State of California
AIR RESOURCES BOARD

METHOD 3

Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight

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Amended ________________________

Note: this document consists of the text of the proposed amendment to Method 3. Proposed deletions are noted by graphic screen and proposed additions are noted by underline.

METHOD 3

**Gas Analysis for Carbon Dioxide,
Oxygen, Excess Air, and Dry Molecular Weight**

1 Principle and Applicability

1.1 Principle

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 carbon dioxide (CO_2), percent oxygen (O_2), and, if necessary, percent carbon monoxide (CO). If a For dry molecular weight determination is to be made, either an Orsat or a Fyrite[1] analyzer or other analyzers specified in Method 100 may be used for the analysis; for excess air or emission rate correction factor determination, an Orsat analyzer or analyzers specified in Method 100 must be used.

1.2 Applicability

1.2.1
This method is applicable for determining CO_2 and O_2 concentrations, excess air, and dry molecular weight of the a sample from a gas stream of a fossil-fuel combustion process. The method may also be applicable to other processes where it has been determined that compounds other than CO_2, O_2, CO, and nitrogen (N_2) are not present in concentration sufficient to affect the results.

1.2.2
Other methods, as well as modifications to the procedure described herein, are also applicable for some or all of the above determinations. Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative. 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; (2) a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight and excess air; (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Control Agency's Authorized RepresentativeExecutive Officer.

1.2.3

[1] Mention of trade names or specific products does not consitute endorsement by the Air Resources Board.

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2 Apparatus

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 Executive OfficerControl Agency's Authorized Representative.

2.1 Grab Sampling (Figure 3-1)

2.1.1 Probe

The probe should be made of sStainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other material inert to O_2, CO_2, CO, and N_2 and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

2.1.1 Pump

A one-way squeeze bulb, or equivalent, is used to transport the gas sample to the analyzer.

2.2 Integrated Sampling (Figure 3.2)

2.2.1 Probe

A probe such as that describedSame as in Section 2.1.1 is suitable.

2.2.2 Condenser

An air-cooled or water-cooled condenser, or other condenser no greater than 250 ml 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.

2.2.3 Valve

A needle valve, is used to adjust sample gas flow rate.

2.2.4 Pump

A leak-free, diaphragm-type pump, or equivalent, is used to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.2.5 Rate Meter

AThe rotameter, or equivalent rate meter, used should be capable of measuring flow rate to within ±2 percent of the selected flow rate. A flow rate range of 500 to 1000 cccm^3/min is suggested.

2.2.6 Flexible Bag

Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and time length of the test run, may be used. A capacity in the range of 55 to 90 liters is suggested.

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow to stand for for 10 minutes. Any displacement of the water manometer indicates a leak. An alternative method is to pressurize the bag to 5 to 10 cm (2 to 4 in.) H_2O and allow to stand overnight. A deflated bag indicates a leak.

2.2.7 Pressure Gauge

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

2.2.8 Vacuum Gauge

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

2.3 Analysis

For Orsat and Fyrite analyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

2.3.1 Dry Molecular Weight Determination

An Orsat analyzer or Fyrite-type combustion gas analyzer may be used.

2.3.2 Emission Rate Correction Factor or Excess Air Determination

An Orsat analyzer must be used. For low CO_2 (less than 4.0 percent) or high O_2 (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions.

3 Dry Molecular Weight Determination

Any of the three sampling and analytical procedures described below may be used for determining the dry molecular weight.

3.1 Single-Point, Grab Sampling and Analytical Procedure

3.1.1

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 1.00 m (3.3 ft), unless otherwise specified by the Executive OfficerControl Agency's Authorized Representative.

3.1.2

Set up the equipment as shown in Figure 3-1, making sure all connnections ahead of the analyzer are tight and leak-free. If an Orsat analyzer is used, it is recommended that the analyzer be leak-checked by following the procedure in Section 5; however, the leak check is optional.

3.1.3

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 5 exchanges. Draw a sample into the analyzer and immediately analyze it for percent CO_2 and percent O_2. Determine the percentage of the gas that is N_2 and CO by subtracting the sum of the percent CO_2 and percent O_2 from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.1.4

Repeat the 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). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2 Single-Point, Integrated Sampling and Analytical Procedure

3.2.1

The sampling point in the duct shall be located as specified in Section 3.1.1.

