

Section 3.2

METHOD 3 - DETERMINATION OF CARBON DIOXIDE, OXYGEN,
EXCESS AIR, AND DRY MOLECULAR WEIGHT

OUTLINE

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SUMMARY

In this procedure, a gas sample is extracted from a stack by one of the following methods: single-point grab sampling; single-point integrated sampling; or multipoint integrated sampling. The gas sample is then analyzed for carbon dioxide (CO_2), oxygen (O_2), and if necessary carbon monoxide (CO). Depending on the desired accuracy of the subsequent analysis, either an Orsat or other type of gas absorption analyzer such as a Fyrite⁺ analyzer may be used for the analysis.

This method is used for determining CO_2 and O_2 concentrations $>0.2\%$ by volume and for calculating excess air and the dry molecular weight of gas streams from combustion processes. 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 concentrations sufficient to affect the results. Sulfur dioxide (SO_2), for example, can affect CO_2 readings since it would be absorbed with the CO_2 .

Other methods and modifications to measure these constituents include: a multipoint sampling method using an Orsat apparatus to directly analyze individual grab samples obtained at each point; assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements for processes burning natural gas, coal, or oil; or a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight and excess air. These methods and modifications may be used, but are subject to the approval of the administrator, U.S. Environmental Protection Agency.

The Method Description which follows is based on the Reference Method promulgated on August 18, 1977. A complete copy

⁺Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

respectively, with diameters <0.61 m (24 in.). A minimum of 12 traverse points shall be used for all other cases. The sampling run must be simultaneous with and for the same total length of time as the pollutant emission rate determination. The Orsat analyzer must be leak checked before and after the analysis. When analyzing low concentrations of CO₂ (<4.0%) or high concentrations of O₂ (>15.0%), the measuring burette of the Orsat must have at least 0.1% subdivisions. The sample must be analyzed within 4 h of collection.

The Method Highlights checklist at the end of this section may be removed from the Handbook and used in pretest, test, and posttest operations. Each form has a subtitle (i.e., Method 3, Figure 3.1) to aid the user in finding a similar filled-in form in the Method Description. Each item on the checklist that can cause significant errors are designated with an asterisk. Most of the Method Description and forms are designed for use in calculating excess air corrections, and therefore contain many more controls than would be required for molecular weight determination only.

1. Procurement of Equipment

Section 3.2.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and materials required to perform Method 3 tests. This subsection is designed to provide the tester with a guide for the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.2.1 can be used as a quick reference, and is a summary of the corresponding written descriptions.

2. Pretest Preparations

Section 3.2.2 (Calibration of Apparatus) provides a step-by-step description of the recommended calibration procedure for the Orsat analyzer and the flow rate meter.

Section 3.2.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field

METHOD HIGHLIGHTS

Specifications described in this method (Section 3.2) are for determining excess air and dry molecular weight of gas streams from fossil-fuel combustion processes. This method may also be applicable to other processes where it has been determined that compounds other than CO_2 , O_2 , CO , and N_2 are not present in sufficient concentrations to affect the results. 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) multipoint integrated sampling. The gas sample is analyzed for percent CO_2 , percent O_2 , and if necessary percent CO .

Determination of dry molecular weight can be made using either an Orsat or Fyrite¹ analyzer and any of the three sampling methods listed above. When using the single-point grab sampling or single-point integrated sampling methods, the sampling point should either be at the centroid of the cross section or at a point >1.00 m (3.3 ft) from the stack wall, unless otherwise specified by the administrator. The sample collected for molecular weight determination must be analyzed within 8 h of collection.

Excess air or emission rate correction factors must be determined using an Orsat analyzer and the sample collection procedure specified in the applicable subpart of the standard. When using the single-point grab or single-point integrated sampling method, the sampling point should be located as specified above for molecular weight determinations. When using the multipoint integrated sampling method, a minimum of eight and nine traverse points should be used for circular and rectangular stacks,

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respectively, with diameters <0.61 m (24 in.). A minimum of 12 traverse points shall be used for all other cases. The sampling run must be simultaneous with and for the same total length of time as the pollutant emission rate determination. The Orsat analyzer must be leak checked before and after the analysis. When analyzing low concentrations of CO₂ (<4.0%) or high concentrations of O₂ (>15.0%), the measuring burette of the Orsat must have at least 0.1% subdivisions. The sample must be analyzed within 4 h of collection.

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Section 3.2.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field

tests. The method for packing and the description of packing containers should help protect the equipment but are not required.

3. On-site Measurements

Section 3.2.4 (On-site Measurements) contains procedures for sampling and analysis. Subsection 4.1 outlines the step-by-step procedure for determination of dry molecular weight. Subsection 4.2 outlines the step-by-step procedure for determination of excess air and emission rate correction factor. Subsection 4.3 includes a list of precautions that will aid in using the Orsat analyzer and improve the validity of the results.

4. Posttest Operations

Section 3.2.5 (Postsampling Operations) outlines a data comparison procedure which will allow detection of gross measurement error. A visual inspection procedure is also included to detect any change in the sampling and analysis apparatus that could have adversely affected the measured values.

Section 3.2.6 (Calculations) provides the tester with the required equations and nomenclature for calculating percent excess air and dry molecular weight.

Section 3.2.7 (Maintenance) outlines the necessary equipment maintenance which will help ensure high quality data.

5. Auditing Procedure

Section 3.2.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The performance audit of the analytical phase can be conducted using certified gas samples. Auditing procedures for the analytical, data processing, and systems phases are described in this section. A checklist for a systems audit is also included in this section.

Section 3.2.9 (Recommended Standards for Establishing Traceability) recommends the primary standards for use in assessing the accuracy of test data.

6. References

Sections 3.2.10 and 3.2.11 contain the Reference Method and the suggested references.

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PRETEST PREPARATIONS
 (Method 3, Figure 3.1)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
Probe type: Borosilicate glass _____ Stainless steel _____ Other _____							
Filter In-stack _____ Out-stack _____ Glass wool _____ Other _____							
Pump One-way squeeze _____ Diaphragm _____ Other _____ Leak checked* _____							
Condenser Type _____							
Flexible Bag Tedlar _____ Mylar _____ Teflon _____ Other _____ Leak checked* _____							
Pressure Gauge Type _____							
Analyzer Orsat _____ Fyrite _____ Other _____ Leak checked* _____ Spare reagents _____							

*Most significant items/parameters to be checked.

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ON-SITE MEASUREMENTS CHECKLIST
(Method 3, Figure 4.1)

Sampling

Method: single-point grab _____ single-point integrated _____
 multipoint integrated _____
Is a filter used to remove particulate matter? _____
*Sampling train leak checked? _____
*Orsat analyzer leak checked? _____
All connections tight and leak free? _____
Sampling port properly sealed? _____
Sampling rate held constant? _____
Sampling train purged? _____

Analysis

Molecular Weight Determination

Analyzer: Orsat _____ Fyrite _____ Other _____

Fyrite:

Reagent at proper level and zeroed?* _____
Leak-free connection between analyzer and sample line? _____
Sampling line purged?* _____

Orsat:

Reagents at proper level?* _____
Analyzer level? _____
Leak checked?* _____
Sample analyzed within 8 h?* _____
Sample lines purged?* _____

Excess Air-Emission Rate Correction

Orsat analyzer leak checked?* Before _____ After _____
Reagents at proper level?* _____
Sampling lines purged?* _____
Analysis repeated by drawing a new sample until the following
criteria are met?

CO₂ - any three analyses differ by
a) <0.3% when CO₂ >4.0% _____
b) <0.2% when CO₂ <4.0% _____

O₂ - any three analyses differ by
a) <0.3% when O₂ <15.0% _____
b) <0.2% when O₂ >15.0% _____

CO - any three analyses differ by <0.3% _____

All readings averaged and reported to nearest 0.1% _____

*Most significant items/parameters to be checked.

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1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

Diagrams of the sampling trains used in the method are shown in Figures 1.1 and 1.2. Specifications, criteria, and/or applicable design features are given in this section to aid in the selection of equipment to assure the collection of good quality data. Procedures and, where applicable, limits for acceptance checks are given. During the procurement of equipment and supplies, it is suggested that a procurement log be used to record the descriptive title of equipment, the identification number (if applicable), and the results of acceptance checks. An example procurement log is shown in Figure 1.3; a blank form is given in Section 3.2.12 for the user. If calibration data are required as part of the acceptance check, the data should be recorded in a calibration log. Table 1.1 at the end of this section contains a summary of the quality assurance activities for procurement and acceptance of apparatus and supplies.

As alternatives to the sampling systems described herein, others (e.g., liquid displacement) may be used if they are capable of obtaining a representative sample, maintaining a constant sampling rate, and yielding acceptable results. Use of such systems is subject to the approval of the administrator.

1.1 Grab Sample (Figure 1.1)

1.1.1 Probe - The probe or probe liner should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack (preferred) or an out-stack filter to remove particulate matter. A plug of glass wool is generally a satisfactory filter. The probe tip should be designed to prevent the glass-wool filter from being drawn from the probe when sampling a source that has a substantial negative pressure. Any material inert to O₂, CO₂, CO, and N₂ and resistant to temperature at the sampling conditions may be used for the probe; examples of such

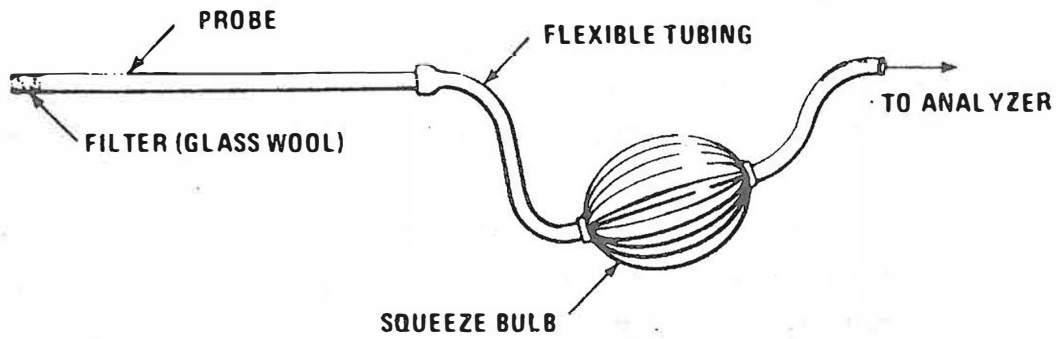


Figure 1.1 Grab sampling train.

