

SOUTH COAST QUALITY MANAGEMENT DISTRICT

METHOD 3.1

GAS ANALYSIS FOR DRY MOLECULAR WEIGHT AND EXCESS AIR

OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 3.1

GAS ANALYSIS FOR DRY MOLECULAR WEIGHT AND EXCESS AIR

TABLE OF CONTENTS

Section

1. Overview

1.1 Principle

1.2 Applicability

2. Field Procedure

2.1 Apparatus

2.2 Dry Molecular Weight Determination

2.3 Emission Rate Correction Factor, Excess Air
Determination, or Dry Molecular Weight
Determination

2.4 Leak Check Procedures for Orsat Analyzers

3. Engineering Calculations and Reporting

3.1 Nomenclature

3.2 Percent Excess Air

3.3 Dry Molecular Weight

METHOD 3.1

GAS ANALYSIS FOR DRY MOLECULAR WEIGHT AND EXCESS AIR

Section 1 of 3

1. Overview

1.1 Principle

A gas sample is extracted from a stack by single-point grab sampling, single-point integrated sampling, or multi-point integrated sampling. The sample is analyzed for percent carbon dioxide (CO₂), percent oxygen (O₂), and, if necessary, percent carbon monoxide (CO). An Orsat analyzer or other analyzer specified in Method 10.1 may be used. Method 10.1 is an alternative method requiring laboratory analysis.

1.2 Applicability

This method determines CO₂ and O₂ concentrations, excess air from fossil fuel combustion sources, and dry molecular weight of a sample from a gas stream consisting primarily of CO₂, O₂, CO, and nitrogen (N₂).

Other methods, as well as modifications to this procedure, may apply for some or all of the above determinations. Specific methods and modifications include:

- a. A multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point.
- b. Methods 10.1 or 100.1.
- c. A method using CO₂ or O₂ and stoichiometric calculations to determine dry molecular weight and excess air.
- d. Assigning a value of 29.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil.

These methods and modifications may be subject to the approval of the Executive Officer.

METHOD 3.1

GAS ANALYSIS FOR DRY MOLECULAR WEIGHT AND EXCESS AIR

Section 2 of 3

2. Field Procedures

2.1 Apparatus

As alternatives to the sampling apparatus and systems described here, other sampling systems (e.g. liquid displacement) may be used provided they are capable of obtaining a representative sample, maintaining a constant sampling rate, and are otherwise capable of yielding acceptable results. Use of such systems is subject to the approval of the Executive Officer.

2.1.1 Grab Sampling

Refer to Figure 3.1-1.

a. Probe

The probe should be made of stainless steel or borosilicate glass tubing, equipped with an in-stack or out-of-stack filter to remove particulate matter. (A plug of glass wool is satisfactory for this purpose.) Any other material inert to O₂, CO₂, CO, and N₂ and resistant to temperature at sampling conditions may be used for the probe.

b. Pump

Use a one-way squeeze bulb, or equivalent, to transport the sample to the analyzer or evacuated flask.

2.1.2 Integrated Sampling

Refer to Figure 3.1-2.

a. Probe

Options described above for the grab sampling probe are suitable.

b. Condenser

An air-cooled or water-cooled condenser, or other condenser that will not remove O_2 , CO_2 , CO , and N_2 , may be used to remove excess moisture which would interfere with the operation of the pump and flow meter.

c. Valve

Use a needle valve to adjust sample gas flow rate.

d. Pump

A leak-free peristaltic pump, or equivalent, transports sample gas to the flexible bag. Install a small surge tank between the pump

and rate meter to eliminate the pulsation effect of a diaphragm pump on the rotameter, if used.

e. Rate Meter

The rotameter, or equivalent rate meter used, should be capable of measuring flow rate to within ± 5 percent of the selected flow rate. A flow rate range of 500 to 1000 cm^3/min is suggested. The rotameter is not needed if a speed control is used on the pump.

f. Flexible Bag

Use any leak-free bag made with plastic (e.g. Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g. aluminized Mylar) film, or equivalent, having a capacity consistent with the selected flow rate and time interval for the test run. The suggested capacity is in the range of 15 to 90 liters.

