoring And Fuel Analysis

For both the alternative procedures presented above, a duplicate background/ambient sample shall be collected and analyzed for CO₂ and CO using the procedures described in Section 3.3 of this document. The placement of the background/ambient sampler is critical, and requires forethought with respect to the representativeness of the combustion air composition. Generally, collecting a sample at the device combustion air inlet is sufficient, but complications occur if multiple intake locations or burner zones are present. Also, the proximity of other CO₂ and CO sources must also be considered. The final report must provide a schematic of the background/ambient sampling locations, and justification for placement of the samplers. Agreement in the results between the canister samples shall meet the data quality requirements in Section 5.1 of Method 25.3.

As an alternate to the above paragraph, a default value of 500 ppm may be assumed for ambient CO₂ concentrations of equipment which is not enclosed by a structure, and has a combustion air inlet composition that is free of CO₂ or CO sources. Written justification with supporting data must be provided when applying this alternative.

For fuels which are not listed in EPA Method 19, a representative fuel sample must be collected over the same time interval as the CO₂ sampling period. An analysis of the fuel composition and subsequent calculation of the Fd and Fc factors must be performed per EPA Method 19. Additionally, all raw laboratory data and calculations must be submitted for evaluation.

4.0 Calculation And Data Reporting

The pollutant concentration at the required oxygen concentration shall be calculated according to the formula below:

$$\text{Pollutant @ C\% O}_2 = P^{\text{stk}} \left(\frac{100}{\text{CO}_2^{\text{stk}} - \text{CO}_2^{\text{amb}}} \right) \left(\frac{20.9 - \text{C\%}}{20.9} \right) \left[\frac{F_c}{F_d} - \frac{\text{CO}_2^{\text{amb}}}{100} \right]$$

where:

- C% = the oxygen correction required for rule or permit compliance (i.e., 3% or 15%);
- P^{stk} = the pollutant concentration measured in the stack (ppm);
- CO₂^{stk} = the dry CO₂ concentration measured in the stack (%);
- CO₂^{amb} = the dry background/ ambient CO₂ concentration (%);
- F_c = EPA Method 19 carbon dioxide based F-Factor (dscf/MMBtu); and,
- F_d = EPA Method 19 dry oxygen based F-Factor (dscf/MMBtu).

It should be noted that analytical CO₂ results from canister samples may be expressed in units of parts per million (ppm), and need to be converted to a percent basis for use in the calculation formulae presented in this protocol.

For typical natural gas compositions which may be adequately represented by standard EPA Method 19 F-Factors, the formulae for pollutant concentrations corrected to 3% and 15%, respectively, are shown below. Note the following formulae are valid for ambient CO₂ concentrations that are less than 500 ppm:

$$\text{Pollutant @ 3\% O}_2 = P^{\text{stk}} \left(\frac{10.23}{\text{CO}_2^{\text{stk}} - \text{CO}_2^{\text{amb}}} \right)$$

$$\text{Pollutant @ 15\% O}_2 = P^{\text{stk}} \left(\frac{3.371}{\text{CO}_2^{\text{stk}} - \text{CO}_2^{\text{amb}}} \right)$$

If a default value of 500 ppm is assumed for the ambient CO₂ per Section 3.4 of this protocol, a value of 0.05 shall be substituted for the variable CO₂^{amb} in the above two formulae.

Calculations should be carried out to at least one significant digit beyond that of the acquired data, and then should be rounded off after final calculation to two significant digits. All rounding off of numbers should be in accordance with the ASTM E380-82 procedures.