

CONVERSION OF PID READINGS TO METHANE EQUIVALENT OR HEXANE EQUIVALENT FID RESPONSE

INTRODUCTION

Many regulatory agencies request inventories of chemicals released to the air to be provided in units of methane equivalents. This is done as a way of normalizing the overall environmental impact of a broad variety of different chemical types to a common unit, i.e., the total number of carbon atoms released. Traditionally, methane equivalents of a mixture of organic compounds have been measured using a laboratory gas chromatograph (GC) calibrated with methane using a flame ionization detector (FID). Portable FIDs and PIDs provide a convenient, cost-saving method of making measurements in the field. Portable FIDs function on the same principle as the laboratory FIDs; however the sample inlet designs of many portable FIDs often result in responses that are not proportional to the number of carbons in the organic compound. Therefore, methane equivalents measured on a portable FID do not necessarily correspond to the desired laboratory FID equivalents, which are proportional to carbons.

Portable PIDs offer advantages over portable FIDs in their ease of use, smaller size and weight, lower cost, and lack of need for hydrogen cylinders. In addition, methane, which is exempt from most regulatory emissions limits, does not respond on a PID. Methane is prevalent from both biogenic sources and from natural gas distribution leaks, and thus use of a PID will reduce the number of false positive responses. This article describes methods for converting PID measurements to laboratory GC-FID methane equivalents. Conversion of PID readings to hexane equivalents is performed by analogous equations.

Empirical Correlations

The conceptually simplest conversion approach is to make PID measurements simultaneous with taking gas samples that are sent to a laboratory for GC-FID analysis. When the results are compared, a PID-FID correlation factor or curve can be developed. For example, Coy, *et al.* (1) found the following correlation when calibrating the PID to isobutylene and sampling with charcoal for GC:

log(GC total ppm) = -0.042 + 1.05*log(PID ppm)

This calibration applied to vapors from painting operations, including such compounds as petroleum distillates, mineral spirits, isobutyl acetate, isobutyl alcohol, isopropanol, toluene, xylenes, ethylbenzene, and MEK.

For gasoline vapors sampled with an isobutylene-calibrated PID and by charcoal tubes for lab GC, Drummond (2) found:

Benzene ppm = 0.20*(PID ppm)

In these cases the GC results gave actual concentrations of the individual components in ppm, but could have easily given methane equivalents by calibrating the GC-FIDs to methane.

The advantage of this approach is its simplicity and accuracy once the correlation has been obtained. It also can be used on highly complex and unknown mixtures. The disadvantage is that it applies to only one mixture and more laboratory tests are needed to establish a new correlation for each new mixture encountered. The methods described below allow estimation of PID-FID conversion factors for many mixtures without the need for sampling and laboratory measurements.

PID Lamp Selection

RAE Systems offers both 10.6 eV and 11.7 eV lamps for general hydrocarbon monitoring. The 10.6 eV lamp responds to pentane and higher hydrocarbons, and the 11.7 eV lamp responds to ethane (weakly), propane and higher hydrocarbons. As mentioned above, methane and ethane are exempt from most regulations. Unless propane or butane are specifically known to be present, the 10.6 eV lamp is preferred because it responds broadly to many solvents and fuels and has a considerably longer working life than the 11.7 eV lamp. Even if propane or butane are present, their proportion of the total hydrocarbons can be measured in a few laboratory tests and then the ratio used to correct the 10.6 eV PID readings. Therefore, the 10.6 eV lamp is recommended unless compounds that require an 11.7 eV lamp dominate the emissions scenario. See Technical Note 106 for an extended list of compounds and their responses on these two lamps.

Procedure

To convert PID readings to methane equivalent FID readings, proceed as follows:

- 1. Calibrate the PID to isobutylene using the standard procedures
- 2. Measure the gas or gas mixture.
- **3.** Multiply the observed readings by the PID-FID Correction Factor listed in one of the last two columns in Table 1 below.

