

## Method 3B—Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air

Note: This method does not include all of the specifications ( *e.g.*, equipment and supplies) and procedures ( *e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and 3.

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Oxygen (O <sub>2</sub> )	7782-44-7	2,000 ppmv
Carbon Dioxide (CO <sub>2</sub> )	124-38-9	2,000 ppmv
Carbon Monoxide (CO)	630-08-0	N/A.

1.2 Applicability. This method is applicable for the determination of O<sub>2</sub>, CO<sub>2</sub>, and CO concentrations in the effluent from fossil-fuel combustion processes for use in excess air or emission rate correction factor calculations. Where compounds other than CO<sub>2</sub>, O<sub>2</sub>, CO, and nitrogen (N<sub>2</sub>) are present in concentrations sufficient to affect the results, the calculation procedures presented in this method must be modified, subject to the approval of the Administrator.

1.3 Other methods, as well as modifications to the procedure described herein, are also applicable for all of the above determinations. Examples of specific methods and modifications include: (1) A multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point, and (2) a method using CO<sub>2</sub> or O<sub>2</sub> and stoichiometric calculations to determine excess air. These methods and modifications may be used, but are subject to the approval of the Administrator.

1.4 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 A gas sample is extracted from a stack by one of the following methods: (1) Single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent CO<sub>2</sub>, percent O<sub>2</sub>, and, if necessary, percent CO using an Orsat combustion gas analyzer.

### 3.0 Definitions[Reserved]

### 4.0 Interferences

4.1 Several compounds can interfere, to varying degrees, with the results of Orsat analyses. Compounds that interfere with CO<sub>2</sub> concentration measurement include acid gases ( *e.g.*, sulfur dioxide, hydrogen chloride); compounds that interfere with O<sub>2</sub> concentration measurement include unsaturated hydrocarbons ( *e.g.*, acetone, acetylene), nitrous oxide, and ammonia. Ammonia reacts chemically with the O<sub>2</sub> absorbing solution, and when present in the effluent gas stream must be removed before analysis.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. A typical Orsat analyzer requires four reagents: a gas-confining solution, CO<sub>2</sub> absorbent, O<sub>2</sub> absorbent, and CO absorbent. These reagents may contain potassium hydroxide, sodium hydroxide, cuprous chloride, cuprous sulfate, alkaline pyrogallic acid, and/or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

## 6.0 Equipment and Supplies

Note: As an alternative to the sampling apparatus and systems described herein, other sampling systems ( *e.g.*, liquid displacement) may be used, provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are, otherwise, capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

6.1 Grab Sampling and Integrated Sampling. Same as in Sections 6.1 and 6.2, respectively for Method 3.

6.2 Analysis. An Orsat analyzer only. For low CO<sub>2</sub> (less than 4.0 percent) or high O<sub>2</sub> (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions. For Orsat maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

## 7.0 Reagents and Standards

7.1 Reagents. Same as in Method 3, Section 7.1.

7.2 Standards. Same as in Method 3, Section 7.2.

## 8.0 Sample Collection, Preservation, Storage, and Transport

Note: Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator. A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determinations, unless approved by the Administrator. If both percent CO<sub>2</sub> and percent O<sub>2</sub> are measured, the

analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight (see Method 3).

### 8.1 Single-Point, Grab Sampling and Analytical Procedure.

8.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

8.1.2 Set up the equipment as shown in Figure 3–1 of Method 3, making sure all connections ahead of the analyzer are tight. Leak-check the Orsat analyzer according to the procedure described in Section 11.5 of Method 3. This leak-check is mandatory.

8.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer. For emission rate correction factor determinations, immediately analyze the sample for percent CO<sub>2</sub> or percent O<sub>2</sub>, as outlined in Section 11.2. For excess air determination, immediately analyze the sample for percent CO<sub>2</sub>, O<sub>2</sub>, and CO, as outlined in Section 11.2, and calculate excess air as outlined in Section 12.2.

8.1.4 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 11.5 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak-test before and after the analysis.

### 8.2 Single-Point, Integrated Sampling and Analytical Procedure.

8.2.1 The sampling point in the duct shall be located as specified in Section 8.1.1.

8.2.2 Leak-check (mandatory) the flexible bag as in Section 6.2.6 of Method 3. Set up the equipment as shown in Figure 3–2 of Method 3. Just before sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe, and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag, and make sure that all connections are tight.