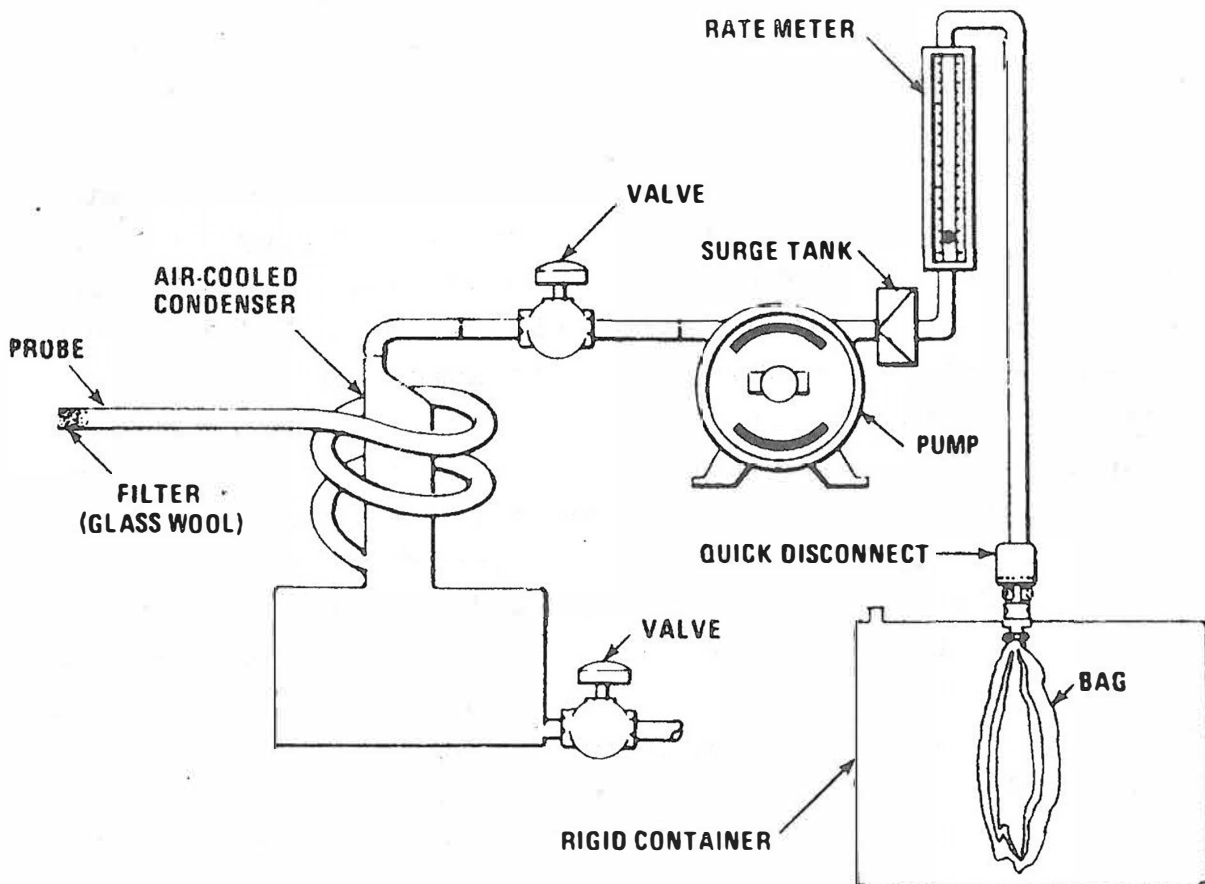


Figure 1.2 Integrated gas sampling train.

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
Orsat Analyzer	1	22481A	Lacy Inc.	7/29/79	8/15/79	\$1000	In service	

Figure 1.3 Example of a procurement log.

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materials are aluminum, steel, glass, PVC plastic, and Teflon^R. Since the gases to be sampled are relatively inert, the key criterion in probe selection is the stack gas temperature.

1.1.2 Pump - A one-way squeeze bulb, or the equivalent, is used to draw the gas sample into the analyzer.

1.2 Integrated Sample (Figure 1.2)

1.2.1 Probe - A probe equipped in the manner just described in Subsection 1.1.1 is suitable.

1.2.2 Condenser - An air or water-cooled condenser that will not remove O₂, CO₂, CO, and N₂ should be used to remove excess moisture if the gas stream contains >2% moisture by volume. (This includes most combustion processes.) The main consideration is that the condenser volume be kept to the minimum size necessary to sufficiently cool the sample gas, because the larger the volume the more difficult it is to completely purge the sampling train before collecting a sample. A 0.63-cm (0.25-in.) stainless steel coil or equivalent connected to a water collection chamber with a capacity of about 40 ml is sufficient.

1.2.3 Valve - Needle valves are needed to adjust the sample gas flow rate.

1.2.4 Pump - A leak-free diaphragm pump, or the equivalent, is needed to transport the sample gas to the flexible bag. A small surge tank should be installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter. Upon receipt, the pump, surge tank, and rate meter (Subsection 1.2.5 below) should be checked in the following manner:

1. Assemble the pump, surge tank, and rate meter.
2. Place a needle valve and vacuum gauge at the pump inlet using a T-connector.
3. Turn on the pump and close the needle valve until a vacuum of 125 mm (5 in.) Hg is obtained. The pumping rate at this vacuum is suggested to be at least 1 l/min (0.035 ft³/min),

^RRegistered trademark.

and the rate meter when the flow is adjusted between 0.5 and 1.0 ℓ /min (0.018 and 0.035 ft^3 /min) should yield steady readings.

If the pump capacity is insufficient, repair, replace, or return it to the manufacturer. If rotameter readings fluctuate >2% of the full-scale reading, use a larger surge tank. Be sure that the rotameter is clean and dry.

1.2.5 Rate Meter - A rotameter or an equivalent rate meter, capable of measuring flow rates within $\pm 2\%$ of the selected flow rate should be used.

The calibration curve (Figure 1.4) supplied by the manufacturer should be checked by comparing the rotameter readings against the wet test meter readings. If the rotameter is not within $\pm 5\%$ of the manufacturer's calibration curve, recalibrate and construct a new curve.

Changes in sample gas pressure, density, and viscosity will affect the sampling rate. However, since sampling is performed at a constant rate and since the total volume sampled need not be measured accurately, these changes are not significant.

1.2.6 Flexible Bag - Any leak-free inert plastic (e.g., Tedlar^R, Mylar^R, Teflon^R) bag, or the equivalent, having a capacity adequate for the selected flow rate and time length of the test run may be used. A capacity of 90 ℓ (3.2 ft^3) is usually required. To leak check the bag (Figure 1.5):

1. Connect it to a manometer and pressurize the bag to from 5 to 10 cm (2 to 4 in.) H_2O .
2. Allow it to stand for 10 min.

Any displacement in the water manometer will indicate a leak and a need to repair the bag. An alternative leak check is to pressurize the flexible bag to 5 to 10 cm (2 to 4 in.) H_2O and allow it to stand overnight. A deflated bag indicates a leak.

1.2.7 Pressure Gauge - A water-filled U-tube manometer, or the equivalent, of about 28 cm (12 in.) is needed for the flexible

^R Registered trademark.

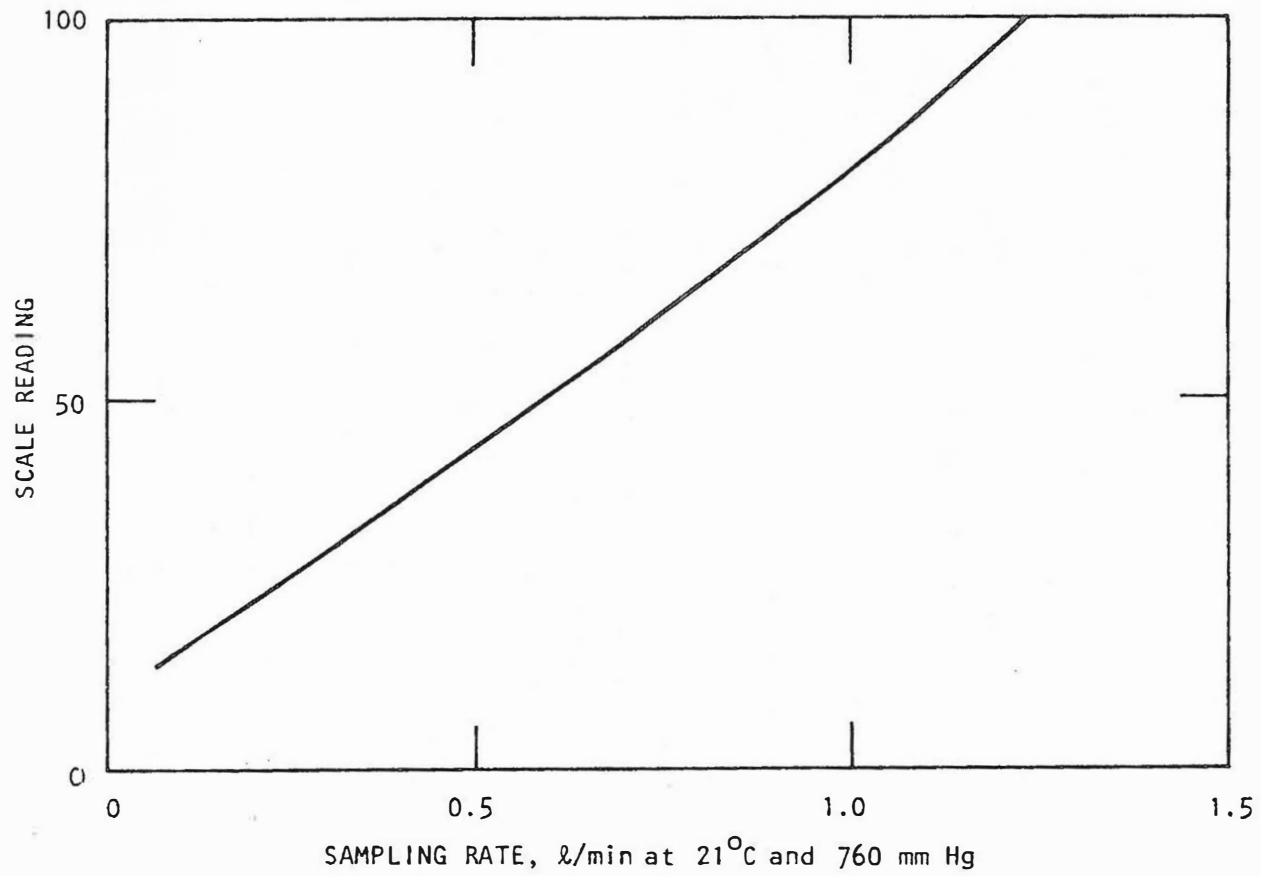


Figure 1.4 Example rotameter calibration curve.

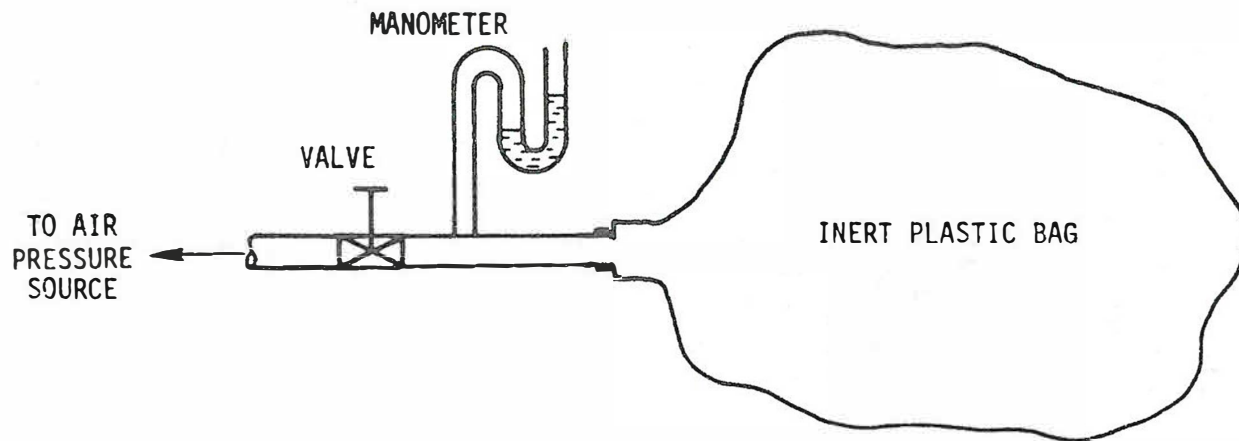


Figure 1.5 Plastic bag leak-check system.

bag leak check. The gauge should be leak checked upon receipt as follows:

1. Place a flexible tube on the gauge opening.
2. Apply a positive pressure of from 5 to 10 cm (2 to 4 in.) H₂O on the gauge by blowing on and then pinching off the tube. The pressure reading should remain stable for 10 min.
3. Check each side of the gauge separately.