Ideally, the value selected is the measured factor in the secondto-last column. In the absence of a measured value, an upper limit to the methane-equivalent response can be estimated from the number of carbons in the molecule (last column).

PID-FID CORRECTION FACTOR DERIVATION FOR METHANE EQUIVALENTS

The rationale behind the PID-FID correction factors (CFs) is as follows:

The PID CF is defined as the value by which the readings are multiplied in order to obtain the true ppmv concentrations, when the unit has been calibrated to isobutylene:

True ppmv = PID reading x PID CF (1)

The Lab FID Response Factor (RF) is defined as the relative response of the compound compared to methane. The methane equivalent FID response is

CH₄ Equivalents = True ppmv x FID RF (2a)

An estimate of the FID RF is the number of carbon atoms in the molecule, in which case Eq (2a) becomes:

CH₄ Equivalents = True ppmv x #C Atoms (2b)

Combining Eqs (2a) or (2b) with Eq (1) yields:

CH₄ Equivs = PID read x PID CF x FID RF (3a) CH₄ Equivs = PID read x PID CF x #Cs (3b)

The PID-FID CFs are thus:

PID-FID CF (Meas.) = PID CF x FID RF (4a) PID-FID CF (Calc.) = PID CF x #Cs (4b)

If the PID is calibrated using the gas of interest, then it reads directly in true ppmv and therefore it is not necessary to multiply by the PID CF, only by the FID RF or the number of carbon atoms.

Example 1. Single Compound

1. Toluene is the only compound being measured. The Lab FID RF is available in Table 1 and therefore the PID-FID CF is known (column 5).

- **a.** The reading is 10 ppm with the PID calibrated to isobutylene. The lab FID equivalent is $10 \times 2.6 = 26$ ppm methane units.
- **b.** With the PID calibrated directly to toluene (or calibrated to isobutylene but using the built-in correction factor to read in toluene units) the display reading is 5 ppm. The lab FID equivalent is $5 \times 5.1 = 26$ ppm methane units.

2. Methyl cellosolve (2-methoxyethanol) is the only compound. The Lab FID RF is not available and therefore the PID-FID CF is estimated from the number of carbon atoms (Table 1, column 6). The PID reading of 10 ppm corresponds to $10 \times 7.2 = 72$ ppm FID equivalents. This value can be considered a safe, upper limit, because the true factor is almost certainly less than the 7.2 estimated from the number of carbons.

Example 2. Compound Mixture

The vapors consist of the following mixture:

60% Ethyl acetate (EA) 25% Methyl ethyl ketone (MEK) 15% Toluene (Tol)

The unit is calibrated to isobutylene and the reading is 50 ppm. As described in Technical Note 106, the average CF for this mixture is calculated as:

 $CFmix = 1/(X_{EA}/CF_{EA} + X_{MEK}/CF_{MEK} + X_{Tol}/CF_{Tol} (5)$ CFmix = 1/(0.60/4.6 + 0.25/0.86 + 0.15/0.50) = 1.4

The true total concentration is $50 \times 1.4 = 70$ ppm, which consists of 42 ppm ethyl acetate, 17.5 ppm MEK, and 10.5 ppm toluene. Multiplying each compound by their respective FID RF factors from Table 1:

CH₄ Equivalents = 42 x 2.0 + 17.5 x 2.2 + 10.5 x 5.1 = 176 ppm

To simplify, an average FID RF can be calculated for the mixture as:

 $\begin{array}{l} \text{RFmix} = X_{\text{EA}} \ x \ \text{RF}_{\text{EA}} + X_{\text{MEK}} \ x \ \text{RF}_{\text{MEK}} + X_{\text{Tol}} \ x \ \text{RF}_{\text{Tol}} \ (6) \\ \text{RFmix} = 0.60 \ x \ 2.0 + 0.25 \ x \ 2.2 + 0.15 \ x \ 5.1 = 2.5 \end{array}$

Then, according to Eq. 3a:

CH₄ Equivs = PID read x PID CF x FID RF (3a) CH₄ Equivs = $50 \times 1.4 \times 2.5 = 175$ ppm CH₄ Equivs = PID reading x 3.5 = 175 ppm

Example 3. Mixture with Non-Responding Compounds

The vapors consist of the following mixture:

60% Ethyl acetate (EA) 25% Methylene chloride (MC) 15% Toluene (Tol)

The unit is calibrated to isobutylene and the reading is 50 ppm. There is no response to methylene chloride with the 10.6 eV lamp, therefore its correction factor is infinite. The average CF for this mixture is calculated as:

 $\begin{array}{l} CFmix = 1/(X_{EA}/CF_{EA} + X_{MC}/CF_{MC} + X_{Tol}/CF_{Tol}) \\ CFmix = 1/(0.60/4.6 + 0.25/\infty + 0.15/0.50) = 2.3 \end{array}$

The average FID RF is calculated as (Eq. 6):

RFmix = 0.60 x 2.0 + 0.25 x 0.94 + 0.15 x 5.1 = 2.2

According to Eq. 3a:

CH₄ Equivs = 50 x 2.3 x 2.2 = 253 ppm

Note that the 50 ppm PID response is equivalent to a higher methane equivalent response in this example than in Example 2 because the PID is blind to 25% of the total VOC.

Example 4. Mixture with Unknown FID RF

If the lab FID RFs were unknown in Examples 2 and 3 above, one would estimate the RFs as the number of carbons, which usually leads to a safe overestimation:

For Example 2:

 $\label{eq:RFmix} \begin{array}{l} \mathsf{RFmix} = 0.60 \ x \ 4 + 0.25 \ x \ 4 + 0.15 \ x \ 7 = 4.5 \\ \mathsf{CH}_4 \ \mathsf{Equivs} = 50 \ x \ 1.4 \ x \ 4.5 = 315 \ \mathsf{ppm} \end{array}$

compared to a value of 175 ppm from actual RFs.

For Example 3:

RFmix = 0.60 x 4 + 0.25 x 1 + 0.15 x 7 = 3.7 CH₄ Equivs = 50 x 2.3 x 3.7 = 426 ppm

compared to a value of 253 ppm from actual RFs. It is clear that the availability of accurate response factors will help avoid false positive alarms.

PID-FID CORRECTION FACTOR DERIVATION FOR HEXANE EQUIVALENTS

Although a PID with 10.6 eV lamp can be calibrated with hexane, the resulting PID hexane equivalents are different than FID hexane equivalents. Therefore, the same procedures should be used for hexane as described above for methane, by substituting the factors in Table 2 in place of those in Table 1. Table 2 assumes calibration with isobutylene. If the instrument is calibrated with hexane instead, the values in Table 2 should be divided by 4.3.

The values in Table 2 are calculated as :

#Cs in compound x PID CF / #Cs in hexane, or #Cs in compound x PID CF / 6 (isobutylene calib.) #Cs in compound x PID CF / 25.8 (hexane calib.)

Example 5. Compound Mixture

For the same compound mixture as in Example 2, the unit is calibrated to isobutylene and reads 50 ppm:

60% Ethyl acetate (EA) 25% Methyl ethyl ketone (MEK) 15% Toluene (Tol)

CFmix = 1/(0.60/4.6 + 0.25/0.86 + 0.15/0.50) = 1.4

The true total concentration is $50 \times 1.4 = 70$ ppm, which consists of 42 ppm ethyl acetate, 17.5 ppm MEK, and 10.5 ppm toluene. Multiplying each compound by their respective FID RF factors from Table 2:

Hexane Equivalents = 42 x 0.42 + 17.5 x 0.48 + 10.5 x 1.1 = 38 ppm

To simplify, an average FID RF can be calculated for the mixture as:

$$\label{eq:RFmix} \begin{split} \text{RFmix} &= X_{\text{EA}} \times \text{RF}_{\text{EA}} + X_{\text{MEK}} \times \text{RF}_{\text{MEK}} + X_{\text{Tol}} \times \text{RF}_{\text{Tol}} \text{ (6)} \\ \text{RFmix} &= 0.60 \times 0.42 + 0.25 \times 0.48 + 0.15 \times 1.1 = 0.54 \end{split}$$