3.2.2

Leak-check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in Hg), plugged 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 and leak free.

3.2.3
Sample at a constant rate. The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 30 liters (1.00 ft^3) of sample gas is recommended; however, smaller volumes may be collected, if desired.

3.2.4

Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO_2 and percent O_2 using either an Orsat analyzer or a Fyrite-type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that the Orsat leak-check described in Section 5 be performed before this determination; however the check is optional. Determine the percentage of the gas that is N_2 and CO by subtracting the sum of percent CO_2 and percent O_2 from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.2.5

Repeat the 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).

Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

3.3 Multi-Point, Integrated Sampling and Analytical Procedure

3.3.1

Unless otherwise specified by the Executive OfficerControl Agency's Authorized Representative, 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 twelve traverse points shall be used for all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to approval of the Executive OfficerControl Agency's Authorized Representative.

3.3.2

Follow the procedures outlined in Sections 3.2.2 through 3.2.5, 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.

4 Emission Rate Correction Factor or Excess Air Determination

NOTE: A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determination, unless approved by the Executive OfficerControl Agency's Authorized Representative. If both percent CO_2 and percent O_2 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight.

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 Executive OfficerControl Agency's Authorized Representative.

4.1 Single Point, Grab Sampling and Analytical Procedure

4.1.1

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 1.00 m (3.3 ft), unless otherwise specified by the Executive Officeradministrator.

4.1.2

Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. Leak check the Orsat analyzer according to the procedure described in Section 35. This leak check is mandatory.

4.1.3

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 5 exchanges. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO_2 or percent O_2. If excess air is desired, proceed as follows: (1) immediately analyze the sample, as in Sections 4.1.4 and 4.1.5, for percent CO_2, O_2 and CO; (2) determine the percentage of the gas that is N_2 by subtracting the percent CO_2, percent O_2 and percent CO from 100 percent; and (3) calculate percent excess air as outlined in Section 6.2.

4.1.4

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.

4.1.5

After the analysis is completed, leak check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis. Note: Since this single-point, grab sampling and analytical procedure is normally conducted in connection 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 CO_2 or O_2 is required, is is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data and that Section 4.4 be used to validate the analytical data.

4.2 Single-Point, Integrated Sampling and Analytical Procedure

4.2.1

The sampling point in the duct shall be located as specified in Section 4.1.1.

4.2.2

Leak check (mandatory) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to 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 shall 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 and leak-free.

4.2.3

Sample at a constant rate or as specified by the Executive OfficerControl Agency's Authorized Representative. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 30 liters (1.00 ft^3) of sample gas is recommended; however, smaller volumes may be collected if desired, subject to approval of the Control Agency's Authorized Representative.

4.2.4

Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor detrmination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-checked (see Section 5) 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 4.2.5 through 4.2.7) for percent CO_2, O_2, and CO; (2) 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; (3) calculate percent excess air, as outlined in Section 6.2.

4.2.5

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 3 consecutive readings, replace the absorbing solution.)

4.2.6

Repeat the analysis until the following criteria are met:

4.2.6.1

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

4.0 percent. Average the three acceptable values of percent CO_2 and report the results to the nearest 0.1 percent.

4.2.6.2

For percent O_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than or equal to 15.0 percent. Average the three acceptable values of percent O_2 and report the results to the nearest 0.1 percent.

4.2.6.3

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

4.2.7

After the analysis is completed, leak-check the Orsat Analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis. Note: Although in most cases only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography carbon balance calculations considering the composition of the fuel be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure

4.3.1

Both the minimum number of sampling points and the sampling point location shall be as specified in Section 3.3.1 of this method. The use of fewer points is subject to the approval of the Executive OfficerControl Agency's Authorized Representative.

4.3.2

Follow the procedures outlined in Sections 4.2.2 through 4.2.7, 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.

4.4 Quality Control Procedures

4.4.1 Data Validation when Both CO_2 and O_2 are measured

Although in most instances, only CO_2 or O_2 measurement is required, it is recommended that both CO_2 and O_2 be measured to provide a check on the quality of the data. The following quality control procedure is suggested. Note: Since the method for validating the CO_2 and O_2 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_2 or O_2 through processes other than combustion (2) add

O_2 (e.g. oxygen enrichment) and N_2 in proportions different from that of air, (3) add CO_2 (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 CO_2 and O_2 for the fuel type, but the method does not detect sample dilution resulting from leaks during or after sample collection. This method is applicable for samples collected downstream of most lime or limestone flue-gas desulfurization units as the CO_2 added or removed from the gas stream is not significant in relation to the total CO_2 concentration. The CO_2 concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F_o check minimally useful.