If a deflection is noted, repair, replace, or return the gauge to the manufacturer.

1.2.8 Vacuum Gauge - A mercury manometer, or the equivalent, of at least 760 mm (30 in.) Hg is needed for the sampling train leak check. If a mercury manometer is used, leak check the system by pulling a 380 mm (15 in.) Hg vacuum on the gauge and then pinching off the tube. No deflection should be noted in the reading over a 10-min period. If another type of gauge is used, compare the gauge reading with a mercury manometer reading at about 380 mm (15 in.) Hg. The gauge reading should be within ± 25 mm (1 in.) Hg of the mercury manometer reading. If the gauge fails the leak check or the comparison with the mercury manometer, repair, replace, or return the manometer to the manufacturer.

1.3 Analyzer

An Orsat or a similar absorption type analyzer is required for measuring constituents of combustion gases. The latter is used only for molecular weight determinations, since it is less accurate than the Orsat.

1.3.1 Orsat Gas Analyzer - The Orsat analyzer^{6,7} is used to determine the CO₂, O₂, and CO stack gas concentrations. A sample is analyzed by successively passing it through absorbents that remove specific gaseous components. The difference in gas volume before and after the absorption represents the amount of the constituent gas in the sample. Constant pressure and temperature must be maintained throughout the analysis. Results are reported as dry volume percentages.

The Orsat analyzer illustrated in Figure 1.6 includes a glass burette to accurately measure the gas volume, a water

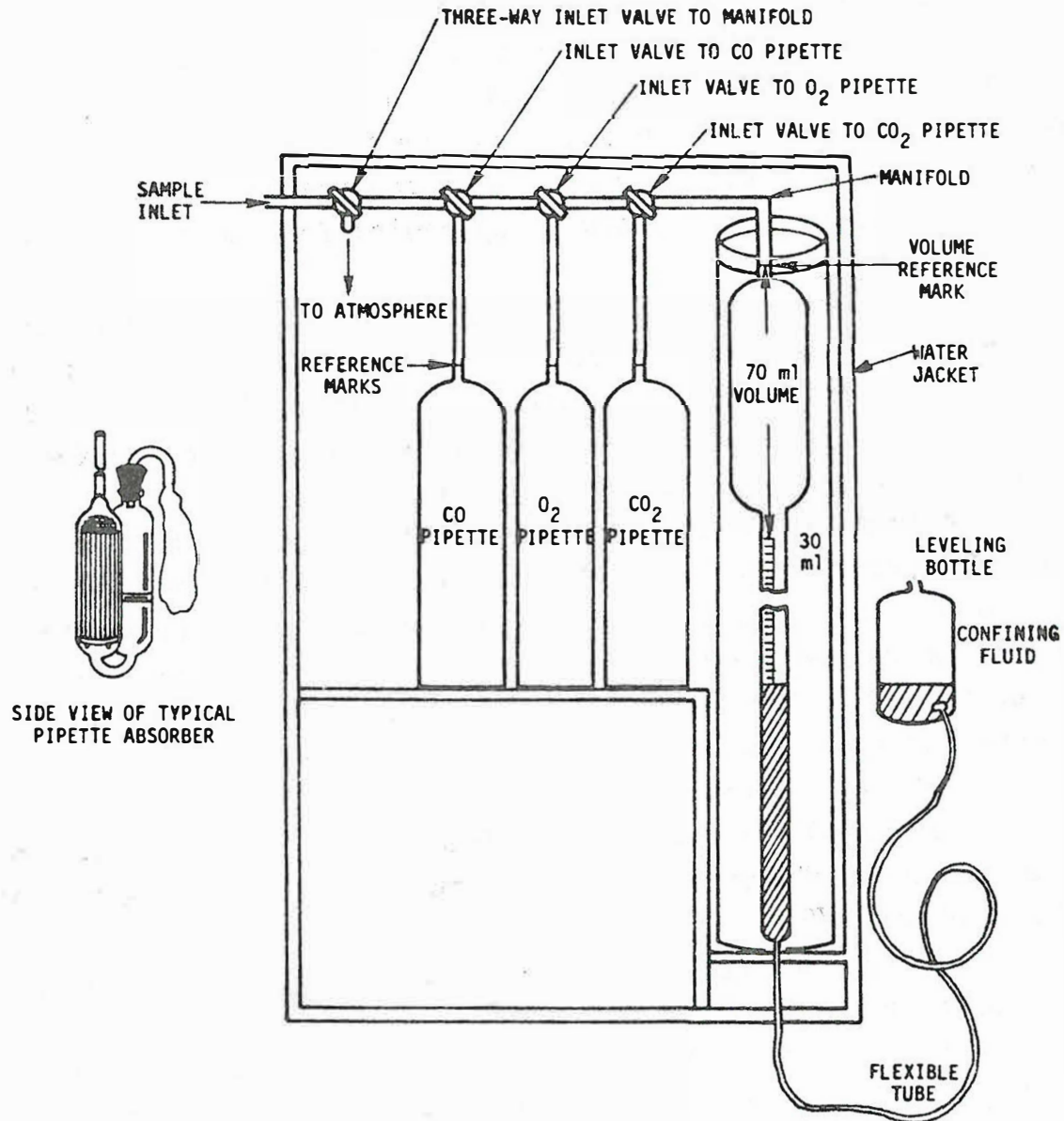


Figure 1.6 Orsat apparatus.

jacket to maintain constant temperature, a manifold to control the gas flow, three absorption pipettes (CO , O_2 , and CO_2), rubber expansion bags, and a liquid-filled leveling bottle to move the gases. The apparatus is usually assembled inside a case that has front and rear doors and a carrying handle.

For expected CO_2 readings $>4.0\%$, a standard Orsat analyzer containing a burette with 0.2-ml divisions and spacings between divisions of about 1 mm (0.04 in.) is satisfactory. For lower CO_2 values or for O_2 values $>15\%$, an analyzer equipped with a burette having 0.1-ml divisions with spacings of ≥ 1 mm (0.04 in.) should be used.

Upon receipt of the analyzer, wash and dry all components and assemble the apparatus according to the manufacturer's instructions. Then properly lubricate all glass valves with silicone stopcock lubricant. If the apparatus is to be used promptly, add the liquid reagents and check for leaks as follows:

1. Allow the apparatus to reach ambient temperature with the manifold valve open and the three pipette valves closed.
2. Bring the liquid in each absorption pipette up to the reference mark by opening the pipette valves one at a time and by slowly lowering the leveling bottle. Pinch off the rubber tube to the leveling bottle with the heel of the hand to quickly stop liquid flow. Close the pipette valves.
3. Displace the indicating fluid until a reading is obtained in the narrow part of the burette, and quickly close the manifold inlet valve.
4. Place the leveling bottle on top of the Orsat case, and read the meniscus in the burette.
5. Wait at least 4 min; then read the meniscus again. A change of ≥ 0.2 ml in the reading indicates a leak in the system which must be repaired. A drop in reagent level to below the capillary tube over a 4-min period indicates a leak in that pipette.

If leaks are detected, correct them so that the above criteria will be met.

Desirable Design Qualities - There is a variety of Orsat analyzer designs on the market. Some design features increase the precision and accuracy. Some of these desirable features are described below.

Precision and probably accuracy are improved with a glass burette configuration as shown in Figure 1.6; that is, the burette column has a large diameter having a volume of about 70 ml joined onto a narrow 30-ml burette graduated in 0.1-ml divisions.⁺ Such designs result in less error in reading the gas volume than with designs having larger graduations and less spacing between divisions. To further reduce reading error, the volume line should be scribed completely around the burette at the reference point. For processes in which CO₂ is released from the product (e.g., in a limestone kiln), the cumulative total of O₂ and CO₂ may be >25%. For these processes, the graduated portion of the burette must be long enough to provide a reading. (Graduated burettes are available up to 100 ml.) A burette with a vertical dark line behind the graduations is easier to read.

The volume reference mark should be on the capillary tube at the top of the glass burette, not on the larger diameter burette. Having the mark on the small capillary tube increases the precision from test to test and increases the accuracy of the burette calibration--both for a more accurate sample volume determination.

The connecting manifold should have as small a volume as possible to reduce the possibility of diluting the sample due to incomplete purging of the manifold. It also minimizes the increase in sample volume; the volume of gas in the manifold between the reference mark on the burette and that on the pipette is small.

⁺ These burettes are commercially available.

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The Orsat apparatus and case should be designed so that the leveling bottle and the glass burette can be viewed side by side when leveling the liquid. The liquid levels in both the burette and the bottle must be at the same height when reading the volumes; otherwise, the sample gas will not be at atmospheric pressure.

The inlet manifold valve should be three-way to allow purging of the manifold without causing the sample bag or the inlet gas to be diluted by ambient air.

Reagents - Four reagents are required by a standard Orsat apparatus for analyzing flue gas. These are the gas-confining solution, the CO₂ absorbent, the O₂ absorbent, and the CO absorbent. Due to the solubility of CO₂ in water, a colored aqueous acidic salt solution is used as the confining solution; it contains sodium sulfate, sulfuric acid, and methyl orange. The CO₂ absorbent is a solution of potassium or sodium hydroxide, and the O₂ absorbent is a solution of alkaline pyrogallic acid or chromous chloride. The CO absorbent is usually a cuprous chloride or sulfate solution, but other solutions may be used.⁶ All of these solutions can be purchased from most chemical suppliers. Note the shelf-life requirements, since some reagents deteriorate with time.

1.3.2 Other Absorption Type Analyzers - Absorption type analyzers which determine CO₂ or O₂ concentrations are also available. These devices are simpler and easier to use than an Orsat, and they are more rugged. However, they provide less precision and can thus be used only for molecular weight determinations of the gases. These devices operate similarly to the Orsat by absorbing the gas in a colored solution; then the volume absorbed is read directly on a scale as percentage by volume. A commonly used O₂ analyzer is shown in Figure 1.7. The use of continuous monitors for determining O₂ content must be approved by the administrator.

