

**State of California
Air Resources Board**

METHOD 4

Determination of Moisture Content in Stack Gases

**Adopted June 29, 1983
Amended: July 1, 1999**

METHOD 4

Determination of Moisture Content in Stack Gases

1 Principle and Applicability

1.1 Principle

A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

1.2 Applicability

This method is applicable for determining the moisture content of stack gas.

1.2.1

Two procedures are given. The first is a reference method, for accurate determinations of moisture content (such as are needed to calculate emission data). The second is an approximation method, which provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content, e.g., drying tubes, wet bulb - dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc., are also acceptable.

1.2.2

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon results of the approximation method, unless the approximation method is shown, to the satisfaction of the Executive Officer, to be capable of yielding results within 1 percent H₂O of the reference method. Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

1.2.3

NOTE: The reference method may yield questionable results when applied to saturated gas streams or to streams that contain water droplets. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to $\pm 1^{\circ}\text{C}$ (2°F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see Section 2.2.1) during the reference method traverse; calculate the average stack gas temperature. Next, determine

the moisture percentage, either by: (1) using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternate methods, subject to the approval of the Executive Officer, shall be used.

2 Reference Method

The procedure described in Method 5 for determining moisture content is acceptable as a reference method.

2.1 Apparatus

A schematic of the sampling train used in this reference method is shown in Figure 4-1. All components shall be maintained and calibrated according to the procedure outlined in Method 5.

2.1.1 Probe

Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (e.g., a plug of glass wool inserted into the end of the probe) or heated out-stack (e.g., as described in Method 5) to remove particulate matter.

When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Executive Officer.

2.1.2 Condenser

See ARB Method 5 Section 2.1.7, *Almpinger Train®*, for a description of an acceptable type of condenser and for alternative measurement systems.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump, to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.3 Cooling System

An ice bath container and crushed ice (or equivalent), to aid in condensing moisture.

2.1.4 Metering System

Same as in ARB Method 5, Section 2.1.8, *AMetering System®*, except do not use sampling systems designed for flow rates higher than 0.0283 m³/min (1.0 cfm). Other metering systems, capable of maintaining a constant sampling rate to

within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Executive Officer.

2.1.5 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg may be used. See note in ARB Method 5, Section 2.1.9, ABarometer®, regarding weather station readings and elevation adjustments.

2.1.6 Graduated Cylinder and/or Balance

To measure condensed water and moisture caught in the silica gel to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. These balances are suitable for use here.

2.2 Procedure

The following procedure is written for a condenser system (such as the impinger system described in ARB Method 5 Section 2.1.7, AImpinger Train®) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1

Unless otherwise specified by the Executive Officer, 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 points 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 in all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Executive Officer. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Place known volumes of water in the first two impingers. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

2.2.2

Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected at a rate no greater than 0.021 m³/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

2.2.3

Set up the sampling train as shown in Figure 4-1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of about 120°C (248°F), to prevent water condensation ahead of the condenser; allow time for the temperature to stabilize. Place crushed ice in the ice bath container. It is recommended but not required that a leak check be done as follows: disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder) and pull a 380 mm (15 in.) Hg vacuum; a lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

2.2.4

During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Executive Officer. For each run, record the data required on the example data sheet shown in Figure 4-2. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point, at least once during each time increment.

2.2.5

To begin sampling, position the probe tip at the first traverse point. Immediately start the pump and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the silica gel outlet.

2.2.6

After collecting the sample, disconnect the probe from the filter holder (or from the first impinger) and conduct a leak check (mandatory) as described in Section 2.2.3. Record the leak rate. If the leakage rate exceeds the allowable rate, the tester shall either reject the test results or shall correct the sample volume as in Section 6.3 of Method 5. Next, measure the volume of the moisture condensed to the nearest ml. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4-3) and calculate the moisture percentage, as described in 2.3 below.

2.2.7

A quality control check of the volume metering system at the field site is suggested before collecting the first sample, following the procedure in ARB Method 5, Section 4.4, *Quality Control Procedures*.

