

DETERMINING F-FACTORS FROM GAS CHROMATOGRAPHIC ANALYSES

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INTRODUCTION

EPA Method 19 provides equations for calculating F-factors for determining particulate matter (PM), sulfur dioxide (SO₂), and nitrogen oxides (NO_x) emission rates in mass per unit calorific value, i.e., in pounds per million Btu (lb/mmBtu). Gaseous fuels (e.g., natural gas, coke oven gases, refinery gases, landfill gases, etc), however, are commonly analyzed by gas chromatography (GC) and the composition is given as mole or volume percent of the individual compounds. Therefore, to use the equations in Method 19, the gas analysis must first be converted to weight percent.

In addition, a commonly accepted idea about the equations in Method 19 is that the calculated F-factors are at 70°F, rather than at 68°F, which is the EPA standard condition for temperature.¹ Therefore, after using the equations in Method 19, the F-factors are often multiplied by the temperature ratio of 528/530 to obtain the F-factors at 68°F. However, a re-calculation of the conversion factors shows that the present conversion factors give F-factors close to the standard temperature condition of 68°F, depending on the amount of hydrogen in the fuel.

Presented below are the methodology used to calculate F-factors directly from GC analysis, the derivation of factors used in the calculations, and derivations of the conversion factors used in the Method 19 equations. All F-factors are at 29.92 in. Hg (760 mm Hg, 14.696 psia) and 68°F (20°C). Using the methodology and conversion factors, spreadsheets can easily be established to run the calculations. A spreadsheet may be downloaded from the Emission Monitoring Inc.'s website at <http://www.emissionmonitoring.com>.

DERIVATION OF CONVERSION FACTORS FOR F-FACTOR CALCULATIONS

Standard Conditions, Conversion Factors, and Assumptions

In deriving the conversion factors, several conditions and reference conversion factors must be established. Those used in this paper are as follows:

1. Standard conditions are 29.92 in. Hg (760 mm Hg, 14.696 psia) and 68°F (20°C).
2. The composition of air is assumed to be 20.9% oxygen and 71.9% nitrogen. Therefore, the amount of N₂ associated with O₂ is 71.9/20.9 O₂.
3. The value used to convert to the absolute temperature scale is 460°F. Although the exact value is 459.69, the former value, i.e., 460°F, is commonly used in the field to convert to the absolute scales. The errors introduced are quite small. For example, the conversion factor to standard conditions would be 528/29.92 = 17.647 vs. 527.69/29.92 = 17.637. If a volume of gas at 100°F is adjusted to standard conditions using 17.637 and 528, rather than 527.69, the error introduced would be (460+100)/(459.69+100) = 1.00055 or 0.055% error. By using 460°F in both the conversion factor to standard conditions (i.e., 17.647) and in the field, no error is introduced.
4. The molar volume is 22.414 liters at 32°F and standard pressure. Using the conversion factors of 1 lb = 453.59237 g and 1 cf = 28.317 liters, the molar volume in cubic feet at the standard conditions of 68°F and 29.92 in. Hg is 22.414 *(528/492)*453.59237/28.317 = 385.3068 cf.
5. The following molecular weights are used: H₂ = 2.01588; O₂ = 31.9988; N₂ = 28.0134; C = 12.01115; S = 32.064; H₂O = 18.01528.

Derivation of Conversion Factors

When fossil fuels are burned with theoretical air, the resulting components are carbon dioxide, water, and nitrogen. Sulfur dioxide, if present, is also a product. To determine the volume of combustion gases per cubic of fuel burned, stoichiometric calculations are used. The amount can be calculated as follows:

- Moles of carbon dioxide = number of carbon atoms (C) in the component.
- Moles of water (W) = number of hydrogen atoms (H) divided by two.
- Moles of oxygen (Ox) required for stoichiometric combustion = $C + H/4 - O_c/2$, where O_c is the number of oxygen atoms in the compound being burned.
- Moles of nitrogen (N) in the combustion gases = $79.1/20.9 * O_x$.