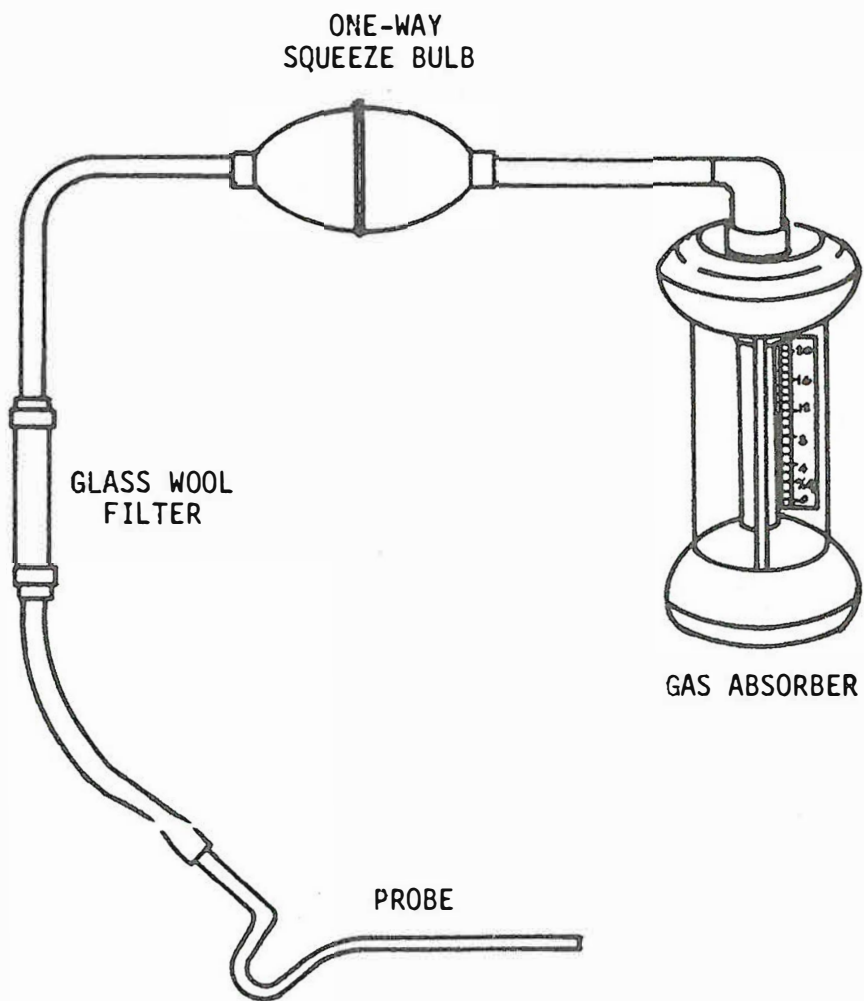


Figure 1.7 Absorption type analyzer.

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Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Grab Sampling Train</u>			
Probe	Stainless steel, borosilicate glass, or equivalent; not damaged or corroded; no leakage	Visual observation upon receipt	Discard or return defective equipment to supplier, as appropriate
Pump	One-way squeeze bulb or equivalent; not damaged or corroded	As above, plus manual operating check	As above
<u>Integrated Gas Sampling Train</u>			
Probe	Stainless steel, borosilicate glass, or equivalent; no leakage	As above	As above
Air-cooled condenser	No leakage; keep the condenser volume to a minimum necessary to cool the sample with air	As above	As above
Valve	Needle valve	As above	As above
Pump	Diaphragm type, leak free, and 1 l/min (0.035 ft ³ /min) capacity	Check for leaks and capacity upon receipt	As above
Rate meter (rotameter)	Check flow range from 0 to 1 l/min (0 to 0.035 ft ³ /min) must be accurate to within $\pm 2\%$ of selected flow rate	Check upon receipt for damage; calibrate against WTM	Recalibrate and construct new calibration curve
Flexible bag	Capacity of 55 ₃ to 90 l (1.9 to 3.2 ft ³); leak test not mandatory	Check for leaks and capacity	Return to supplier

(continued)

Table 1.1 (continued)

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Pressure gauge	28-cm (12-in.) water-filled U-tube or equivalent for flexible bag leak check	Visually observe and leak check upon receipt	As above
Vacuum gauge	At least 760-mm (30-in.) Hg gauge for the sampling train leak check	Check against a mercury U-tube manometer and leak check	As above
<u>Orsat Analyzer</u>			
Glass burette	0.1-ml divisions with spacings of about 1mm	Visually inspect upon receipt	Return to supplier
Pipettes, manifolds, etc.	Air tight	Initially and before tests	Repair or discard
Leveling bottle	Can be viewed side-by-side with glass burette	Visually check for damages	As above
<u>Other Analyzers</u>	<0.5% divisions	Visually check for damage and leaks	As above

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2.0 CALIBRATION OF APPARATUS

Calibration of sampling apparatus is one of the most important functions in maintaining data quality. Only limited initial calibration is required for gas absorption using an analyzer such as an Orsat. Continued maintenance, reagent checks, and most importantly, the operator's technique and diligence are required for good quality data. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration.

2.1 Analyzers

Calibration is recommended upon receipt, before every third field test, and before any field test in which the Orsat or other absorption type analyzer has not been checked during the previous 3 mo.

To check the O₂-absorbing reagent and the operator's technique, the percentage of O₂ in air should be determined. The average of three replicates should be 20.8 ±0.7% when using the standard Orsat. A measured average value >21.5% generally indicates poor operator technique, while a value <20.1% generally indicates leaking valves, spent absorbing reagent (for O₂ only), and/or poor operator technique. (See Section 4.1 of Reference 1 for the derivation of the above limits.) The three replicates and their averages should be reported on an \bar{X} and R chart, as illustrated by Figure 2.1; a blank copy of this form is in Section 3.2.12.

A more thorough check, if required equipment is available, would be to take a sample from a manifold containing a known mixture of CO₂ and O₂. This is applicable to grab samples or to the integrated samples. In both cases, the sample is analyzed for CO₂ and O₂ using the Orsat. The average of three replicates should be ±0.5% (absolute) of the known concentration of each gas. Again, high measured values indicate poor operator technique, while low values indicate leaking valves, spent absorbing reagent, and/or poor operator technique.

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If the above limits are exceeded, corrective action should be equipment maintenance and/or operator training.

2.2 Rate Meter

Clean and calibrate the rate meter in the integrated gas sampling train every 6 mo and at any sign of erratic behavior. Calibrate using either a wet test meter or a volume meter which has been recently calibrated against a primary standard.

1. Place the calibrated volume meter or wet test meter in series with the rate meter.

2. Adjust the flow rate to 1 ℓ/min ($0.035 \text{ ft}^3/\text{min}$) on the rate meter.

3. Take readings with the wet test meter and stopwatch. If the flow rate is not near the desired 1 ℓ/min ($0.035 \text{ ft}^3/\text{min}$) on the rate meter, adjust the valve and repeat the reading with the wet test meter and stopwatch; repeat until the desired flow rate is obtained for the rate meter setting.

4. Take readings at 0.5, 0.75, and 1.0 ℓ/min (0.18, 0.027, and $0.035 \text{ ft}^3/\text{min}$) on the rate meter. Record the readings from the calibrated meter and the rate meter in the calibration log.

5. Construct a calibration curve of rate meter reading versus flow rate for the meter using corrected wet test meter stopwatch readings.

6. Number each rate meter and include the number and the date of calibration on the calibration curve.

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Table 2.1 ACTIVITY MATRIX FOR THE CALIBRATION OF APPARATUS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Orsat analyzer	Average of three replicates should be 20.8 $\pm 0.5\%$ (absolute) or known concentration ± 0.5 (absolute)	Upon receipt and before any test in which the analyzer has not been checked during the previous 3 mo; determine % O_2 in ambient air, or use a calibration gas with known CO, CO_2 , O_2 concentrations	Check Orsat analyzer for leaking valves, spent absorbing reagent, and/or operator techniques; take corrective action
Rotameter or rate meter	Smooth curve of rotameter actual flow rates with no evidence of error	Check with wet test meter or volume meter at 6-mo intervals or at indication of erratic behavior	Repeat calibration steps until limits are attained

3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling operations are summarized in Table 3.1 at the end of this section. See Section 3.0 of this Handbook for details on site selection.

3.1 Apparatus and Calibration Checks

Figure 3.1 or a similar form is recommended to aid the tester in preparing an equipment checklist, status report form, and packing list.

3.1.1 Grab Sample Train - The grab sample train (Figure 1.1) should be checked before each field test as follows:

1. Clean the probe with soap and water, rinse it with water, and allow it to dry. Check it visually for leaks indicated by cracks or corrosion. Cap both ends of the probe tightly to prevent contaminants from entering while it is not in use. If particulates are expected, insert a plug of glass wool into the sampling end of the probe.

2. Check the pump--either a one-way squeeze bulb or a leak-free diaphragm type pump--to see if it is operating properly. Check all connectors and tubes for leaks; do this by slightly pressurizing the system and by applying soap to the connections and joints and watching for bubbles.

3.1.2 Integrated Sample Train - The integrated gas sampling train (Figure 1.2) should be checked before each field test as follows:

1. Clean the probe with soap and water, rinse it with water, and allow it to dry. Visually check it for leaks indicated by cracks or corrosion. Cap both ends of the probe tightly to prevent contaminants from entering it while it is not in use. If particulates are expected, insert a plug of glass wool into the sampling end of the probe.

2. Clean the air-cooled condenser, or equivalent, and leak check it by slightly pressurizing the unit, applying soap to joints and connections, and watching for bubbles.

(3.2.3)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe type:</u> Borosilicate glass _____ Stainless steel <input checked="" type="checkbox"/> _____ Other _____	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Filter</u> In-stack <input checked="" type="checkbox"/> _____ Out-stack _____ Glass wool _____ Other _____	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Pump</u> One-way squeeze _____ Diaphragm <input checked="" type="checkbox"/> _____ Other _____ Leak checked* _____	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Condenser</u> Type <u>air cooled</u>	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Flexible Bag</u> Tedlar _____ Mylar <input checked="" type="checkbox"/> _____ Teflon _____ Other _____ Leak checked* <u>yes</u>	<input checked="" type="checkbox"/>		6	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Pressure Gauge</u> Type <u>Hube</u>	<input checked="" type="checkbox"/>			<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Analyzer</u> Orsat <input checked="" type="checkbox"/> _____ Fyrite <input checked="" type="checkbox"/> _____ Other _____ Leak checked* <u>yes</u> Spare reagents <input checked="" type="checkbox"/> _____	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	2 2	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
	<input checked="" type="checkbox"/>		1	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	

*Most significant items/parameters to be checked.

Figure 3.1 Pretest preparation.

3. Disassemble, clean, and reassemble the needle valve and rate meter at any sign of foreign matter in the rotameter or erratic behavior of the rotameter.

4. Leak check the flexible bag by pressurizing and by observing for any loss in pressure as described in Section 3.2.1.

3.1.3 Orsat Gas Analyzer - The Orsat apparatus should be checked and serviced before each field test in the following manner:

1. Check the confining fluid levels in the leveling bottle and the burette. Be sure the approximately 300 ml of fluid in the leveling bottle is clear, orange, and sufficient to fill the burette. Be sure the solution in the leveling bottle is distilled water containing approximately 5% by volume of concentrated sulfuric acid and 2 to 3 ml of methyl orange acidic indicator; then saturate the solution with a salt, usually sodium sulfite or sodium chloride, at the temperature at which the Orsat is expected to operate. (The sulfuric acid acts as a drying agent to remove any moisture from the sample, and the saturated salt solution prevents the absorption of sample gases by the leveling solution.) This leveling bottle solution should be prepared as a stock solution and taken to the field in case it is needed.

2. Remove and clean the stopcocks. Carefully apply stopcock grease to prevent system leaks, and do it without plugging the air passages. Stopcocks are generally not interchangeable, so replace each one in the same port from which it was originally taken.