8.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 28 liters (1.0 ft<sup>3</sup>) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

8.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO<sub>2</sub> or percent O<sub>2</sub> (as outlined in Section 11.2).

### 8.3 Multi-Point, Integrated Sampling and Analytical Procedure.

8.3.1 Unless otherwise specified in an applicable regulation, or by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of 12 traverse points shall be used for all other cases. The traverse points shall be located according to Method 1.

8.3.2 Follow the procedures outlined in Sections 8.2.2 through 8.2.4, except for the following: Traverse all sampling points, and sample at each point for an equal length of time. Record sampling data as shown in Figure 3–3 of Method 3.

## 9.0 *Quality Control*

9.1 **Data Validation Using Fuel Factor.** Although in most instances, only CO<sub>2</sub> or O<sub>2</sub> measurement is required, it is recommended that both CO<sub>2</sub> and O<sub>2</sub> be measured to provide a check on the quality of the data. The data validation procedure of Section 12.3 is suggested.

Note: Since this method for validating the CO<sub>2</sub> and O<sub>2</sub> analyses is based on combustion of organic and fossil fuels and dilution of the gas stream with air, this method does not apply to sources that (1) remove CO<sub>2</sub> or O<sub>2</sub> through processes other than combustion, (2) add O<sub>2</sub> (e.g., oxygen enrichment) and N<sub>2</sub> in proportions different from that of air, (3) add CO<sub>2</sub> (e.g., cement or lime kilns), or (4) have no fuel factor, F<sub>O</sub>, values obtainable (e.g., extremely variable waste mixtures). This method validates the measured proportions of CO<sub>2</sub> and O<sub>2</sub> for fuel type, but the method does not detect sample dilution resulting from leaks during or after sample collection. The method is applicable for samples collected downstream of most lime or limestone flue-gas desulfurization units as the CO<sub>2</sub> added or removed from the gas stream is not significant in relation to the total CO<sub>2</sub> concentration. The CO<sub>2</sub> concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the fuel factor check minimally useful.

## 10.0 *Calibration and Standardization*

10.1 **Analyzer.** The analyzer and analyzer operator technique should be audited periodically as follows: take a sample from a manifold containing a known mixture of CO<sub>2</sub> and O<sub>2</sub>, and analyze according to the procedure in Section 11.3. Repeat this procedure until the measured concentration of three consecutive samples agrees with the stated value  $\pm 0.5$  percent. If necessary, take corrective action, as specified in the analyzer users manual.

10.2 **Rotameter.** The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

## 11.0 *Analytical Procedure*

11.1 **Maintenance.** The Orsat analyzer should be maintained according to the manufacturers specifications.

11.2 **Grab Sample Analysis.** To ensure complete absorption of the CO<sub>2</sub>, O<sub>2</sub>, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.) Although in

most cases, only CO<sub>2</sub> or O<sub>2</sub> concentration is required, it is recommended that both CO<sub>2</sub> and O<sub>2</sub> be measured, and that the procedure in Section 12.3 be used to validate the analytical data.

Note: Since this single-point, grab sampling and analytical procedure is normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis.

11.3 Integrated Sample Analysis. The Orsat analyzer must be leak-checked (see Section 11.5 of Method 3) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in Sections 11.3.1 through 11.3.3) for percent CO<sub>2</sub>, O<sub>2</sub>, and CO; (2) determine the percentage of the gas that is N<sub>2</sub> by subtracting the sum of the percent CO<sub>2</sub>, percent O<sub>2</sub>, and percent CO from 100 percent; and (3) calculate percent excess air, as outlined in Section 12.2.

11.3.1 To ensure complete absorption of the CO<sub>2</sub>, O<sub>2</sub>, or if applicable, CO, follow the procedure described in Section 11.2.

Note: Although in most instances only CO<sub>2</sub> or O<sub>2</sub> is required, it is recommended that both CO<sub>2</sub> and O<sub>2</sub> be measured, and that the procedures in Section 12.3 be used to validate the analytical data.

11.3.2 Repeat the analysis until the following criteria are met:

11.3.2.1 For percent CO<sub>2</sub>, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO<sub>2</sub> is greater than 4.0 percent or (b) 0.2 percent by volume when CO<sub>2</sub> is less than or equal to 4.0 percent. Average three acceptable values of percent CO<sub>2</sub>, and report the results to the nearest 0.2 percent.