To leak check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H₂O (2 to 4 in. H₂O) and allow to stand overnight. A deflated bag indicates a leak.

g. Pressure Gauge

A water-filled U-tube manometer, or equivalent, of about 30 cm (12 in.) is used for the flexible bag leak check.

h. Vacuum Gauge

A mercury manometer, or equivalent, of at least 760 mm (30 in.) Hg is used for the sampling train leak-check.

2.1.3 Orsat Analyzer

An Orsat analyzer may be used for on-site analysis. For Orsat analyzer maintenance and operation procedures,

follow manufacturer's instructions unless otherwise specified herein.

Appropriate leak-free sample containers (two-liter glass or stainless steel flasks, or Tedlar bags) may be used to store samples for later laboratory analysis. Method 100.1 may be used for on-site continuous monitoring.

2.2 Dry Molecular Weight Determination

Use one of the three sampling and analytical procedures described below to determine dry molecular weight.

2.2.1 Single-Point Grab Sampling and Analytical Procedure

The sampling point in the duct should either be at the centroid of the cross section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Executive Officer.

Set up equipment as shown in Figure 3.1-1, making sure all connections ahead of the analyzer are tight and leak-free. If an Orsat analyzer is used, the analyzer should be leak checked by following the procedure in Section 2.4.

Place the probe in the stack with the tip of the probe positioned at the sampling line. Purge the sampling line. Draw a sample into the analyzer and immediately analyze it for percent CO₂ and percent O₂.

Determine the percentage of the gas that is N₂ and CO by subtracting the sum of the percent CO₂ and percent O₂ from 100 percent.

Calculate the dry molecular weight as outlined in Section 3.3.

Repeat sampling, analysis, and calculation procedures until the dry molecular weights of any three grab samples differ from their

mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole).

Report this mean value to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

2.2.2 Single-Point Integrated Sampling and Analytical Procedure

Locate the sampling point in the duct as specified in Section 2.2.1.

Leak check the flexible bag as in Section 2.1.2 (f). Set up equipment as shown in Figure 3.1-3. Just prior to sampling, leak check the train by placing a vacuum gauge at the probe inlet, pulling a vacuum of at least 250 mm (10 in.) Hg, plugging the outlet at the bag inlet, and then turning off the pump. The vacuum should remain stable for at least 30 seconds.

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. Connect the bag and make sure that all connections are tight and leak-free.

Sample at a constant rate throughout the total time of the pollutant emission rate determination, or as specified by the Executive Officer. Collection of at least 15 liters (0.5 ft³) of sample gas is recommended.

Obtain one integrated flue gas sample during each pollutant emission rate determination.

Within 24 hours after the sample is taken, analyze it for percent CO₂ and percent O₂ using either an Orsat analyzer, Method 100.1, or Method 10.1. If an Orsat analyzer is used, an optional Orsat leak check (described in Section 2.4) may be performed before this determination. Determine the percentage of the gas that is N₂ and CO by subtracting the sum of percent CO₂ and percent O₂ from 100 percent.

Calculate the dry molecular weight as indicated in Section 3.3.

Repeat analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole).

Report this mean value to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

2.2.3 Multi-Point Integrated Sampling and Analytical Procedure

Unless otherwise specified by the Executive Officer, use a minimum of eight traverse points for circular stacks with diameters less than 61 cm (24 in.), a minimum of nine points for rectangular stacks with equivalent diameters less than 61 cm (24 in.), and a minimum of twelve points for all other cases. Traverse points should be located according to Method 1.1. The use of fewer points is subject to approval of the Executive Officer.

Follow the procedures outlined in Section 2.2.2. but traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3.1-3.

2.3 Emission Rate Correction Factor, Excess Air Determination, or Dry Molecular Weight Determination

2.3.1 Single-Point Grab Sampling and Analytical Procedure

See Section 2.2.1.

If an excess air determination is desired, proceed as follows:

- a. Immediately analyze the sample as in Sections 2.2.2. for percent CO₂, O₂, and CO.

- b. Determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2 , percent O_2 , and percent CO from 100 percent.
- c. Calculate percent excess air as outlined in Section 3.2.