3. Change the absorbing solutions if >10 passes are needed to obtain a constant reading for any gas component. If in doubt, change the solution (following the manufacturer's instructions) by emptying the absorber and adding fresh absorbing reagents. Add new reagents when required, 6 to 8 h prior to field use. Prior to adding the O₂ reagent, flush the absorbing pipette and the expansion bag with N₂, and pass N₂ over the reagent while adding it to the pipette.

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4. Leak check the Orsat analyzer thoroughly on site before using it, since moving an Orsat to the site may have caused it to leak. (Use the procedure in Section 3.2.1) If there are leaks, check all connections and stopcocks 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, the leak-check procedure must be repeated.

3.1.4 Fyrite Gas Analyzer - Check the absorption analyzer visually for leaking of reagents prior to each test.

3.2 Equipment Packaging

Logistics of the method, time of sampling, and quality of data are dependent on the packing of the sampling and analytical equipment for (1) accessibility in the field, (2) ease of movement on site, and (3) optimum functioning in the field. Equipment should be packed to withstand severe treatment during shipment and field operations.

1. Pack probes, pumps, and condenser in cases or wooden boxes filled with packing material or lined with styrofoam. The cases should have handles or hooks that can withstand hoisting and should be rigid enough to prevent bending or twisting during shipping and handling.

2. Pack rate meters, needle valves, and all small glassware individually in shipping containers.

3. Use the rigid container with the integrated sampling bag for its shipping container.

4. Disassemble the Orsat and pack each item individually in suitable packing material and rigid containers for long trips or for shipping as freight. Ship the spare parts and the absorbent solutions in separate containers.

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Table 3.1 ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Grab Sample Train</u>	No visual sign of breakage	Visual observation before each field test	Replace as necessary
Probe	As above	As above	As above
Pump	As above	As above	As above
<u>Integrated Gas Sampling Train</u>			
Probe	As above	As above	As above
Air-cooled condenser	As above	As above	Clean and replace as necessary
Needle valve and rotameter	No foreign matter or erratic behavior	As above	Clean and reassemble as necessary
Flexible bag	No visual indication of leakage	As above	Replace as necessary
Pump	According to manufacturer's criteria	Before each field test, use manufacturer's directions	Service or return to supplier as necessary
<u>Gas Analyzer Orsat</u>			
Leveling solution	Distilled water containing approximately 5% by volume of concentrated H_2SO_4 and saturated with a salt		Prepare fresh solution
Absorbing solution	<10 passes needed for constant readings with any component gas	Performance check using any component gas	Use fresh reagent

(continued)

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Table 3.1 (continued)

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stopcocks	No leakage	Visual observation	Remove, clean, regrease as necessary
Assembly	No leaks present	See text	Eliminate leaks before test
<u>Gas Analyzer</u> <u>(Fyrite)</u>	Fill with reagents; no leaks	Visual observation	Add fresh reagent; repair as necessary
<u>Package Equip-</u> <u>ment for Ship-</u> <u>ment</u>	Not applicable	See packing instructions	Not applicable

4.0 ON-SITE MEASUREMENTS

The choice of procedure to be used at the sampling site depends on whether an emission rate factor (F-factor), an excess air determination, or a molecular weight determination is required. The applicable measurement is specified in the emission standard, and the quality assurance activities are summarized in Table 4.1 in this section. In any case, the equipment is unpacked at the sampling site and visually inspected for damage during shipment from the laboratory; the Orsat analyzer, especially, is carefully checked for reagent levels and leaks as described in Section 3.2.1. Figure 4.1 (On-site Measurement Checklist) can be used as a guide for sampling and analysis of molecular weight, excess air, and emission rate determination.

4.1 Determination of CO₂ and O₂ for Dry Molecular Weight Calculations

Three methods are described in the Federal Register for measuring a gas stream's dry molecular weight. These are discussed in order of increasing complexity, and their uses are determined by the applicable standards or by expected variations in gas composition.

4.1.1 Single-Point Grab Sampling and Analysis - Set up the grab sampling train as depicted in Figure 1.1. Visually check each connection for leaks.

1. Be sure the sampling point in the duct is either at the centroid of the cross section or at a point ≥ 1 m (3.28 ft) from the walls of larger ducts, unless otherwise specified by the administrator.

2. Place the probe securely in the stack at the sampling point.

3. Seal the sampling port as well as possible with a sponge or rag to prevent dilution of the stack gas by ambient air if the stack pressure is negative.

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Sampling

Method: single-point grab single-point integrated _____
multipoint integrated _____

Is a filter used to remove particulate matter? yes

*Sampling train leak checked? yes

*Orsat analyzer leak checked? yes

All connections tight and leak free? yes

Sampling port properly sealed? yes

Sampling rate held constant? N/A

Sampling train purged? yes

Analysis

Molecular Weight Determination

Analyzer: Orsat Fyrite _____ Other _____

Fyrite:

Reagent at proper level and zeroed?* _____

Leak-free connection between analyzer and sample line? _____

Sampling line purged?* _____

Orsat:

Reagents at proper level?* yes

Analyzer level? yes

Leak checked?* yes

Sample analyzed within 8 h?* yes

Sample lines purged?* yes

Excess Air-Emission Rate Correction N/A

Orsat analyzer leak checked?* Before _____ After _____

Reagents at proper level?* _____

Sampling lines purged?* _____

Analysis repeated by drawing a new sample until the following criteria are met?

- CO₂ - any three analyses differ by
 - a) <0.3% when CO₂ >4.0% _____
 - b) <0.2% when CO₂ <4.0% _____

- O₂ - any three analyses differ by
 - a) <0.3% when O₂ <15.0% _____
 - b) <0.2% when O₂ >15.0% _____

CO - any three analyses differ by <0.3% _____

All readings averaged and reported to nearest 0.1% _____

*Most significant items/parameters to be checked.

Figure 4.1 On-site measurement checklist.

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4. Check the Orsat analyzer for leaks as described in Section 3.2.1. (Though this step is not mandatory, it is highly recommended.) If another gas absorption device is used, it must be zeroed before use.

5. Purge the sampling line several times by squeezing the one-way squeeze bulb and then attaching the gas analyzer (either the Orsat or another gas absorption device).

6. Draw a gas sample into the analyzer and immediately analyze it for CO_2 and O_2 . Record the data on data form shown in Figure 4.2 or on a similar form.

7. Calculate the molecular weights as described in Section 3.2.6.

8. Repeat steps 5 through 7 until the calculated molecular weights of any three samples differ from their mean by ≤ 0.3 g/mole.

4.1.2 Single-Point Integrated Sampling and Analysis - Set up the sampling train as shown in Figure 1.2. Visually check for leaks.

1. Be sure the sampling point in the duct is either at the centroid of the cross section or at a point ≥ 1 m (3.28 ft) from the walls of larger ducts, unless otherwise specified by the administrator.

2. Place the probe securely in the stack at the sampling point.

3. Seal the sampling port as well as possible with a sponge or rag to prevent dilution of the stack gas by ambient air if the stack pressure is negative.

4. Leak check the flexible bags as described in Section 3.2.1, and then evacuate the selected bag. Leak check the sampling system by attaching a vacuum gauge to the condenser inlet, drawing a vacuum of 250 mm (10 in.) Hg, and plugging the outlet fitting where the bag is usually attached. Turn off the pump and observe the vacuum reading for 30 s; it should remain stable. If the vacuum drops, check the system for leaks, then repair if necessary, and finally recheck. (These leak checks are optional, but highly recommended.)

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PLANT Valley Power Company
 DATE 8-1-79 TEST NO 0-1
 SAMPLING TIME (24-hr CLOCK) 1335-1454
 SAMPLING LOCATION ESP Outlet
 SAMPLE TYPE (BAG, INTEGRATED, CONTINUOUS) Integrated bag
 ANALYTICAL METHOD Orsat
 AMBIENT TEMPERATURE 60°F
 OPERATOR T. Clark

COMMENTS:

RUN 0-1 GAS	1		2		3		AVERAGE NET VOLUME	MULTIPLIER	MOLECULAR WEIGHT OF STACK GAS (DRY BASIS) M _d
	ACTUAL READING	NET	ACTUAL READING	NET	ACTUAL READING	NET			
CO ₂	8.0	8.0	8.0	8.0	8.0	8.0	8.0	44/100	3.52
O ₂ (NET IS ACTUAL O ₂ READING MINUS ACTUAL CO ₂ READING)	19.2	11.2	19.2	11.2	19.2	11.2	11.2	32/100	3.58
CO (NET IS ACTUAL CO READING MINUS ACTUAL O ₂ READING)	19.2	0	19.2	0	19.2	0	0	28/100	0
N ₂ (NET IS 100 MINUS ACTUAL CO READING)	80.8		80.8	80.8	80.8	80.8	80.8	28/100	22.62
TOTAL									29.72

Figure 4.2 Gas analysis data form.

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 Revision No. 0
 Date January 15, 1980
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5. Connect the probe, open the quick disconnect at the bag connection, and purge the sampling system with stack gas by running the pump for about 1 min at a high rate. Make sure that the condenser drain valve is closed tightly.

6. Connect the evacuated flexible bag, and begin the sampling. Record the time, flow rate, and other appropriate data on a form like the one shown in Figure 4.3.

7. Sample at a constant rate so that about 30 to 90 l (1 to 3 ft³) of gas are collected simultaneously with the pollutant emission rate test.

8. Disconnect, seal, and remove the flexible sampling bag to a suitable area for performing the analysis. Allow the collected sample to sit for about 30 min to ensure thorough mixing and temperature equilibrium. It is recommended that the analysis be performed as soon as practical after the 30-min waiting period, but not more than 8 h after sampling. If an Orsat analyzer is used, leak check it as described in Section 3.2.1. (Though not mandatory, this step is highly recommended.) If a gas absorption device is used, zero it before use.

9. Calculate the molecular weights as described in Section 3.2.6. A data form similar to the one shown in Figure 4.2 can be used for recording the results of the calculations.

10. Repeat steps 8 and 9 until the calculated molecular weights of any three analyses differ from their mean by ≤ 0.3 g/mole.

4.1.3 Multipoint Integrated Sampling and Analysis - This procedure is similar to the single-point integrated sampling procedure, but it is used when the stack cross section is traversed.

1. Locate the sampling points according to the procedures described in Method 1. Determine the minimum number of traverse points, as follows:

- a. 8 points for a round stack with < 0.61 m (24 in.) diameter,
- b. 9 points for a rectangular stack with an equivalent diameter of < 0.61 m (24 in.), or

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Run number 0-1

Date January 9, 1980 Plant Valley Power Company

Sampling location CSP Outlet

Barometric pressure 29.57 in.

Ambient temp. °C 30.5 Stack temp. °C 152

Operator B. C. Blagum

Time	Traverse point	Rate meter flow rate (Q), cm ³ /min	% Dev. ^a
13:00	W-1	500	0
13:05	2	500	0
13:10	3	500	0
13:15	4	500	0
13:20	5	500	0
13:25	6	500	0
13:45	N-1	500	0
13:50	2	500	0
13:55	3	500	0
14:00	4	500	0
14:05	5	500	0
14:10	6	500	0
		Avg = 500	0

^a

$$\% \text{ Dev.} = \left(\frac{Q - Q_{\text{avg}}}{Q_{\text{avg}}} \right) 100; \text{ must be } \leq 10\%.$$

Figure 4.3 Integrated bag sampling field data.