11.3.2.2 For percent O<sub>2</sub>, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O<sub>2</sub> is less than 15.0 percent or (b) 0.2 percent by volume when O<sub>2</sub> is greater than or equal to 15.0 percent. Average the three acceptable values of percent O<sub>2</sub>, and report the results to the nearest 0.1 percent.

11.3.2.3 For percent CO, repeat the analytical procedure until the results of any three analyses differ by no more than 0.3 percent. Average the three acceptable values of percent CO, and report the results to the nearest 0.1 percent.

11.3.3 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 11.5 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak-test before and after the analysis.

11.4 Standardization. A periodic check of the reagents and of operator technique should be conducted at least once every three series of test runs as indicated in Section 10.1.

## 12.0 Calculations and Data Analysis

12.1 Nomenclature. Same as Section 12.1 of Method 3 with the addition of the following:

%EA=Percent excess air.

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

12.2 Percent Excess Air. Determine the percentage of the gas that is N<sub>2</sub>by subtracting the sum of the percent CO<sub>2</sub>, percent CO, and percent O<sub>2</sub>from 100 percent. Calculate the percent excess air (if applicable) by substituting the appropriate values of percent O<sub>2</sub>, CO, and N<sub>2</sub>into Equation 3B–1.

$$\%EA = \frac{\%O_2 - 0.5 \%CO}{0.264 \%N_2 - (\%O_2 - 0.5 \%CO)} \times 100 \quad Eq. 3B-1$$

Note: The equation above assumes that ambient air is used as the source of O<sub>2</sub>and that the fuel does not contain appreciable amounts of N<sub>2</sub>(as do coke oven or blast furnace gases). For those cases when appreciable amounts of N<sub>2</sub>are present (coal, oil, and natural gas do not contain appreciable amounts of N<sub>2</sub>) or when oxygen enrichment is used, alternative methods, subject to approval of the Administrator, are required.

12.3 Data Validation When Both CO<sub>2</sub>and O<sub>2</sub>Are Measured.

12.3.1 Fuel Factor, F<sub>o</sub>. Calculate the fuel factor (if applicable) using Equation 3B–2:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \quad Eq. 3B-2$$

Where:

%O<sub>2</sub>=Percent O<sub>2</sub>by volume, dry basis.

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

20.9=Percent O<sub>2</sub>by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O<sub>2</sub>and CO<sub>2</sub>values using Equations 3B–3 and 3B–4 before performing the calculation for F<sub>o</sub>:

$$\%CO_2(adj) = \%CO_2 + \%CO \quad Eq. 3B-3$$

$$\%O_2(adj) = \%O_2 - 0.5 \%CO \quad Eq. 3B-4$$

Where:

%CO=Percent CO by volume, dry basis.

12.3.2 Compare the calculated F<sub>o</sub>factor with the expected F<sub>o</sub>values. Table 3B–1 in Section 17.0 may be used in establishing acceptable ranges for the expected F<sub>o</sub>if the fuel being burned is known. When fuels are burned in combinations, calculate the combined fuel F<sub>d</sub> and F<sub>c</sub> factors (as

defined in Method 19, Section 12.2) according to the procedure in Method 19, Sections 12.2 and 12.3. Then calculate the  $F_o$  factor according to Equation 3B-5.

$$F_o = \frac{0.209 F_d}{F_c} \quad \text{Eq. 3B-5}$$

12.3.3 Calculated  $F_o$  values, beyond the acceptable ranges shown in this table, should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should be reviewed and verified. An acceptability range of  $\pm 12$  percent is appropriate for the  $F_o$  factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate; i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time consuming and costly.

*13.0 Method Performance[Reserved]*

*14.0 Pollution Prevention[Reserved]*

*15.0 Waste Management[Reserved]*

*16.0 References*

Same as Method 3, Section 16.0.

*17.0 Tables, Diagrams, Flowcharts, and Validation Data*

Table 3B-1—F<sub>o</sub> Factors for Selected Fuels

Fuel type	F <sub>o</sub> Range
Coal:	
Anthracite and lignite	1.016–1.130
Bituminous	1.083–1.230
Oil:	
Distillate	1.260–1.413
Residual	1.210–1.370
Gas:	
Natural	1.600–1.836
Propane	1.434–1.586
Butane	1.405–1.553
Wood	1.000–1.120
Wood bark	1.003–1.130