

# Correction Factors, Ionization Energies, And Calibration Characteristics For BW Ultra

## Correction Factors & Ionization Energies\*

Photoionization Detector sensors (PIDs) can be used for the detection of a wide variety of gases that exhibit different responses. In general, any compound with ionization energy (IE) lower than that of the lamp photons can be measured.\* The best way to calibrate a PID to different compounds is to use a standard of the gas of interest. However, correction factors have been determined that enable the user to quantify a large number of chemicals using only a single calibration gas, typically isobutylene. In our PIDs, correction factors can be used in one of three ways:

1. Calibrate the monitor with isobutylene in the usual fashion to read in isobutylene equivalents. Manually multiply the reading by the correction factor (CF) to obtain the concentration of the gas being measured.
2. Calibrate the unit with isobutylene in the usual fashion to read in isobutylene equivalents. Call up the correction factor from the instrument memory or download it from a personal computer and then call it up. The monitor will then read directly in units of the gas of interest.
3. Calibrate the unit with isobutylene, but input an equivalent, "corrected" span gas concentration when prompted for this value. The unit will then read directly in units of the gas of interest.

*\* The term "ionization energy" is more scientifically correct and replaces the old term "ionization potential." High-boiling ("heavy") compounds may not vaporize enough to give a response even when their ionization energies are below the lamp photon energy. Some inorganic compounds like  $H_2O_2$  and  $NO_2$  give weak response even when their ionization energies are well below the lamp photon energy.*

### Example 1:

With the unit calibrated to read isobutylene equivalents, the reading is 10 ppm with a 10.6 eV lamp. The gas being measured is butyl acetate, which has a correction factor of 2.6. Multiplying 10 by 2.6 gives an adjusted butyl acetate value of 26 ppm. Similarly, if the gas being measured were trichloroethylene (CF = 0.54), the adjusted value with a 10 ppm reading would be 5.4 ppm.

### Example 2:

With the unit calibrated to read isobutylene equivalents, the reading is 100 ppm with a 10.6 eV lamp. The gas measured is m-xylene (CF = 0.43). After downloading this factor, the unit should read about 43 ppm when exposed to the same gas, and thus read directly in m-xylene values.

### Example 3:

The desired gas to measure is ethylene dichloride (EDC). The CF is 0.6 with an 11.7 eV lamp. During calibration with 100 ppm isobutylene, insert 0.6 times 100, or 60 at the prompt for the calibration gas concentration. The unit then reads directly in EDC values.

## Conversion to mg/m<sup>3</sup>

To convert from ppm to mg/m<sup>3</sup>, use the following formula:

$$\text{Conc. (mg/m}^3\text{)} = \frac{[\text{Conc. (ppmv)} \times \text{mol. wt. (g/mole)}]}{\text{molar gas volume (L)}}$$

For air at 25°C (77°F), the molar gas volume is 24.4 L/mole and the formula reduces to:

$$\text{Conc. (mg/m}^3\text{)} = \text{Conc. (ppmv)} \times \text{mol. wt. (g/mole)} \times 0.041$$

For example, if the instrument is calibrated with a gas standard in ppmv, such as 100 ppm isobutylene, and the user wants the display to read in mg/m<sup>3</sup> of hexane, whose m.w. is 86 and CF is 4.3, the overall correction factor would be 4.3 x 86 x 0.041 equals 15.2.

## Correction Factors for Mixtures

The correction factor for a mixture is calculated from the sum of the mole fractions  $X_i$  of each component divided by their respective correction factors  $CF_i$ :

$$CF_{\text{mix}} = 1 / (X_1/CF_1 + X_2/CF_2 + X_3/CF_3 + \dots X_i/CF_i)$$

Thus, for example, a vapor phase mixture of 5% benzene and 95% n-hexane would have a  $CF_{\text{mix}}$  of  $CF_{\text{mix}} = 1 / (0.05/0.53 + 0.95/4.3) = 3.2$ . A reading of 100 would then correspond to 320 ppm of the total mixture, comprised of 16 ppm benzene and 304 ppm hexane.

For a spreadsheet to compute the correction factor and TLV of a mixture see the appendix at the end of the CF table.

## TLVs and Alarm Limits for Mixtures

The correction factor for mixtures can be used to set alarm limits for mixtures. To do this one first needs to calculate the exposure limit for the mixture. The Threshold Limit Value (TLV) often defines exposure limits. The TLV for the mixture is calculated in a manner similar to the CF calculation:

In the above example, the 8-h TLV for benzene is 0.5 ppm and for n-hexane 50 ppm. Therefore, the TLV of the mixture is  $TLV_{\text{mix}} = 1 / (0.05/0.5 + 0.95/50) = 8.4$  ppm, corresponding to 8.0 ppm hexane and 0.4 ppm benzene. For an instrument calibrated on isobutylene, the reading corresponding to the TLV is:

$$TLV_{\text{mix}} = 1 / (X_1/TLV_1 + X_2/TLV_2 + X_3/TLV_3 + \dots X_i/TLV_i)$$

A common practice is to set the lower alarm limit to half the TLV, and the higher limit to the TLV. Thus, one would set the alarms to 1.3 and 2.6 ppm, respectively.