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c. 12 points for a larger stack.

2. Leak check and purge the bag and the sampling train as described in Subsection 4.1.2.

3. Sample each point at the same rate and for the same time increment. Record the sampling data as shown in Figure 4.3. Collect from 30 to 90 l (1 to 3 ft³) of gas simultaneously with the pollutant emission rate test.

4. Disconnect, seal, and remove the bag to a suitable area for performing the analysis within 8 h, as described in Subsection 4.1.2.

5. Calculate the molecular weight, and repeat the analysis until the results from any three analyses differ from their mean by ≤ 0.3 g/mole.

4.2 Determination of Gas Composition for Emission Rate Factor or Excess Air Calculations

The same three sampling procedures may be used as previously described (Subsections 4.1.1, 4.1.2, and 4.1.3), but in all cases the Orsat analyzer must be used for analysis, and it must be leak checked before and after analysis. In addition, the integrated sampling train (when used) and the flexible bags must be leak checked prior to sampling. Care in using the Orsat and in assuring the accuracy of the results is also required, as described in this section.

4.2.1 Single-Point Grab Sampling and Analysis - Set up, check, and purge the system as described in Subsection 4.1.1. Perform the Orsat analysis immediately according to the manufacturer's instructions and as follows:

1. Draw sample gas into the Orsat and flush (i.e., allow to bubble through the burette) at least three times to saturate the liquid in the burette with the gas being analyzed and to ensure that the air remaining in the manifold is of the same composition as the sample to be analyzed. Caution: Once the flushing has begun, ambient air must not be allowed to enter the manifold.

2. Draw in a fixed volume (usually 100 ml) of the sample gas, following the manufacturer's instructions. Allow a minimum of 5 min for the sample gas to come to temperature equilibrium with the water jacket around the burette (unless the sample and the analyzer have both been at the same temperature for at least 5 min).

3. Proceed with the sequential determinations of CO_2 , O_2 , and CO as directed by the instructions supplied by the manufacturer of the gas analyzer. Make repeated analyses of each component until two consecutive readings are identical. Always make two or three passes through the absorbing solution between readings. Note: If more than three readings of two or three passes are required to reach a constant reading for any component gas, replace the absorbing reagent and repeat the entire sampling sequence.

4. Record the readings on the data form (Figure 4.1), and determine the average value for each component of interest.

5. Leak check the Orsat after analysis. If it does not pass the leak test, repair it and repeat the analysis.

4.2.2 Integrated Single-Point and Multipoint Sampling and Analysis - The sampling procedures are identical to those described in Subsections 4.1.2 and 4.1.3. The flexible bag and the sampling train must be checked for leaks prior to sampling, and the Orsat must be leak checked before and after analysis.

After taking the sample, remove the flexible bag to the analysis area and let it remain there for at least 30 min before analyzing with the Orsat. Analysis must be completed within 4 h of sampling. Perform the analysis according to the manufacturer's instructions and as outlined in Subsection 4.2.1. Repeat the analyses by drawing in new samples of CO_2 , O_2 , or CO from the bag until the following criteria are met:

For CO_2 - Repeat until any three analyses differ by $\leq 0.3\%$ (absolute) when CO_2 is $> 4.0\%$, or by $\leq 0.2\%$ (absolute) when CO_2 is $\leq 4.0\%$. Average the three acceptable readings, and report to the nearest 0.1%.

For O₂ - Repeat until any three analyses differ by $\leq 0.3\%$ when the O₂ is $\leq 15.0\%$, or by $\leq 0.2\%$ when the O₂ is $> 15.0\%$. Average the three acceptable readings and repeat to the nearest 0.1%.

For CO, if required - Repeat until any three results differ by $\leq 0.3\%$.

4.3 Special Precautions

The Orsat analyzer is a simple instrument, but the validity of results depends on operator technique, care, and patience. Special precautions for using an Orsat analyzer include:

1. Do not allow ambient air to enter the Orsat analyzer during testing.

2. Always perform the analysis in the following sequence: absorber No. 1 - CO₂, absorber No. 2 - O₂, and absorber No. 3 - CO. This sequence is necessary because absorber No. 2 will also absorb CO₂, and absorber No. 3 will absorb O₂ and possibly CO₂; double absorption will yield erroneous data.

3. Be sure to saturate the indicating solution in the burette with salt at the operating temperature to prevent absorption of sample gases prior to analysis. Be sure the solution is acidic (as indicated by methyl orange) to enable it to absorb any moisture in the sample gas.

4. Keep the absorber solution from entering the capillary column manifold. Void the test if any absorber solution enters the manifold, and clean the sample manifold with acetone.

5. Allow a minimum of 5 min for gas samples to come to temperature equilibrium with the water jacket before the analysis.

6. Operate the Orsat analyzer under constant temperature and pressure. Be sure that the levels of solutions in the burette and the leveling bottle are the same to ensure equal pressures before taking a reading from the Orsat. The water jacket acts as a buffer for temperature changes.

7. Measure SO₂ concentrations quantitatively (Method 6) if the source being tested is known to have or is suspected of

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having high SO₂ concentrations, and subtract the value from that of the CO₂ determination. Measure and correct the values when the SO₂ concentration is suspected to be $\geq 3\%$ (relative) of the CO₂ concentration and when the data are to be used to correct emission rates or to calculate gas flows. If the data are to be used for calculating just the molecular weight (M_d), then SO₂ interferences as high as 0.5% (absolute) or 5000 ppm are acceptable; this level of interference will result in an error of only about 0.1 g/g-mole (0.1 lb/lb-mole) in M_d .

Table 4.1 ACTIVITY MATRIX FOR ON-SITE MEASUREMENTS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Grab Sampling</u> Sampling train	No leaks	Visually check before each field test	Eliminate leaks before proceeding with test
Sampling points	At the centroid of the cross section or at a point >1 m (3.28 ft) from the walls	Not applicable	Not applicable
<u>Integrated Sampling</u> Locate sampling points	8-12 points; see Sub-sec 4.1.3	Not applicable	Not applicable
Flexible bag	No leaks	Check before each field test; see Sec 3.2.1	Replace as necessary
Train	No leaks; vacuum stable for >30 s	Pull vacuum of at least 250 mm (10 in.) Hg	Check all connections, replace items as necessary
Sampling rate	Constant rate	Check using Fig 4.2	Repeat sampling to meet 10% deviation limit
<u>Orsat Analyzer</u> Leak check	No leaks for 4 min	Varies with test method; mandatory for emission rate factor and excess air calculations; Sec 3.2.1	Check rubber connections and stopcocks until cause of leak is identified; leak check after repair and reassembly

(continued)

Table 4.1 (continued)

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Test Results</u> For M_d	M_d from each of three grab samples and analyses differ from their mean by <0.3 g/g mole (0.3 lb/lb mole)	For each field test, compare calculated M_d 's to their means	Repeat analysis, perhaps by another operator
For emission rate factor or excess air calculations	<ol style="list-style-type: none"> 1. Make repeated passes thru the absorbing solution until two consecutive readings are the same; compare three readings 2. Make repeated analyses; see Subsec 4.2.2 for criteria 	<ol style="list-style-type: none"> 1. Compare readings 2. Compare analyses of component gases 	<ol style="list-style-type: none"> 1. Replace absorbing solution 2. Repeat analyses by another operator; check the apparatus and technique

5.0 POSTSAMPLING OPERATIONS

Table 5.1 at the end of this section summarizes the quality assurance activities for the postsampling operations.

5.1 Compare Measured Values Against Theoretical Values

After the analyses have been performed and before the apparatus is disassembled, the measured and the theoretical results (if available) should be compared as a quick check for gross measurement errors.

Combustion nomographs are available for estimating the percentages by volumes of CO₂ and O₂ when the fuel composition is known.^{8,9} Also the nomograph can be used to calculate the molecular weight of the stack gas.

Perform the calculations on the measured data as directed in Section 3.2.6 and perform the following comparison:

$$D_{\text{CO}_2} = \% \text{CO}_2(\text{m}) - \% \text{CO}_2(\text{e})$$

where

D_{CO_2} = difference in measured and estimated values, %,

$\% \text{CO}_2(\text{m})$ = measured CO₂ (average of r replicates), %, and

$\% \text{CO}_2(\text{e})$ = estimated or theoretical CO₂, %.

Accept the measured value if D_{CO_2} is <2% (absolute); otherwise, check the apparatus, the technique, and the estimating procedures before collecting and analyzing more samples.

Record the estimated or theoretical values on a form similar to Figure 4.1. (Theoretical values may have been calculated and recorded before the field test if sufficient knowledge of the process was available.)

A second method to help eliminate gross errors is the use of the Fyrite sampler at several points during the test. This will indicate whether a problem does exist, but will not reveal which value is indeed correct.

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5.2 Disassemble and Inspect Apparatus

When disassembling the apparatus, visually inspect the sampling train components and the Orsat analyzer for damages that could have adversely affected the measured values. Any identified damage that was not detected during the test should be documented on the field data form and thoroughly evaluated by the appropriate apparatus check in the laboratory. After checking if it is concluded that the damage could have biased the measurements, a description of potential bias in the data should be included in the field test report. If possible, repeat the field test.

5.3 Pack Apparatus for Shipment to Laboratory

Pack the apparatus for shipment to the laboratory as described in Section 3.2.3. Return the data forms, prepared in duplicate, to the laboratory--one copy should be sent by mail, and one copy handcarried.

Table 5.1 ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Compare measured vs. estimated values of %CO ₂	%CO _{2(m)} - %CO _{2(e)} ≤2% (absolute) suggested	As suggested by administrator; e.g., for each incinerator test when an estimate of %CO ₂ is to be used to correct particulate emission levels	Repeat the analysis for additional samples
Disassemble and inspect apparatus	No damage that could have adversely affected the measurement	Visual inspection	Report damage and its possible bias on measurements to the administrator; use Fig 4.1
Pack apparatus for shipment	Follow specified packing instructions	After each field test	Not applicable



6.0 CALCULATIONS

Table 6.1 at the end of this section summarizes the quality assurance checks pertaining to calculations.

6.1 Excess Air

Use Equation 6-1 to calculate the percentage of excess air. Use the average value for each of the component gases, as follows:

$$\%EA = \left(\frac{\%O_2 - 0.5 \%CO}{0.264 \%N_2 (\%O_2 - 0.5 \%CO)} \right) 100 \quad \text{Equation 6-1}$$

where

$\%EA$ = percent excess air, %,

$\%O_2$ = percent O_2 by volume (dry basis), average of three O_2 values, %,

$\%CO$ = percent CO by volume (dry basis), average of three CO values, %,

$\%N_2$ = percent N_2 by volume (dry basis), average of three N_2 values, %, and

0.264 = ratio of O_2 to N_2 in air, v/v.

The average value for each of the gases is computed from the Orsat analyses satisfying the criteria in Section 3.2.4. Round each average to the nearest 0.1%. In many cases, $\%CO$ will be close to zero and can be dropped to simplify Equation 6-1. Equation 6-1 is applicable whenever most of the N_2 in the flue gas comes from N_2 in the combustion air, as is the case with most fuel and refuse combustion processes. If the fuel contains appreciable amounts of N_2 or if O_2 enrichment is used, Equation 6-1 cannot be used; alternate methods, subject to the approval by the administrator, are required.