4.4.1.1

Calculate a fuel factor, F_o using the following equation:

$F_o = (20.9 - \%O_2) / (\%CO_2)$ Eq. 3-3

Where:
$\%O_2$ = Percent O_2 by volume (dry basis).
$\%CO_2$ = Percent CO_2 by volume (dry basis).
20.9 = Percent O_2 by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values before performing the calculation for F_o as follows:

$\%CO_2 \text{ (adj)} = \%CO_2 + \%CO$
$\%O_2 \text{ (adj)} = \%O_2 - 0.5\ \%CO$

Where:
%CO = Percent CO by volume (dry basis).

4.4.1.2

Compare the calculated F_o factor with the expected F_o values. The following table may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combination, calculate the combined fuel F_d and F_c factors (as defined in EPA Method 19, 40 CFR 60 Appendix A) according to the procedure in EPA Method 19 Section 5.2.3. Then calculate the F factor as follows:

$F_o = 0.209\ F_d / F_c$ Equation 3-4

	Fuel Type	F_o range
Coal:		
	Anthracite and Lignite	1.0186 - 1.130
	Bituminous	1.083 - 1.230
Oil		
	Distillate	1.260 - 1.413
	Residual	1.2710 - 1.370
Gas		

Natural	1.600 - 1.838
Propane	1.434 - 1.586
Butane	1.405 - 1.553
Wood	1.000 - 1.120
Wood Bark	1.003 - 1.130

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 anayzing 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 this test would not significantly change the compliance status of the source and would be unnecessarily time consuming and costly.

5. LEAK-CHECK PROCEDURE FOR ORSAT ANALYZER

Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be thoroughly leak checked on site before the flue gas sample is introduced into it. The procedure for leak checking an Orsat analyzer is as follows:

5.1.1

Bring the liquid level in each pipette up to the reference mark on the capillary tubing, and then close the pipette stopcock.

5.1.2

Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette and then close the manifold stopcock.

5.1.3

Record the meniscus position.

5.1.4

Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

5.1.5

For the Orsat analyzer to pass the leak check, two conditions must be met:

5.1.5.1

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

5.1.5.2

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

5.1.6

If the analyzer fails the leak-check procedure, check all rubber connections and stopcocks to determine whether they might be the cause of the leak. Disassemble, clean and regrease leaking stopcocks. Replace leaking rubber connections. should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned and regreased. Leaking rubber connections must be replaced. After the analyzer is reassembled, repeat the leak-check procedure must be repeated.

6. Calculations

6.1 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 CO_2 divided by 100.

6.2 Percent Excess Air

Calculate the percent excess air (if applicable), by substituting the appropriate values of percent O_2, CO and N_2 (obtained from Section 4.1.3 or 4.2.4) into Equation 3-1.

Equation to be deleted:

$$percent\ EA = \left[\frac{percent\ O_2 - 0.5\ percent\ CO}{0.264\ percent\ N_2 - (percent\ O_2 - 0.5\ percent\ CO)} \right] x\ 100$$

Equation 3-1

Equation to be added:

$\%EA = [(\%O_2) - 0.5(\%CO)]\ x100/ [0.264(\%N_2) - (\%O_2) + 0.5(\%CO)]$ Equation 3-1

Note: The equation above assumes that ambient air is used as the source of O_2 and that the fuel does not contain appreciable amounts of N_2 (as do coke or blast furnace gases). For those cases when appreciable amounts of N_2 are present (coal, oil and natural gas do not contain appreciable amounts of N_2) or when oxygen enrichment is used, alternate methods, subject to approval of the Executive OfficerControl Agency's Authorized Representative, are required.

6.3 Dry Molecular Weight.

Use Equation 3-2 to calculate the dry molecular weight of the stack gas.

$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO)$ Equation 3-2

Note: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. The tester may choose to include argon in the analysis using procedures subject to approval of the Executive OfficerControl Agency's Authorized Representative.