## CALIBRATION CHARACTERISTICS

**A. Flow Configuration.** PID response is essentially independent of gas flow rate as long as it is sufficient to satisfy the pump demand. Four main flow configurations are used for calibrating a PID:

1. Pressurized gas cylinder (Fixed-flow regulator): The flow rate of the regulator should match the flow demand of the instrument pump or be slightly higher.
2. Pressurized gas cylinder (Demand-flow regulator): A demand-flow regulator better matches pump speed differences, but results in a slight vacuum during calibration and thus slightly high readings.
3. Collapsible gas bag: The instrument will draw the calibration gas from the bag at its normal flow rate, as long as the bag valve is large enough. The bag should be filled with enough gas to allow at least one minute of flow (~ 0.5 L for a MiniRAE3000+, ~0.3 L for MultiRAE).
4. T (or open tube) method: The T method uses a T-junction with gas flow higher than the pump draw. The gas supply is connected to one end of the T, the instrument inlet is connected to a second end of the T, and excess gas flow escapes through the third, open end of the T. To prevent ambient air mixing, a long tube should be connected to the open end, or a high excess rate should be used. Alternatively, the instrument probe can be inserted into an open tube slightly wider than the probe. Excess gas flows out around the probe.

The first two cylinder methods are the most efficient in terms of gas usage, while the bag and T methods give slightly more accurate results because they match the pump flow better.

**B. Pressure.** Pressures deviating from atmospheric pressure affect the readings by altering gas concentration and pump characteristics. It is best to calibrate with the instrument and calibration gas at the same pressure as each other and the sample gas. (Note that the cylinder pressure is not relevant because the regulator reduces the pressure to ambient.) If the instrument is calibrated at atmospheric pressure in one of the flow configurations described above, then (1) pressures slightly above ambient are acceptable but high pressures can damage the pump and (2) samples under vacuum may give low readings if air leaks into the sample train.

**C. Temperature.** Because temperature effects gas density and concentration, the temperature of the calibration gas and instrument should be as close as possible to the ambient temperature where the unit will be used. We recommend that the temperature of the calibration gas be within the instrument's temperature specification (typically, 14° to 113° F, or -10° to 45° C). Also, during actual measurements, the instrument should be kept at the same or higher temperature than the sample temperature to avoid condensation in the unit.

**D. Matrix.** The matrix gas of the calibration compound and VOC sample is significant. Some common matrix components, such as methane and water vapor can affect the VOC signal. PIDs are most commonly used for monitoring VOCs in air, in which case the preferred calibration gas matrix is air. For a MiniRAE3000+, methane, methanol, and water vapor reduce the response by about 20% when their concentration is 15,000 ppm and by about 40% at 30,000 ppm. Despite earlier reports of oxygen effects, RAE PID responses with 10.6 eV lamps are independent of oxygen concentration, and calibration gases in a pure nitrogen matrix can be used. H<sub>2</sub> and CO<sub>2</sub> up to 5 volume % also have no effect.

**E. Concentration.** Although Honeywell PIDs have electronically linearized output, it is best to calibrate in a concentration range close to the actual measurement range. For example, 100 ppm standard gas for anticipated vapors of 0 to 250 ppm, and 500 ppm standard for expected concentrations of 250 to 1,000 ppm.

The correction factors in this table were typically measured at 50 to 100 ppm and apply from the ppb range up to about 1,000 ppm. Above 1000 ppm the CF may vary and it is best to calibrate with the gas of interest near the concentration of interest.

**F. Filters.** Filters affect flow and pressure conditions and therefore all filters to be used during sampling should also be in place during calibration. Using a water trap (hydrophobic filter) greatly reduces the chances of drawing water aerosols or dirt particles into the instrument. Regular filter replacements are recommended because dirty filters can adsorb VOCs and cause slower response time and shifts in calibration.