Then, analogous to Eq. 3a:

Hexane Equivs = PID read x PID CF x FID RF Hexane Equivs = $50 \times 1.4 \times 0.54 = 38$ ppm Hexane Equivs = PID reading x 0.76 = 38 ppm

Example 6. Hexane Calibration

To calibrate with hexane instead of isobutylene, proceed as follows. For a compound with known FID CF, divide the PID-FID CF in Table 2 by 4.3. For example, for isopropanol, the new factor is 2.1/4.3 = 0.49 and for gasoline, the new factor is about 1.3/4.3 = 0.30. For a compound with unknown PID-FID CF, such as aniline, the new factor is 3/4.3 = 0.70. For a compound not on Table 2, such as methyl propyl ketone (#Cs = 5, CF = 0.93), the new factor is:

Calibrate with hexane gas and set the CF to the factors listed in this paragraph to read directly in FID hexane equivalents.

When using a **MiniRAE 2000**, it is easiest to use Memory 0 for this procedure because when other memories are calibrated, the CF cannot be changed from 1.0. Therefore, enter Memory 0, set the gas to hexane, change the CF to the value calculated above (for example, 0.49 for isopropanol or 0.30 for gasoline, not 4.3 for hexane), and set the span value to the hexane gas cylinder concentration. During calibration the monitor will ask for isobutylene, but hexane gas should be applied. During readings, the monitor will indicate hexane measurements, and it will be set up to read directly in FID hexane equivalents of the gas being measured. When using a **ToxiRAE PID**, set the span value to the hexane calibration gas concentration and calibrate with this same hexane gas. Then under the "Select Gas?" menu, choose hexane gas and change the correction factor to the value in Table 2 for the gas of interest, divided by 4.3 (for example, 0.49 for isopropanol or 0.30 for gasoline).

REFERENCES

J.D. Coy, P.L. Bigelow, R.M. Buchan, J.D. Tessari & J.O. Parnell, Field Evaluation of a Portable Photoionization Detector for Assessing Exposure to Solvent Mixtures, *Amer. Ind. Hygiene Assoc. J.* **61**, 268-274, 2000.

I. Drummond, On-the-Fly Calibration of Direct Reading Photoionization Detectors, *Amer. Ind. Hygiene Assoc.* J. **58**, 820-822, 1997.

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Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)			
Acetaldehyde	2	6			12			
Acetic acid	2	22			44			
Acetone	3	1.1	1.8	2.0	3.3			
Acetonitrile	2	NR		NR	NR			
Acetylene	2	NR		NR	NR			
Acrolein	3	3.9			11.7			
Acrylonitrile	3	NR		NR	NR			
Allyl alcohol	3	2.4			7.2			
Allyl chloride	3	~4			~12			
Aniline	6	3.0			18			
Benzene	6	0.53	4.3	2.3	3.2			
Benzyl chloride	7	0.6			4.2			
Bromoethane	2	~1.6			~3.2			
Bromoform	1	2.5			2.5			
Bromoproane, 1-	3	1.5			4.5			
Butadiene, 1,3-	4	0.85			3.4			
Butane, iso-	4	~100			~400			

