

8.2 If only O₂ is measured using Method 3A, measurements of the sample stream CO₂ concentration should be obtained at the sample by-pass vent discharge using an Orsat or Fyrite analyzer, or equivalent. Duplicate samples should be obtained concurrent with at least one run. Average the duplicate Orsat or Fyrite analysis results for each run. Use the average CO₂ values for comparison with the O₂ measurements in accordance with the procedures described in Section 4.4 of Method 3.

8.3 If only CO₂ is measured using Method 3A, concurrent measurements of the sample stream CO₂ concentration should be obtained

using an Orsat or Fyrite analyzer as described in Section 8.2. For each run, differences greater than 0.5 percent between the Method 3A results and the average of the duplicate Fyrite analysis should be investigated.

9. Emission Calculation

For all CO₂ analyzers, and for O₂ analyzers that can be calibrated with zero gas, follow Section 8 of Method 6C, except express all concentrations as percent, rather than ppm.

For O₂ analyzers that use a low-level calibration gas in place of a zero gas, calculate the effluent gas concentration using Equation 3A-1.

$$C_{\text{gas}} = \frac{C_{\text{ma}} - C_{\text{oa}}}{C_{\text{m}} - C_{\text{o}}} (\bar{C} - C_{\text{m}}) + C_{\text{ma}} \quad \text{Eq. 3A-1}$$

Where:

C_{gas}=Effluent gas concentration, dry basis, percent.

C_{ma}=Actual concentration of the upscale calibration gas, percent.

C_{oa}=Actual concentration of the low-level calibration gas, percent.

C_m=Average of initial and final system calibration bias check responses for the upscale calibration gas, percent.

C_o=Average of initial and final system calibration bias check responses for the low-level gas, percent.

\bar{C} =Average gas concentration indicated by the gas analyzer, dry basis, percent.

10. Bibliography

Same as bibliography of Method 6C.

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 ₂)	7782-44-7	2,000 ppmv.
Carbon Dioxide (CO ₂)	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 O₂, CO₂, 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 CO₂, O₂, CO, and nitrogen (N₂) 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 ana-

lyze individual grab samples obtained at each point, and (2) a method using CO₂ or O₂ 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 CO₂, percent O₂, 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 CO₂ concentration measurement include acid gases (*e.g.*, sulfur dioxide, hydrogen chloride); compounds that interfere with O₂ concentration measurement include unsaturated hydrocarbons (*e.g.*, acetone, acetylene), nitrous oxide, and ammonia. Ammonia reacts chemically with the O₂ 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, CO₂ absorbent, O₂ absorbent, and CO absorbent. These reagents may contain potassium hydroxide, sodium hydroxide, cuprous chloride, cuprous sulfate, alkaline pyrogallol 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 CO₂ (less than 4.0 percent) or high O₂ (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 CO₂ and percent O₂ 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 CO₂ or percent O₂, as outlined in Section 11.2. For excess air determination, immediately analyze the sample for percent CO₂, O₂, 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 ft³) 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 CO₂ or percent O₂ (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 CO₂ or O₂ measurement is required, it is recommended that both CO₂ and O₂ 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 CO₂ and O₂ 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 CO₂ or O₂ through processes other than combustion, (2) add O₂ (e.g., oxygen enrichment) and N₂ in proportions different from that of air, (3) add CO₂ (e.g., cement or lime kilns), or (4) have no fuel factor, F_O, values obtainable (e.g., extremely variable waste mixtures). This method validates the measured proportions

of CO₂ and O₂ 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 CO₂ added or removed from the gas stream is not significant in relation to the total CO₂ concentration. The CO₂ 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 CO₂ and O₂, 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 ± 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 CO₂, O₂, 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 CO₂ or O₂ concentration is required, it is recommended that both CO₂ and O₂ 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 CO₂, O₂, and CO; (2) determine the percentage of the gas that is N₂ by

subtracting the sum of the percent CO₂, percent O₂, 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 CO₂, O₂, or if applicable, CO, follow the procedure described in Section 11.2.

NOTE: Although in most instances only CO₂ or O₂ is required, it is recommended that both CO₂ and O₂ 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 CO₂, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO₂ is greater than 4.0 percent or (b) 0.2 percent by volume when CO₂ is less than or equal to 4.0 percent. Average three acceptable values of percent CO₂, and report the results to the nearest 0.2 percent.