**G. Instrument Design.** High-boiling (“heavy”) or very reactive compounds can be lost by reaction or adsorption onto materials in the gas sample train, such as filters, pumps and other sensors. Multi-gas meters, including MultiRAE and AreaRAE Plus / Pro have the pump and other sensors upstream of the PID and are prone to these losses. Compounds possibly affected by such losses are shown in green in the table, and may give slow response, or in extreme cases, no response at all. In many cases the multi-gas meters can still give a rough indication of the relative concentration, without giving an accurate, quantitative reading. The 3GPID+ series instruments have inert sample trains and therefore do not exhibit significant loss; nevertheless, response may be slow for the very heavy compounds and additional sampling time up to a minute or more should be allowed to get a stable reading.

### DISCLAIMER

TN-106F is a general guideline for Correction Factors (CF) for use with PID instruments manufactured by Honeywell. The CF may vary, depending on instrument and operation conditions. For the best accuracy, it is recommended to calibrate the instrument to target gas. Actual readings may vary with age and cleanliness of lamp, relative humidity, and other factors, as well. For accurate work, the instrument should be calibrated regularly under the operating conditions used. The factors in this table on the following pages were measured in dry air (40 to 50% RH) at room temperature, typically at 50 to 100 ppm. CF values may vary above about 1,000 ppm.

### IMPORTANT!

Even though the same sensor may be used in different instruments (MultiRAE Series and ToxiRAE Pro, for example), the firmware and design of the instruments are different, The CF are therefore customized for best performance within the specific instrument, as confirmed by our lab tests.

Note: These CF are specific to the instruments cited in these notes, and do not apply to instruments not manufactured by Honeywell. In addition, these lamps and sensors should not be used in instruments by other manufacturers because their performance cannot be guaranteed.

### Updates

The values in this table on the following pages are subject to change as more or better data become available. Watch for updates of this table on the Internet.

IE data are taken from the CRC Handbook of Chemistry and Physics, 73rd Edition, D.R. Lide (Ed.), CRC Press (1993) and NIST Standard Ref. Database 19A, NIST Positive Ion Energetics, Vers. 2.0, Lias, et.al., U.S. Dept. Commerce (1993).

## TABLE ABBREVIATIONS

**CF** = Correction Factor (multiply by reading to get corrected value for the compound when calibrated to isobutylene)

**ND** = Not Detectable

**NCF** = No Correction Factor

**MW** = Molecular weight

**CAS No.** = CAS Registry Number

**IE** = Ionization Energy

**Note:** The term "ionization energy" is more scientifically correct and replaces the old term "ionization potential." High-boiling ("heavy") compounds may not vaporize enough to give a response even when their ionization energies are below the lamp photon energy. Some inorganic compounds like H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub> give weak response even when their ionization energies are well below the lamp photon energy.

**Note:** The Correction Factors shown here are included in the Correction Factor Library in firmware version v01.018 for the BW Ultra.

Compound Name	IE (eV)	Formula	CAS No.	Molecular Weight (g/mol)	CF 10.6eV
Acetaldehyde	10.23	C <sub>2</sub> H <sub>4</sub> O	75-07-0	44.1	6.5
Acetone	9.71	C <sub>3</sub> H <sub>6</sub> O	67-64-1	58.1	1.08
Ammonia	10.16	NH <sub>3</sub>	7664-41-7	17	8.0
Butadiene	9.07	C <sub>4</sub> H <sub>6</sub>	106-99-0	54.1	0.73
Diesel		----	68334-30-5	226	1.2
Diesel Fuel #2, whole		----	68334-30-5	216	0.7
Ethanol	10.47	C <sub>2</sub> H <sub>6</sub> O	64-17-5	46.1	7.7
Ethene	10.51	C <sub>2</sub> H <sub>4</sub>	74-85-1	28.1	8.4
Gasoline		----	8006-61-9	93	1.0
Hexane	10.13	C <sub>6</sub> H <sub>14</sub>	110-54-3	86.2	10.8
Isobutylene	9.24	C <sub>4</sub> H <sub>8</sub>	115-11-7	56.1	1
Jet A			80008-20-6	150	1.35
Jet fuel JP-8		----	----	165	0.6
Methyl Ethyl Ketone	9.51	C <sub>2</sub> H <sub>6</sub> O	78-93-3	72.1	0.94
Naptha	8.13	C <sub>17</sub> H <sub>30</sub>	8030-30-6	128.3	0.8
Styrene	8.43	C <sub>8</sub> H <sub>8</sub>	100-42-5	104.1	0.6
Toluene	8.82	C <sub>7</sub> H <sub>8</sub>	108-88-3	92.1	0.5
Turpentine	~8	C <sub>10</sub> H <sub>16</sub>	8006-62-2	136.2	0.4
Vinyl Chloride	9.99	C <sub>2</sub> H <sub>3</sub> Cl	75-01-4	62.5	2.0
Xylene, -p	8.44	C <sub>8</sub> H <sub>10</sub>	106-42-3	106.2	0.5