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6.2 Dry Molecular Weight

Use Equation 6-2 to calculate the dry molecular weight from data in Figure 4.1--i.e., the average values of the component gases reported to the nearest 0.1%.

$$M_d = 0.44 (\%CO_2) + 0.32 (\%O_2) + 0.28 (\%N_2 + \%CO) \quad \text{Equation 6-2}$$

where

M_d = dry molecular weight, g/g-mole (lb/lb-mole),

$\%CO_2$ = percent CO_2 by volume (dry basis), average of three analyses, and

$\%O_2$, $\%N_2$, and $\%CO$ are previously defined.

Round M_d to the nearest 0.1, and record the value Figure 4.1.

6.3 Data Reporting

A copy of Figure 4.1 or an equivalent form should be filed in the laboratory log, and the original should be forwarded either to the home laboratory for further internal review or to the user. An independent check of the calculations should be performed, and the corrected values should be indicated on the form if the differences are more than the acceptable roundoff error. The checking analyst should initial the data form.

Table 6.1 ACTIVITY MATRIX FOR CALCULATIONS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Calculations	<p>1. Data form Fig 4.1 contains all data required for calculations of %EA, M_d, and emission rate factor</p> <p>2. Average concentrations calculated to the nearest 0.1%; final calculations rounded to nearest 0.1%</p> <p>3. Independent calculation agrees to the nearest 0.1%</p>	<p>1. Visual observation at each field test</p> <p>2. For each field test, compute the average concentration of three analyses that meet test requirements</p> <p>3. For each field test, repeat calculations starting with raw data</p> <p>4. Visual check</p>	<p>1. Obtain necessary data to complete the form</p> <p>2. Recalculate all results for which computations not consistent with procedure</p> <p>3. Report corrected values of the calculations in Fig 4.1</p> <p>4. Correct calculations</p>
Data reporting	Data report complete with indication of calculation check	Visual observation of each field test	Perform necessary calculation checks

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7.0 MAINTENANCE

Little periodic maintenance is required for the Orsat apparatus--other than visual checks of the glassware, tubes, and expansion bulbs. Keep the valves closed during storage, and avoid freezing temperatures. If the Orsat is to be stored over an extended period, it is generally better to remove all of the absorbing reagents. The flexible bags are generally subjected to extensive wear, and require repair or replacement when leaks occur. The pump and rotameter should be kept clean and should be maintained in accordance with manufacturers' instructions.

Table 7.1 ACTIVITY MATRIX FOR MAINTENANCE

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Glassware, connecting tubing, expansion bulbs	No damage	Visually check before each use	Replace if damaged
Flexible bags	As above	As above	Repair or replace as required
Pump and rotameter	Clean and maintained in accordance with manufacturer's instructions	According to manufacturer's instructions	Adjust/repair or request assistance of supplier

3 1 3

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. It is independent because it is conducted by personnel other than the field crew and by using apparatus and measurement standards that are different from those used by the regular field crew. In the field, routine quality assurance checks are necessary for obtaining good quality data from a series of test runs at one source, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance activities for auditing. Based on the results of collaborative tests, three performance audits and a systems audit are recommended in Subsections 8.1 and 8.2. Both types are to be conducted by auditors.

8.1 Performance Audits

Performance audits are quantitative evaluations of the quality of the data produced and recorded by the total measurement system (sample collection, sample analysis, and data processing). These audits should be conducted by the responsible control agency once during every enforcement source test, regardless of whether the test is conducted by a control agency or by a private company personnel. A source test for enforcement comprises a series of runs at one source.

8.1.1 Audit of M_d - Because the maximum relative error in M_d is approximately 4%, it is not practical to audit M_d unless directed by the administrator.

8.1.2 Audit of Analytical Phase Using Certified Gas Mixtures for Emission Rate Correction Factor and Excess Air Determination -

Analyzer operation and operator technique can be checked by providing audit samples of certified gas mixtures to be analyzed prior to or along with field samples. One sample should contain concentrations of 2-4% O_2 and 14-18% CO_2 , and another sample should contain concentrations of 2-4% CO_2 and about 15% O_2 .

2.75

These gas samples can be transferred from their pressurized storage containers to flexible bags and delivered to the test team on site by the auditor. Replicate samples of the audit gas containing O₂ and CO₂ concentrations similar to the concentrations expected during the test and one sample of the other audit gas should be sufficient for audit of the analytical phase.

The error of the analytical phase can be calculated using Equation 8-1, and should be ≤1.0% for CO₂ and O₂.

$$D = \overline{\%V_a} - \%V_c \qquad \text{Equation 8-1}$$

where

D = difference in the field test results and the certified audit value, %,

$\overline{\%V_a}$ = field team's value as the average of r replicates, %, and

$\%V_c$ = certified value of audit gas, %.

The emission rate correction factor is not directly proportional to the Orsat analyzer error. Therefore, the standard calculation of %D is not applicable. The results of the calculated %D should be included in the enforcement source test report as an assessment of accuracy of the analytical phase of Method 3 during the actual enforcement source test.

8.1.3 Audit of Data Processing - Data processing errors can be detected by auditing the data recorded on the field and the laboratory forms. The original and the field check calculations should agree; if not, all of the remaining data should be rechecked by the auditor, and any errors should be clearly explained to the team to prevent or minimize reoccurrence. The data processing errors may also be detected in copies of data sets compiled and filed in the field and in copies of manual data reductions (or computer printouts, if used) forwarded to the evaluator for audit. Calculation errors are prevalent among users of Method 3.

8.2 Systems Audit

A systems audit is an on-site qualitative inspection and review of the quality assurance checks used by the team for the total measurement system (sample collection, sample analysis, data processing, etc.). Initially, a systems audit specified by a quality assurance coordinator should be conducted for each enforcement source test, which by definition comprises three runs at one source. After the team gains experience with the procedure, the frequency of audit may be reduced, for example, to once for every four tests. The auditor should have extensive experience in source sampling--more specifically, with the characterization technique being audited.

The functions of the auditor are summarized as follows:

1. Observe procedures and techniques of the field team during sample collection.
2. Check/verify the records of apparatus calibration and the quality control charts used in the laboratory analysis.
3. Record the results of the audit and forward them with comments on source team management to the quality assurance coordinator so that any needed corrective actions may be implemented.

8.2.1 Collecting On-Site Information - While on-site, the auditor should observe the field team's overall performance of the source test. Specific operations to observe should include, but not be limited to:

1. Setting up and leak testing the sampling train.
2. Purging the sampling train with stack gas prior to collecting the sample.
3. Proportional sampling.
4. Transferring of the sample from the collapsible bag to the Orsat analyzer.

Table 8.1 is a suggested form for use by the auditor.

8.2.2 Collecting Laboratory Information - When visiting the field team's home laboratory, the auditor should check the records to verify that the performance criteria in Table 4.3 (Section 3.2.4) have been met since the last audit was performed.

		OPERATION
Yes	No	
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<p>Presampling Operation</p> <ol style="list-style-type: none"> 1. Availability of theoretical value 2. Use of modified Orsat analyzer (0.1-ml divisions)
<input checked="" type="checkbox"/>	<input type="checkbox"/>	<p>On-Site Measurements</p> <ol style="list-style-type: none"> 3. Setting up and leak testing the sampling train 4. Purging the sampling train with stack gas prior to collecting the sample 5. Constant rate sampling 6. Transfer of sample from collapsible bag to the Orsat analyzer 7. Maintaining constant pressure throughout the test 8. Exposing the sample to ambient air 9. Spent absorbing reagent
<input checked="" type="checkbox"/>	<input type="checkbox"/>	<p>Postsampling Measurements</p> <ol style="list-style-type: none"> 10. Perform independent calculations using data from audit 11. Compare the audit value with the field team's test value 12. Make sufficient passes for complete absorption of a component gas 13. Minimize volumetric reading error 14. Check/verify applicable records of apparatus calibration checks and quality control charts in the field team's home laboratory
General Comments		

Figure 8.1 Checklist for Method 3 for use by the auditor.

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Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURES

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical audit	$D = \overline{\%V}_a - \%V_c$ $\overline{\%V}_a = \text{mean value of measurements by field team}$ $\%V_c = \text{certified value of audit gas}$	As designated by the administrator	Advise team of sources of errors, and request they seek additional training; rerun test if necessary for determination of compliance
Data processing audit	Agreement of original and check calculations	Once during each enforcement source test; independent calculations starting with raw data	Check and correct all data
Systems audit	Technique described in this section	Once during each enforcement test until experience gained, then every fourth test; observe techniques; use audit checklist Fig 8.1	Explain to team the deviations from recommended techniques, and note deviations on Fig 8.1

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9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To acquire data of good quality, two considerations are essential: (1) the measurement process must be in a state of statistical control at the time of the measurement, and (2) the systematic errors combined with the random variations (errors of measurement) must result in an acceptable level of uncertainty. As evidence of good quality, it is necessary to perform quality control checks and independent audits of the measurement process, to use materials and measurement procedures which can be traced to an appropriate reference standard, and to document data from the checks and audits (e.g., by means of a quality control chart).

Data must be routinely obtained by repeat measurements of standard reference samples, primary, secondary, and/or working standards. The working calibration standards should be traceable to either primary or higher order standards.

In the case of absorption type gas analyzers, operator techniques and analyzer operations can be checked by sampling two certified mixtures of bottled gas containing 2-4% O₂ and 14-18% CO₂, or 2-4% CO₂ and about 15% O₂. Bottled gases used for audit purposes should be traceable to NBS standards.

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10.0 REFERENCE METHOD ^a

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 (CO₂), percent oxygen (O₂), and, if necessary, percent carbon monoxide (CO). If a dry molecular weight determination is to be made, either an Orsat or a Fyrite¹ analyzer may be used for the analysis. For excess air or emission rate correction factor determination, an Orsat analyzer must be used.

1.2 Applicability. This method is applicable for determining CO₂ and O₂ concentrations, excess air, and dry molecular weight of 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 components other than CO₂, O₂, CO, and nitrogen (N₂) are not present in concentrations sufficient to affect the results.

Other methods, as well as modifications to the procedure described herein, are also applicable for some or 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; (2) a method using CO₂ or O₂ 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 Administrator.

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 Administrator.

2.1 Grab Sampling (Figure 3-1).

2.1.1 Probe. The probe should be made of stainless 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 O₂, CO₂, CO, and N₂ and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

2.1.2 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 described in Section 2.1.1 is suitable.

¹ Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser that will not remove O₂, CO₂, CO, and N₂ 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 flow meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.2.5 Rate Meter. The 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 cm³/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 65 to 90 liters is suggested.

Toleak-check the bag, connect it to a watermanometer and pressurize the bag to 5 to 10 cm H₂O (2 to 4 in. H₂O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to 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.

2.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 28 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 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 CO₂ (less than 40 percent) or high O₂ (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 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. 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. 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 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 2.0 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 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 5 liters (1.0 ft³) of sample gas is recommended; however, smaller volumes may be collected, if desired.