11.3.2.2 For percent O₂, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O₂ is less than 15.0 percent or (b) 0.2 percent by volume when O₂ is greater than or equal to 15.0 percent. Average the three acceptable values of percent O₂, 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 O₂ to N₂ in air, v/v.

12.2 Percent Excess Air. Determine the percentage of the gas that is N₂ by subtracting the sum of the percent CO₂, percent CO, and percent O₂ from 100 percent. Calculate the percent excess air (if applicable) by substituting the appropriate values of percent O₂, CO, and N₂ into Equation 3B-1.

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

NOTE: The equation above assumes that ambient air is used as the source of O₂ and that the fuel does not contain appreciable amounts of N₂ (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N₂ are present (coal, oil, and natural gas do not contain appreciable amounts of N₂) or when oxygen enrichment is used, alternative methods, subject to approval of the Administrator, are required.

12.3 Data Validation When Both CO₂ and O₂ Are Measured.

12.3.1 Fuel Factor, F_o. Calculate the fuel factor (if applicable) using Equation 3B-2:

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

Where:

%O₂=Percent O₂ by volume, dry basis.

%CO₂=Percent CO₂ by volume, dry basis.

20.9=Percent O₂ by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O₂ and CO₂ values

using Equations 3B-3 and 3B-4 before performing the calculation for F_o:

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

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

Where:

%CO=Percent CO by volume, dry basis.

12.3.2 Compare the calculated F_o factor with the expected F_o values. Table 3B-1 in Section 17.0 may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combinations, calculate the combined fuel F_d and F_c 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.

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

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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 ± 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_o FACTORS FOR SELECTED FUELS

Fuel type	F_o 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

METHOD 3C—DETERMINATION OF CARBON DIOXIDE, METHANE, NITROGEN, AND OXYGEN FROM STATIONARY SOURCES

1. *Applicability and Principle*

1.1 *Applicability.* This method applies to the analysis of carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), and oxygen (O_2) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart.

1.2 *Principle.* A portion of the sample is injected into a gas chromatograph (GC) and the CO_2 , CH_4 , N_2 , and O_2 concentrations are determined by using a thermal conductivity detector (TCD) and integrator.

2. *Range and Sensitivity*

2.1 *Range.* The range of this method depends upon the concentration of samples. The analytical range of TCD's is generally between approximately 10 ppmv and the upper percent range.

2.2 *Sensitivity.* The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. For CO_2 , CH_4 , N_2 , and O_2 , the sensitivity limit is in the low ppmv range.

3. *Interferences*

Since the TCD exhibits universal response and detects all gas components except the carrier, interferences may occur. Choosing the appropriate GC or shifting the retention times by changing the column flow rate may help to eliminate resolution interferences.

To assure consistent detector response, helium is used to prepare calibration gases. Frequent exposure to samples or carrier gas containing oxygen may gradually destroy filaments.

4. *Apparatus*

4.1 *Gas Chromatograph.* GC having at least the following components:

4.1.1 *Separation Column.* Appropriate column(s) to resolve CO_2 , CH_4 , N_2 , O_2 , and other gas components that may be present in the sample.

4.1.2 *Sample Loop.* Teflon or stainless steel tubing of the appropriate diameter. NOTE: Mention of trade names or specific products does not constitute endorsement or recommendation by the U. S. Environmental Protection Agency.

4.1.3 *Conditioning System.* To maintain the column and sample loop at constant temperature.

4.1.4 *Thermal Conductivity Detector.*

4.2 *Recorder.* Recorder with linear strip chart. Electronic integrator (optional) is recommended.

4.3 *Teflon Tubing.* Diameter and length determined by connection requirements of cylinder regulators and the GC.

4.4 *Regulators.* To control gas cylinder pressures and flow rates.

4.5 *Adsorption Tubes.* Applicable traps to remove any O_2 from the carrier gas.

5. *Reagents*

5.1 *Calibration and Linearity Gases.* Standard cylinder gas mixtures for each compound of interest with at least three concentration levels spanning the range of suspected sample concentrations. The calibration gases shall be prepared in helium.

5.2 *Carrier Gas.* Helium, high-purity.