2.3 Calculations

Carry out the following calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

2.3.1 Nomenclature

B_{ws}	=	Proportion of water vapor, by volume, in the gas stream.
M_w	=	Molecular weight of water, 18.0 g/g mole (18.0 lb/lb-mole).
P_m	=	Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in Hg).
P_{std}	=	Standard absolute pressure, 760 mm Hg (29.92 in Hg).
R	=	Ideal gas constant, 0.06236 (mm Hg) (m ³)/(g-mole) (°K) for metric units and 21.85 (in Hg) (ft ³)/(lb-mole) (°R) for English units.
T_m	=	Absolute temperature at meter. °K (°R).
T_{std}	=	Standard absolute temperature, 293°K (528°R).
V_m	=	Dry gas volume measured by the dry gas meter, dcm (dcf).
ΔV_m	=	Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).
$V_{m(std)}$	=	Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$	=	Volume of water vapor condensed, corrected to standard conditions, scm (scf).
$V_{wsg(std)}$	=	Volume of water vapor collected in silica gel corrected to standard conditions, scm (scf).
V_f	=	Final volume of condenser water, ml.
V_i	=	Initial volume, if any, of condenser water, ml.
W_f	=	Final weight of silica gel plus impinger, g.
W_i	=	Initial weight of silica gel plus impinger, g.
Y	=	Dry gas meter calibration factor.
ρ_w	=	Density of water, 0.9982 g/ml (0.002201 lb/ml).

2.3.2 Volume of Water Vapor Condensed

$$\begin{aligned}V_{wc(std)} &= (V_f - V_i) \rho_w R T_{std} / (P_{std} M_w) \\ &= K_1 (V_f - V_i)\end{aligned}\quad \text{Equation 4-1}$$

where:

$$\begin{aligned}K_1 &= 0.001333 \text{ m}^3/\text{ml} \text{ for metric units} \\ &= 0.04707 \text{ ft}^3/\text{ml} \text{ for English units}\end{aligned}$$

2.3.3 Volume of Water Vapor Collected in Silica Gel

$$\begin{aligned}V_{wsg(std)} &= (W_f - W_i) R T_{std} / (P_{std} M_w) \\ &= K_2 (W_f - W_i)\end{aligned}\quad \text{Equation 4-2}$$

where:

$$\begin{aligned}K_2 &= 0.001335 \text{ m}^3/\text{g} \text{ for metric units} \\ &= 0.04715 \text{ ft}^3/\text{g} \text{ for English units}\end{aligned}$$

2.3.4 Sample Gas Volume

$$\begin{aligned}V_{m(std)} &= V_m Y P_m T_{std} / (P_{std} T_m) \\ &= K_3 Y V_m P_m / T_m\end{aligned}\quad \text{Equation 4-3}$$

where:

$$\begin{aligned}K_3 &= 0.3858 \text{ }^\circ\text{K}/\text{mm Hg} \text{ for metric units} \\ &= 17.65 \text{ }^\circ\text{R}/\text{in. Hg} \text{ for English units}\end{aligned}$$

NOTE: If the post-test leak rate (Section 2.2.6) exceeds the allowable rate, correct the value of V_m in Equation 4-3, as described in Section 6.3 of Method 5.

2.3.5 Moisture Content

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}}\quad \text{Equation 4-4}$$

NOTE: In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see Section 1.2), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

2.3.6 Verification of Constant Sampling Rate

For each time increment, determine the ΔV_m . Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

3 Approximation Method

The approximation method described below is presented only as a suggested method (see Section 1.2).

3.1 Apparatus

See Figure 4-4.

3.1.1 Probe

Stainless steel or glass tubing, sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter. A plug of glass wool, inserted into the end of the probe, is a satisfactory filter.

3.1.2 Impingers

Two midjet impingers, each with 30 ml. capacity, or equivalent.

3.1.3 Ice Bath

Container and ice, to aid in condensing moisture in impingers.

3.1.4 Drying Tube

Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

3.1.5 Valve

Needle valve, to regulate the sample gas flow rate.

3.1.6 Pump

Leak-free, diaphragm-type, or equivalent to pull the gas sample through the train.

3.1.7 Volume Meter

Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, and calibrated over the range of flow rates and conditions actually encountered during sampling.

3.1.8 Rate Meter

Rotameter to measure the flow range from 0 to 3 lpm (0 to 0.11 cfm).