3.2.4 Obtain one integrated line gas sample during each pollutant emission rate determination. Within 5 hours after the sample is taken, analyze it for percent CO₂ and percent O₂ 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 N₂ and CO by subtracting the sum of the percent CO₂ and percent O₂

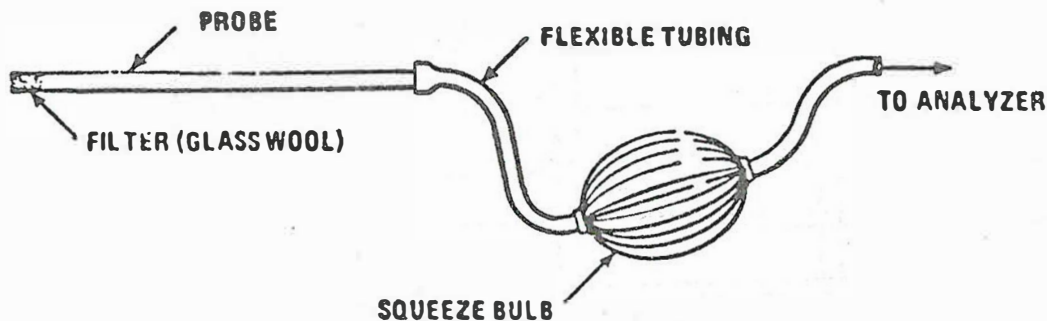


Figure 3-1. Grab-sampling train.

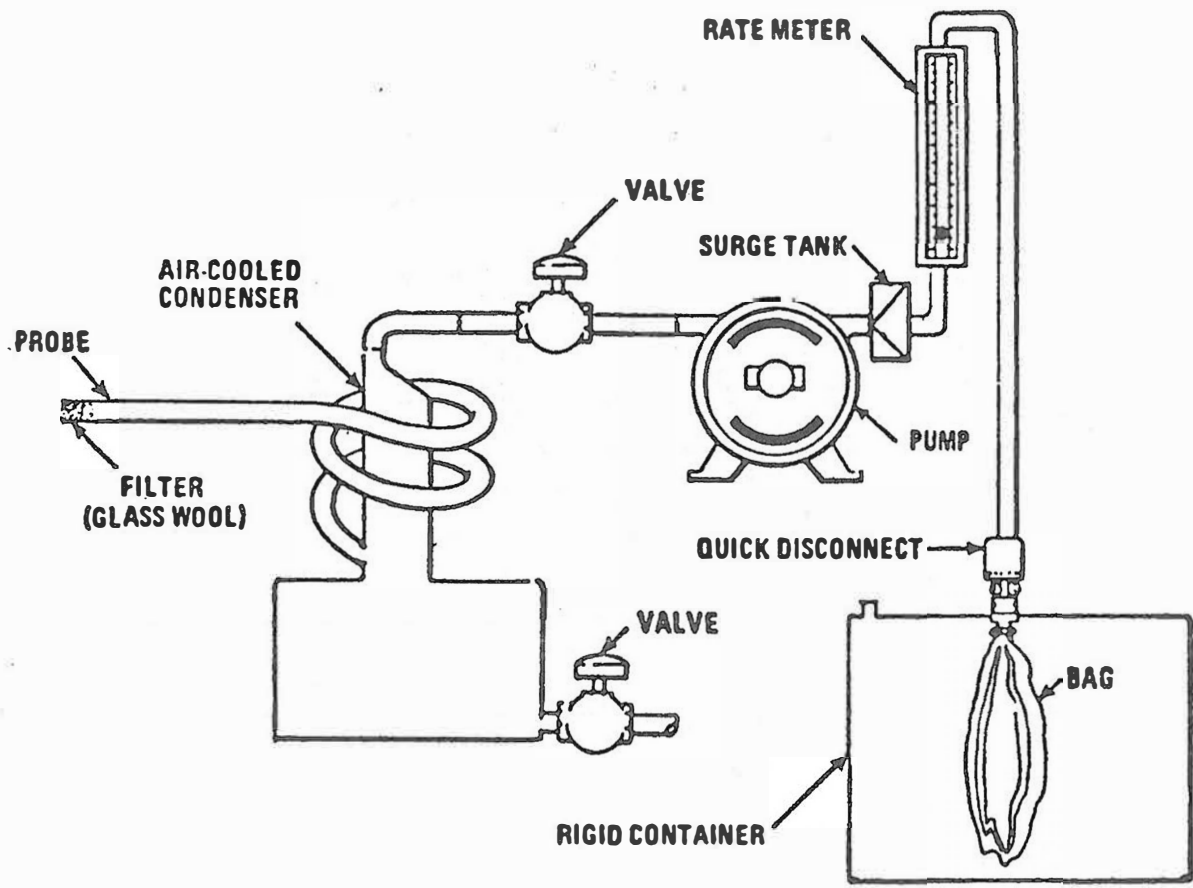


Figure 3-2. Integrated gas-sampling train.

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 3-3. Sampling rate data.

from 100 percent. Calculate the dry molecular weight as indicated in Section 5.3.

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 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 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 Administrator.

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 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.

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.

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 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

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 5. 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. Draw a sample into the analyzer. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO₂ or percent O₂. 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 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 6.2.

4.1.4 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.

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 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 that Citation 5 in the Bibliography 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 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 30 liters (100 ft³) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

4.2.4 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 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 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; (3) calculate percent excess air, as outlined in Section 6.2.

4.2.5 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.

4.2.6 Repeat the analysis until the following criteria are met:

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

4.2.6.2 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 15.0 percent. Average the three acceptable values of percent O₂ 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 percent. 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 (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.—Although in most instances only CO₂ or O₂ is required, it is recommended that both CO₂ and O₂ be measured, and that Citation 5 in the Bibliography 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 than specified is subject to the approval of the Administrator.

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.

5. Leak-Check Procedure for Orsat Analyzers

Moving an Orsat analyzer frequently causes a 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:

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

5.1.2 Raise the leveling bulb sufficiently to bring the containing 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, all rubber connections and stopcocks 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, the leak-check procedure must be repeated.

6. Calculations

6.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

%EA = Percent excess air.

%CO₂ = Percent CO₂ by volume (dry basis).

%O₂ = Percent O₂ by volume (dry basis).

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

%N₂ = Percent N₂ by volume (dry basis).

0.264 = Ratio of O₂ to N₂ in air, v/v.

0.280 = Molecular weight of N₂ or CO, divided by 100.

0.320 = Molecular weight of O₂ divided by 100.

0.440 = Molecular weight of CO₂ divided by 100.

6.2 Percent Excess Air. Calculate the percent excess air (if applicable), by substituting the appropriate values of percent O₂, CO₂, and N₂ into Equation 3-1.

$$\%EA = \left[\frac{\%CO_2 - 0.5\%CO}{0.264\%N_2 - \%O_2 - 0.5\%CO} \right] 100$$

Equation 3-1

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 gas (e.g., 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), alternate methods, subject to approval of the Administrator, are required.

6.3 Dry Molecular Weight. Use Equation 3-2 to calculate the dry molecular weight of the stack gas.

$$M_d = (0.10\%CO + 0.32\%O_2 + 0.28\%N_2 + \%CO_2)$$

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 opt to include argon in the analysis using procedures subject to approval of the Administrator.

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2. Mitchell, William J. On-Site Collaborative Test of Method 3 of the New Source Performance Standards Using Modified Orsat Apparatus. Environmental Protection Agency, Research Triangle Park, N.C., November 1973.
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4. Hamil, H. F. and R. E. Thomas, Collaborative Study of Method for Stack Gas Analysis and Determination of Moisture Fraction with Use of Method 5. Southwest Research Institute. EPA-650/4-74-026, June 1974.
5. Hamil, H. F. and R. E. Thomas, Collaborative Study of Particulate Emissions Measurements by EPA Methods 2, 3, and 5 Using Paired Particulate Sampling Trains. Southwest Research Institute. EPA-600/4-76-014, March 1976.
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7. Burrell Manual for Gas Analysts. 7th Ed. Burrell Corp. Pittsburgh, Penn., 1951.
8. Shigehara, R. T., et al. Validating Orsat Analysis Data from Fossil Fuel-Fired Units. Stack Sampling News 4(2):21-26, August 1976.
9. Steam Its Generation and Use. 37th Ed. Babcock & Wilcox Co., N.Y. 1963. pp. 4-11 and 4-12.
10. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles. EPA-600/9-76-005, Environmental Protection Agency, Research Triangle Park, N. C. March 1976.

12.0 DATA FORMS

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page. However, the section-page documentation in the top right-hand corner of each page of other sections has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section. For example, Form M3-1.3 indicates that the form is Figure 1.3 in Section 3.2.1 of the Method 3 Handbook. Future revisions of these forms, if any, can be documented by 1.3A, 1.3B, etc. Five of the blank forms listed below are included in this section. Two are in the Methods Highlights Section as shown by the MH following the form number.

<u>Form</u>	<u>Title</u>
1.3	Procurement Log
2.1	\bar{X} and R Chart
3.1 (MH)	Pretest Preparations
4.1 (MH)	On-Site Measurements Checklist
4.2	Gas Analysis Data Form
4.3	Integrated Bag Sampling Data Form
8.1	Checklist for Method 3 for Use by the Auditor

9.5

PROCUREMENT LOG

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			

X̄ AND R CHART

PROJECT NAME	MEASUREMENT PERFORMED	MEASUREMENT UNITS
DATE		
MEASUREMENT RESULT CODE	1	
	2	
	3	
MEASUREMENT RESULT	1	
	2	
	3	
SUM		
AVERAGE, \bar{X}		
RANGE, R		
AVERAGES, \bar{X}		
RANGES, R		
Comments (Correct Action, etc.)		

1/19/80

GAS ANALYSIS DATA FORM

PLANT _____ COMMENTS: _____
 DATE _____ TEST NO _____
 SAMPLING TIME (24-hr CLOCK) _____
 SAMPLING LOCATION _____
 SAMPLE TYPE (BAG, INTEGRATED, CONTINUOUS) _____
 ANALYTICAL METHOD _____
 AMBIENT TEMPERATURE _____
 OPERATOR _____

RUN GAS	1		2		3		AVERAGE NET VOLUME	MULTIPLIER	MOLECULAR WEIGHT OF STACK GAS (DRY BASIS) M _d
	ACTUAL READING	NET	ACTUAL READING	NET	ACTUAL READING	NET			
CO ₂								44/100	
O ₂ (NET IS ACTUAL O ₂ READING MINUS ACTUAL CO ₂ READING)								32/100	
CO (NET IS ACTUAL CO READING MINUS ACTUAL O ₂ READING)								28/100	
N ₂ (NET IS 100 MINUS ACTUAL CO READING)								28/100	
TOTAL									



CHECKLIST FOR METHOD 3 FOR USE BY THE AUDITOR

		OPERATION
Yes	No	
		Presampling Operation
— —	— —	1. Availability of theoretical value 2. Use of modified Orsat analyzer (0.1-ml divisions)
		On-Site Measurements
— — — — — — —	— — — — — — —	3. Setting up and leak testing the sampling train 4. Purging the sampling train with stack gas prior to collecting the sample 5. Constant rate sampling 6. Transfer of sample from collapsible bag to the Orsat analyzer 7. Maintaining constant pressure throughout the test 8. Exposing the sample to ambient air 9. Spent absorbing reagent
		Postsampling Measurements
— — — — —	— — — — —	10. Perform independent calculations using data from audit 11. Compare the audit value with the field team's test value 12. Make sufficient passes for complete absorption of a component gas 13. Minimize volumetric reading error 14. Check/verify applicable records of apparatus calibration checks and quality control charts in the field team's home laboratory
General Comments		