To ensure complete absorption of the CO_2 , O_2 , 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.)

After the analysis is completed, leak check (mandatory) the Orsat analyzer once again, as described in Section 2.4. Results will be valid only if the Orsat analyzer passes this leak test before and after the analysis.

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. Although in most cases only CO₂ or O₂ is required, it is recommended that both CO₂ and O₂ be measured and the stoichiometric relation be used to validate the analytical data.

2.3.2 Single-Point Integrated Sampling and Analytical Procedure

See Section 2.2.2.

If an excess air determination is desired, proceed as follows:

- a. Within 24 hour after the sample is taken, analyze it for percent CO₂, O₂, and CO.

- b. Determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2 , percent O_2 , and percent CO from 100 percent.
- c. Calculate percent excess air as outlined in Section 3.2.

To ensure complete absorption of the CO_2 , O_2 , or if applicable, CO , make repeated passes through each absorbing solution until two consecutive readings are the same. Make three or four passes between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

Repeat the analysis until the following criteria are met:

For percent CO_2 , repeat the analytical procedure until the results of any three analyses differ by no more than (1) 0.3 percent by volume when CO_2 is greater than 4.0 percent, or (2) 0.2 percent by volume when CO_2 is less than or equal to

4.0 percent. Average the three acceptable values of percent CO₂ and report the results to the nearest 0.1 percent.

After the analysis is completed, leak check (mandatory) the Orsat analyzer again, as described in Section 2.4. Results will be valid only if the Orsat analyzer passes this leak test before and after the analysis.

Note: Although in most instances only CO₂ or O₂ is required, it is recommended that both CO₂ and O₂ be measured and the stoichiometric relation be used to validate the analytical data.

2.3.3 Multi-Point Integrated Sampling and Analytical Procedure

Both the minimum number of sampling points and the sampling point location are specified in Section 2.2.3. The use of fewer points than specified is subject to the approval of the Executive Officer.

Follow the procedures outlined in
Section 2.2.2 for sample collection.

2.4 Leak Check Procedure for Orsat Analyzers

Since moving an Orsat analyzer frequently causes it to leak, an analyzer should be thoroughly leak checked on-site before the flue gas sample is introduced into it.

Bring the liquid level in each pipet up to the reference mark on the capillary tubing and then close the pipet stopcock. Raise the leveling bulb sufficiently to bring confining liquid meniscus onto the graduated portion of the buret and then close the manifold stopcock. Record the meniscus position. Observe the meniscus in the buret and the liquid level in the pipet for movement over the next 4 minutes. For the Orsat analyzer to pass the leak check, two conditions must be met:

- The liquid level in each pipet must not fall below the bottom of the capillary tubing during this 4-minute interval.

- The meniscus in the buret must not change by more than 0.2 ml during this 4-minute interval.

If the analyzer fails the leak check procedure, check all rubber connections and stopcocks until the cause of the leak is identified.

Disassemble, clean, and regrease leaking stopcocks. Replace leaking rubber connections. Reassemble the analyzer and repeat the leak check procedure.

METHOD 3.1

GAS ANALYSIS FOR DRY MOLECULAR WEIGHT AND EXCESS AIR

Section 3 of 3

3. Calculations

Perform calculations and record values to at least one decimal place more than that of the acquired data.

Round off the final results.

3.1 Nomenclature

M_d	=	Dry molecular weight, g/g-mole (lb/lb-mole)
Percent EA	=	Percent excess air
Percent CO ₂	=	Percent CO ₂ by volume (dry basis)
Percent O ₂	=	Percent O ₂ by volume (dry basis)
Percent CO	=	Percent CO by volume (dry basis)
Percent N ₂	=	Percent N ₂ by volume (dry basis)
0.264	=	Ratio of O ₂ to N ₂ in air, v/v
0.280	=	Molecular weight of N ₂ or CO, divided by 100
0.320	=	Molecular weight of O ₂ divided by 100

0.440 = Molecular weight of CO₂ divided by
100

3.2 Percent Excess Air

Calculate the percent excess air (if applicable) by substituting the appropriate values of percent O₂, CO, and N₂ (obtained from Section 2.3.1 or 2.3.2) in the following equation:

$$\text{Percent EA} = \frac{\text{Percent O}_2 - 0.5 \text{ Percent CO}}{0.264 \text{ Percent N}_2 - (\text{Percent O}_2 - 0.5 \text{ Percent CO})} \times 100$$

This equation assumes that ambient air is used as the source of O₂ and that the fuel does not contain appreciable amounts of N₂ (as does coke or blast furnace gas). For cases where appreciable amounts of N₂ are present (coal, oil, and natural gas do not contain appreciable amounts of N₂) or when oxygen enrichment is used, alternate methods are required, subject to approval of the Executive Officer.