3.1.9 Graduated Cylinder

25 ml.

3.1.10 Barometer

Mercury, aneroid, or other barometer, as described in Section 2.1.5 above.

3.1.11 Vacuum Gauge

At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling leak check.

3.2 Procedure

3.2.1

Place exactly 5 ml water in each impinger. Leak-check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet; then, plug the probe inlet and pull a vacuum of at least 250 mm Hg (10 in Hg). Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0-40 cc/min.) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

3.2.2

Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft³) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

3.2.3

After collecting the sample, combine the contents of the two impingers and measure the volume to the nearest 0.5 ml.

3.3 Calculations

The calculation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content, for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature

B_{wm}	=	Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws}	=	Water vapor in the gas stream, proportion by volume.
M_w	=	Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m	=	Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
P_{std}	=	Standard absolute pressure, 760 mm Hg (29.92 in Hg).
R	=	Ideal gas constant, [0.06236 (mm Hg) (m ³)] / [(g-mole) (°K)] for metric units and [21.85 (in Hg) (ft ³)] / [lb-mole (°R)] for English units.
T_m	=	Absolute temperature at meter, °K (°R).
T_{std}	=	Standard absolute temperature, 293°K (528°R).
V_f	=	Final volume of impinger contents, ml.
V_i	=	Initial volume of impinger contents, ml.
V_m	=	Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$	=	Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$	=	Volume of water vapor condensed, corrected to standard conditions, scm (scf).
Y	=	Dry gas meter calibration factor.
ρ_w	=	Density of water, 0.9982 g/ml (0.002201 lb/ml).

3.3.2 Volume of Water Vapor Collected

$$\begin{aligned} V_{wc(std)} &= (V_f - V_i) \rho_w R T_{(std)} / (P_{std} M_w) \\ &= K_1 (V_f - V_i) \end{aligned} \quad \text{Equation 4-5}$$

where:

$$K_1 = 0.001333 \text{ m}^3/\text{ml} \text{ for metric units}$$

$$= 0.04707 \text{ ft}^3/\text{ml} \text{ for English units}$$

3.3.3 Gas Volume

$$V_{m(\text{std})} = V_m Y (P_m T_{\text{std}}) / (P_{\text{std}} T_m)$$

$$= K_2 V_m Y P_m / T_m$$
Equation 4-6

where:

$$K_2 = 0.3858 \text{ }^\circ\text{K/mm Hg} \text{ for metric units}$$

$$= 17.65 \text{ }^\circ\text{R/in. Hg} \text{ for English units}$$

3.3.4 Approximate Moisture Content

$$B_{ws} = \frac{V_{wc(\text{std})}}{V_{wc(\text{std})} + V_{m(\text{std})}} + B_{wm} = \frac{V_{wc(\text{std})}}{V_{wc(\text{std})} + V_{m(\text{std})}} + (0.025)$$
Equation 4-7

4 Calibration

4.1

For the reference method, calibrate the metering system, temperature gauges, and barometer as specified in the following sections of ARB Method 5 respectively: Section 5.3, *Metering System*, Section 5.5, *Temperature Gauges*, and Section 5.7, *Barometer*. The recommended leak check of the metering system (Section 5.6 of Method 5) also applies to the reference method. For the approximation method, use the procedures outlined in Section 5.1.1, *Initial Calibration*, of ARB Method 6 to calibrate the metering system, and the procedure of ARB Method 5, Section 5.7, *Barometer*, to calibrate the barometer.

5 Bibliography

1. EPA Method 4, Determination of Moisture Content in Stack Gases, CFR40, Part 60, Appendix A
2. ARB Method 5, Determination of Particulate Matter Emissions from Stationary Sources
3. ARB Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources

Figure 4-1 Moisture Sampling Train (Reference Method)