7. Bibliography

1. EPA Method 3, Gas Analysis for Determination of Dry Molecular Weight, CFR40, Part 60, Appendix A

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4. Mitchell, W.J. and M.R. Midgett. Field Reliability of the Orsat Analyzer. Journal of Air Pollution Control Association. 26:491-495. May 1976.

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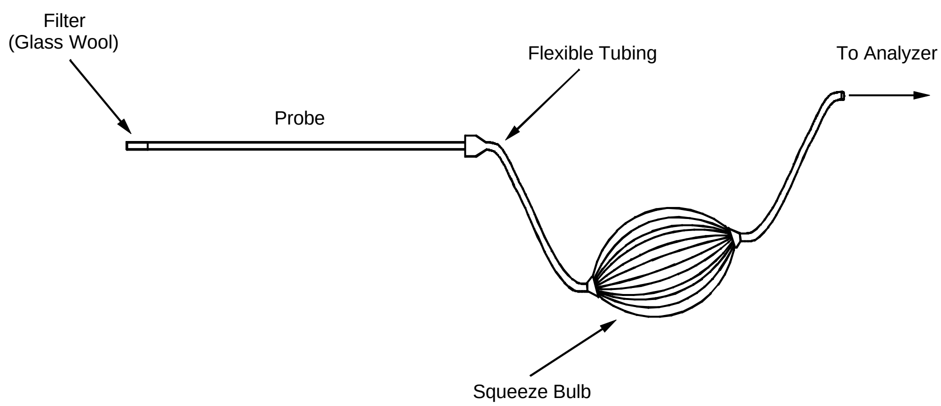

Figure 3-1. Grab-Sampling Train.

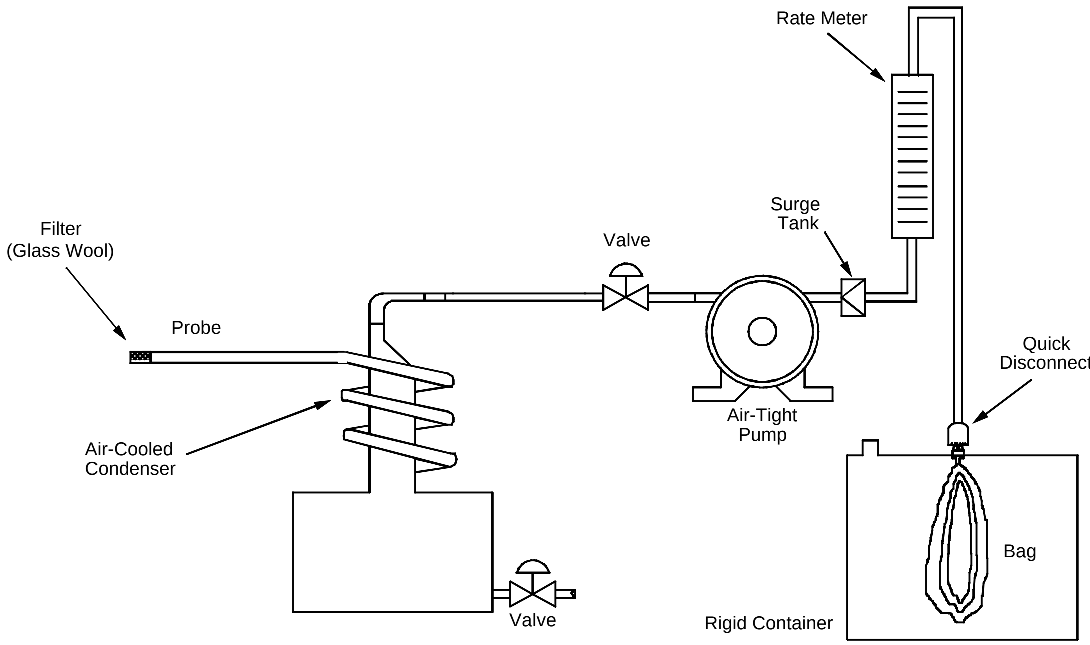

Figure 3-2. Integrated gas-sampling train.

Figure 3-3. Sampling Rate Data.

Time	Traverse Pt.	Q, liter/min	% dev.[a]
Average			

[a] % dev. = $(Q - Q_{avg})/Q_{avg} * 100$ (Must be $\leq$ 10%)