Example 1: $C_2H_6 + 3.5O_2 = 2 CO_2 + 3 H_2O$

$$\begin{aligned} C &= 2 & W &= 6/2 = 3 & O_x &= 2 + 6/4 - 0/2 = 3.5 \\ N &= 79.1/20.9 * 3.5 = 13.246 \end{aligned}$$

$$\begin{aligned} \text{Dry effluent (DE)} &= C + N = 2 + 13.246 = 15.246 \text{ dscf/scf of } C_2H_6 \\ \text{Wet effluent (WE)} &= DE + W = 15.246 + 3 = 18.246 \text{ wscf/scf of } C_2H_6 \\ \text{Carbon dioxide (CE)} &= C = 2 \text{ scf/scf of } C_2H_6 \end{aligned}$$

Example 2: $CH_3OH + 1.5 O_2 = CO_2 + 2 H_2O$

$$\begin{aligned} C &= 1 & W &= 4/2 = 2 & O_x &= 1 + 4/4 - 1/2 = 1.5 \\ N &= 79.1/20.9 * 1.5 = 5.677 \end{aligned}$$

$$\begin{aligned} DE &= C + N = 1 + 5.677 = 6.677 \text{ dscf/scf of } CH_3OH \\ WE &= DE + W = 6.677 + 2 = 8.677 \text{ wscf/scf of } CH_3OH \\ CE &= C = 1 \text{ scf/scf of } CH_3OH \end{aligned}$$

Table 1 contains selected conversion factors for common components of gaseous fuels. Table 2 presents conversion factors for a few more compounds. For other compounds, the methodology provided can be used to calculate the conversion factors.

Determination of F-Factors

To determine the F-factors, DE, WE, and CE are divided by the high heating value (HHV) of the component. When selecting the HHV for each component, care must be taken to ascertain the base conditions for the HHV. In most cases, the base conditions are 60°F and 14.696 psia. In some cases, the HHV is reported at 60°F and 14.73 psia. In the latter cases, the values must be adjusted to the standard conditions of 60°F and 14.696 psia by using the pressure ratio 14.696/14.73. Then, the HHV at 60°F must be adjusted to 68°F by using the temperature ratio 520/528.

Example: For ethane, the HHV is 1769.7 Btu/cf at 60°F and 14.696 psia. To convert this value to standard conditions, i.e., 68°F and 29.92 in. Hg (14.696 psia), HHV must be multiplied by the factor 520/528. Using the effluent volumes from Example 1 above (DE = 15.246; WE = 18.246, and CE = 2), the F-factors for ethane would be as follows:

$$\begin{aligned} F_d &= 15.246/1769.7 * 528/520 * 10^6 = 8,748 \text{ dscf/mmBtu} \\ F_w &= 18.246/1769.7 * 528/520 * 10^6 = 10,469 \text{ wscf/mmBtu} \\ F_c &= 2/1769.7 * 528/520 * 10^6 = 1,148 \text{ scf/mmBtu} \end{aligned}$$

In addition to the conversion factors, Tables 1 and 2 contain HHVs for selected compounds. HHVs for a multitude of compounds are available from the GPA Standard 2145-96, Gas Processors Association, 6526 East 60th, Tulsa, OK 74145.^{2,3}

Table of Conversion Factors for Gaseous Components and Example Calculation

In addition to containing selected conversion factors and HHVs for common components of gaseous, Table 1 presents an example calculation for a fuel gas composition (shown in Column E). To calculate the HHV for a mixture of compounds, the HHVs, DEs, WEs, and CEs must be weighted according to the volume fraction (Columns F, G, H, and J, respectively). Since the HHVs in Table 1 are at 60°F and 14.696 psia (29.92 in. Hg), the only adjustment that must be made is that for temperature. This is done by multiplying the HHVs by 520/528 to provide the HHV at 68°F and 29.92 in. Hg. In the example calculations, the HHV is calculated at 60°F and the temperature adjustment is made in the final step when the F-factors are calculated.