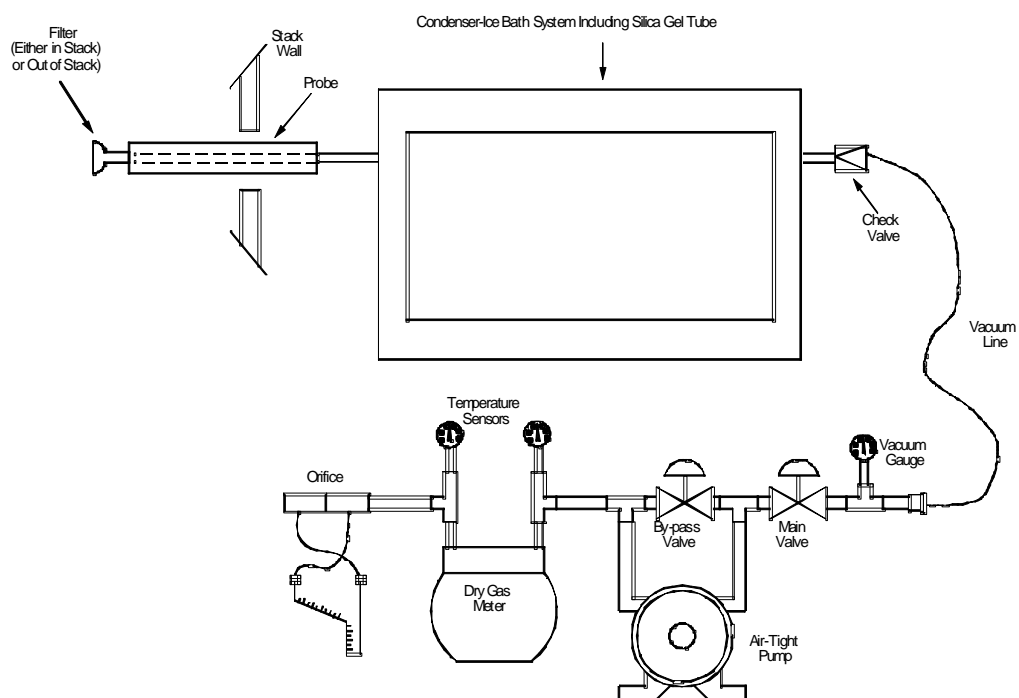


Figure 4-2. Field Moisture Determination Reference Method.

Plant _____
Location _____
Operator _____
Date _____
Run No. _____
Ambient Temperature _____
Barometric pressure _____
Probe Length _____

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Sampling Time (θ), min	Stack Temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H ₂ O	Meter Reading gas sample volume m ³ (ft ³)	ΔV _m m ³ (ft ³)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C(°F)
						Inlet T _{m_{in}} °C(°F)	Outlet T _{m_{out}} °C(°F)	
Average								

Figure 4-3 Analytical Data - reference method

	Impinger volume, ml	Silica gel weight, g
Final	_____	_____
Initial	_____	_____
Difference	_____	_____

FIGURE 4-4 Moisture Sampling Train - approximation method

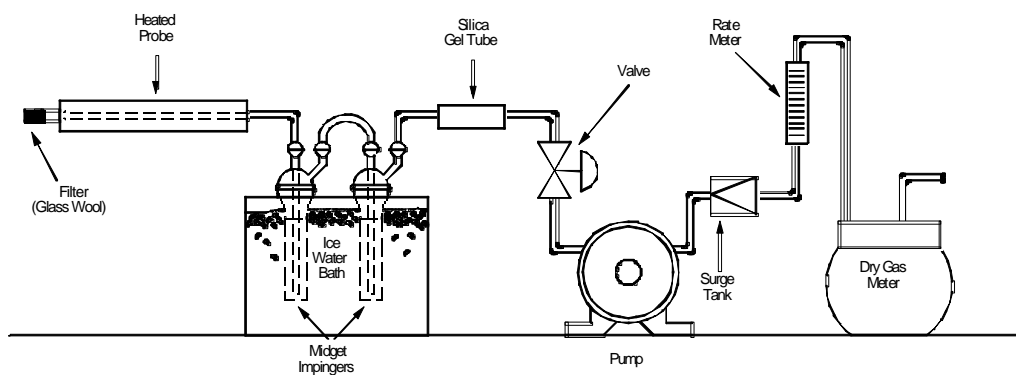


Figure 4-5 Field Moisture Determination - Approximation Method

Location _____ Comments: _____

Test _____

Date _____

Operator _____

Barometric pressure _____

Clock Time	Gas volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature $^{\circ}C$ ($^{\circ}F$)