3.3 Dry Molecular Weight

Use the following equation to calculate the dry molecular weight of the stack gas:

$$M_d = 0.440 (\text{percent CO}_2) + 0.320 (\text{percent O}_2) + 0.280 (\text{percent N}_2 + \text{percent CO})$$

Note: The above equation does not consider the argon present in air (about 0.9 percent, molecular weight of 37.7) which introduces a negative error of about 0.4 percent. The tester may opt to include argon in the analysis using procedures approved by the Executive Officer.

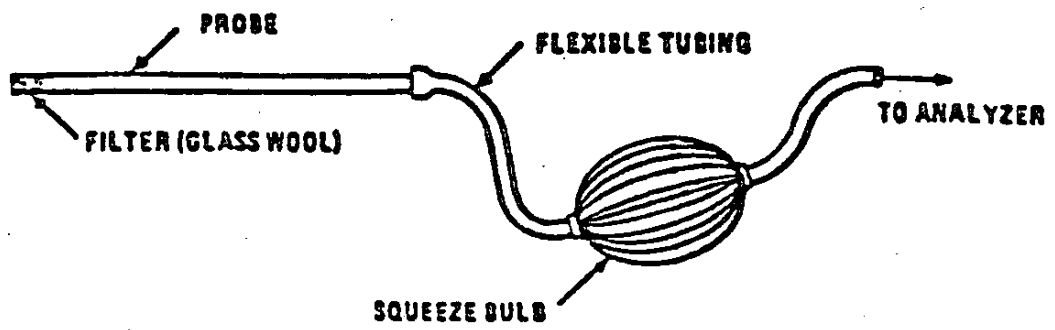
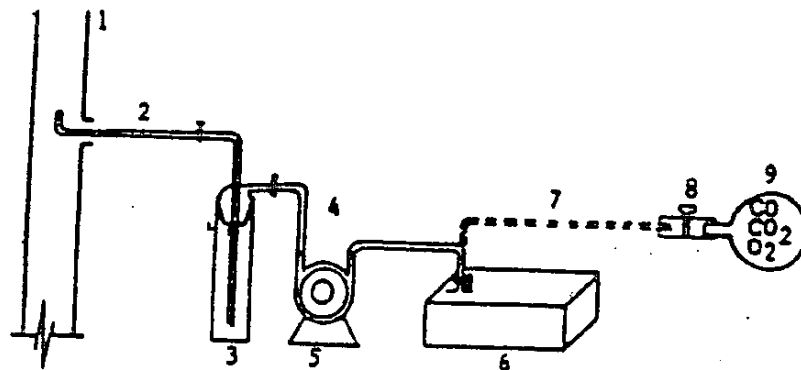


Figure 3.1-1
Grab Sampling Train



- | | |
|------------------|-------------------------------|
| 1. Exhaust Stack | 6. Sample Bag |
| 2. Sample Probe | 7. Transfer Line |
| 3. Condenser | 8. Pinch Line |
| 4. Suction Line | 9. Evacuated 2-Liter Grab Bag |
| 5. Pump | 10. Rate Meter |

Figure 3.1-2

Gas Sample Collection System (with Water and Particulate Dropout).
 Sample is Integrated Over a Minimum Fifteen Minute Interval

TIME	TRAVERSE PT.	Q 1pm	% DEV. ^a
AVERAGE			

$$^a \% \text{ DEV} = \left(\frac{Q - Q_{\text{avg}}}{Q_{\text{avg}}} \right) 100 \quad (\text{MUST BE } < 10\%)$$

Figure 3.1-3
Sampling Rate Data