The calculation of the HHV from GC gas analysis is modeled after ASTM D 3588-91.⁴ In ASTM D 3588-91, a distinction is made between the “ideal” and “real” conditions. The real HHV, which takes into consideration the compressibility factor, should be used only when determining heat input rates when real fuel flow rates are used, i.e., by multiplying the “real” HHV by the “real” fuel flow rates. (*Note:* The compressibility factor is the “ratio of the actual volume of a given mass of gas at a specified temperature and

pressure to its volume calculated from the ideal gas law at the same conditions.”⁴) The real HHV should NOT be used in calculating the F-factors – the ideal HHV must be used.

Table 3 presents a different format from Table 1. The conversion factors are at the top and the composition of the fuel is given as shown. The HHV column is the sum of the mole fractions times the conversion factors (Note that this HHV is at 60°F and 14.696 psia). The F_d , F_w , and F_c columns are the sums of the mole fractions times the conversion factors divided by the weighted HHV, which is then multiplied by 528/520 to adjust the F-factors to 68°F. Several example calculations for various types of gaseous fuels are provided to allow a check of spreadsheets.

DERIVATION OF CONVERSION FACTORS IN METHOD 19

As mentioned earlier, the conversion factors in Method 19 are thought to be at 70°F. However, it will be seen that the conversion factors closely estimate the volume at 68°F. The conversion factors are derived as follows:

Conversion Factors for Carbon

When 1.0 mole (note that mole and cubic foot can be used interchangeably) of C is burned with air ($C + O_2 = CO_2$), the resulting products are 1.0 mole of CO_2 . N_2 will also be present in the amount of $79.1/20.9 * 1.0$, since 1.0 mole of O_2 is required. Thus, $1.0 + 79.1/20.9 * 1.0 = 4.7847$ dscf/cf of carbon.

Since weight percent is being used, the mass of carbon is determined as follows:

$$1.0 \text{ cf of carbon} / 385.3068 \text{ scf/lb-mole} * 12.01115 \text{ lb/lb-mole} * 100\%$$

Dividing this value into the dscf of combustion gas yields $4.7847 * 385.3068 / 12.01115 / 100 = 1.5349$ (scf/lb)/%.

The amount of CO_2 generated would be $1.0 * 385.3068 / 12.0115 / 100 = 0.3208$ (scf/lb)/%

Conversion Factor for Hydrogen

When 1.0 mole of H_2 is burned with air ($H_2 + 0.5 O_2 = H_2O$), the resulting products are 1.0 mole of H_2O . N_2 will also be present in the amount of $79.1/20.9 * 0.5 = 1.892$ dscf/mole of H_2 . Using the same methodology as above, except using 2.01588 for the molecular weight, the conversion factor for the dry basis is obtained by:

$$1.892 * 385.3068 / 2.01588 / 100 = 3.6169 \text{ scf/lb)/}\%$$

For the wet basis, the amount of water must be added to the N_2 .

$$(1.892 + 1) * 385.3068 / 2.01588 / 100 = 5.5283 \text{ (scf/lb)/}\%$$

Conversion Factor for Nitrogen

Nitrogen remains unchanged in the combustion process. Thus, the conversion factor is:

$$1.0 * 385.3068 / 28.0134 / 100 = 0.1375 \text{ (scf/lb)/}\%$$

Conversion Factor for Oxygen

Any oxygen in the fuel is used in the combustion process. As a result, the amount of N_2 is *decreased* by the ratio 79.1/20.9. Thus, the conversion factor for O_2 is a negative number:

$$-1.0 * 79.1/20.9 * 385.3068 / 31.9988 / 100 = -0.4557 \text{ (scf/lb)/}\%$$

Conversion Factor for Sulfur

When 1.0 mole of sulfur is burned with air, the resulting product is 1.0 mole of SO_2 and $79.1/20.9 * 1.0$ moles of N_2 . Thus, the conversion factor for sulfur is:

$$(1.0 + 79.1/20.9) * 385.3068 / 32.064 / 100 = 0.5750 \text{ (scf/lb)/}\%$$

Conversion Factor for Free Water

Free water goes through the combustion process unchanged. Thus, the conversion factor is:

$$1.0 * 385.3068/18.01528/100 = 0.2139 \text{ (scf/lb)/\%}$$

Summary of Method 19 Conversion Factors

A summary of the calculated conversion factors for use in Method 19 at 68°F is given below. The Method 19 conversion factors, as listed in the latest Code of Federal Regulations, are also listed for comparison purposes. Any differences in the final results from using the two sets of values will depend on the composition of the fuel. The greatest effect will be seen when the concentration of hydrogen is high relative to carbon. When carbon is the major constituent, differences will be very slight.

When EPA changed its standard conditions from 70°F to 68°F, EPA derived the average F-factors in Method 19 by multiplying all previously derived values (thought to be at 70°F) by the ratio 528/530 and rounding off to the nearest 10 cubic feet. Therefore, on an average, the F-factors given in Method 19 is about 0.4% lower than would be calculated by both sets of conversion factors listed in the table below.

Component	Conversion Factor @ 68°F	M19 Conversion Factor ⁴ (revised as of 7/1/97)
Carbon, K _C	1.5349	1.53
Hydrogen, K _{hd}	3.6169	3.64
Hydrogen, K _{wd}	5.5283	5.57
Oxygen, K _O	0.4557	0.46
Nitrogen, N ₂	0.1375	0.14
Sulfur, K _S	0.5750	0.57
Water, K _W	0.2139	0.21
Carbon Dioxide, K _{CC}	0.3208	0.321

Example Calculation – Comparison of the Two (Volume vs. Weight) Approaches

Propane (C₃H₈) has 3 atoms of carbon and 8 atoms of hydrogen. Thus, the weight percent of carbon is $C = 3 * 12.01115 / (3 * 12.01115 + 8 * 1.00794) = 0.8171$ or 81.71% C. The weight percent of hydrogen is 18.29%. The HHV is 21,653 Btu/lb or 2516.1 Btu/cf at 60°F

Using the weight conversion factors in the above table, the F-factor is:

$$\begin{aligned} DE &= 1.5349 * 81.71 + 3.6169 * 18.29 = 191.57 \text{ dscf/lb} \\ F_d &= 191.57/21653 * 10^6 = 8,847 \text{ dscf/mmBtu} \end{aligned}$$

Using the volume factors:

$$\begin{aligned} DE &= 21.923 \text{ dscf/cf (from Table 1, Column B)} \\ F_d &= 21.923/2516.1 * 528/520 * 10^6 = 8,847 \text{ dscf/mmBtu} \end{aligned}$$

REFERENCES

1. R.T. Shigehara, R.M. Neulicht, W.S. Smith, and J.W. Peeler, "Summary of F Factor Methods for Determining Emissions from Combustion Sources," Source Evaluation Society Newsletter, Vol. 1, No. 4, November 1976. This paper summarizes the F-factors (dry, carbon, wet) methods, presents the calculated F-factor values for different types of fuels, and discusses the various uses of F-factors and errors involved in certain applications and conditions. Related articles that may be of interest are listed in the "Reference" section.
2. Technical Publication TP-17, "Table of Physical Properties of Hydrocarbons for Extended Analysis of Natural Gases," Gas Processors Association, 6526 East 60th Street, Tulsa, Oklahoma 74145.

3. GPA Standard 2145-96, "*Table of Physical Constants of Paraffin Hydrocarbons and Other Components of Natural Gas,*" Gas Processors Association, 6526 East 60th Street, Tulsa, Oklahoma 74145.
4. ASTM D 3588-91, "*Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density (Specific Gravity) of Gaseous Fuels.*" This practice covers the procedures for calculating the parameters listed in the title at the standard conditions of 14.696 psia and 60°F. In its earlier version (D 3588-81), the standard pressure was 14.73 psia.
5. 40 CFR Part 60, Appendix A, Method 19, "*Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxides Emission Rates.*" This reference method includes the equations used to calculate the various F-factors from fuel compositions in weight percents.