Table 1. PID to FID Correction Factors for Methane Equivalents

Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)
Butane, n-	4	NR		NR	NR
Butanol, n-	4	4.7			18.8
Butanol, iso-	4	3.8			15.2
Butyl mercaptan	4	0.52			2.1
Carbon tetrachloride	1	NR	0.40	NR	NR
Chlorobenzene	6	0.40	4.0	1.6	2.4
Chloroethane	2	NR		NR	NR
Chloroform	1	NR	0.49	NR	NR
Cumene	9	0.54			4.9
Cyclohexane	6	1.4			8.4
Dichlorobenzene, 1,2-	6	0.47			2.8
Dichlorobenzene, 1,4-	6	~0.5			~3
Dichloroethylene, 1,1-	2	~0.9	1.9		~1.8
Dichloroethylene,c-1-2-	2	~0.8			~1.6
Dichloropropane, 1, 2-	3	NR		NR	NR
Dimethylformamide, N-N-	3	~0.8			~2.4
Dioxane, 1,4-	4	~1.3			~5.2

Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)	Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)
Epichlorohydrin	2	8.5			17.0	Methyl t-butyl ether	5	0.9	3.2	2.8	4.5
Ethane	2	NR		NR	NR	Methylene chloride	1	NR	0.94	NR	NR
Ethanol	2	12			24.0	Mineral Spirits	11	0.7			7.7
Ethoxyethanol, 2- (Ethyl cellosolve)	4	~1.3			~5.2	Nonane, n- Octane (mix)	9 8	~1.4			~13
Ethyl acetate	4	4.6	2.0	9.0	18.4	Pentane, n-	5	8.4			42.0
Ethyl acrylate	5	2.4			12.0	Perchloroethylene	2	0.57	1.3	0.8	1.1
Ethylbenzene	8	0.52			4.2	Propane	3	NR	1.0	NR	NR
Ethylene dibromide (1,2-Dibromomethane)	2	1.7			3.4	Propionaldehyde	3	~1.9			~5.7
Ethylene dichloride	_					Propylene oxide	3	6.5			19.5
(1,2-Dichloroethane)	2	NR	1.5	NR	NR	Styrene	8	0.4			3.2
Gasoline	8	~1			~8	Tetrachloroethane, 1,1,2,2-	2	NR		NR	NR
Heptane, n-	7	2.6			18.2	Tetrahydrofuran	4	1.7	2.5	4.2	6.8
Hexane, n-	6	4.3	4.7	20.2	25.8	Toluene	7	0.5	5.1	2.6	3.5
Isobutylene	4	1.0			4.0	Trichloroethane, 1,1,1-	2	NR	1.6	NR	NR
Isoprene	5	0.6			3.2	Trichloroethane, 1,1,2-	2	NR		NR	NR
Isopropanol	3	6.0	1.6	9.9	18.0	Trichloroethylene	2	0.5			1.0
Methane	1	NR	1.0	NR	NR	Trimethylbenzene, 1,2,4-	6	~0.35	3.0	~1	~2
Methanol	1	NR	0.58	NR	NR	Triethylamine	3	0.9			2.7
Methoxyethanol, 2-	<u> </u>		0.00			Vinyl acetate	4	1.2			4.8
(Methyl cellosolve)	3	2.4			7.2	Vinyl bromide	2	0.4			0.8
Methyl bromide	1	1.7			1.7	Vinyl chloride	2	2.0	2.0	4.0	4.0
Methyl chloride	1	NR		NR	NR	Xylene, o-	8	0.59	3.6	2.1	4.7
Methyl ethyl ketone	4	0.86	2.2	1.9	3.4	Xylene, m-	8	0.43			3.4
Methyl isobutyl ketone	6	0.8			4.8	Xylene, p-	8	0.45			3.6
Methyl methacrylate	5	1.5			7.5						

Table 2. PID to FID Correction Factors for Hexane Equivalents

Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)	Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)
Acetaldehyde	2	6			2.0	Benzene	6	0.53	0.92	0.49	0.53
Acetic acid	2	22			7.3	Benzyl chloride	7	0.6			0.7
Acetone	3	1.1	0.39	0.42	0.55	Bromoethane	2	~1.6			~0.5
Acetonitrile	3	NR		NR	NR	Bromoform	1	2.5			0.42
Acetylene	2	NR		NR	NR	Bromoproane, 1-	3	1.5			0.75
Acrolein	3	3.9			2.0	Butadiene, 1,3-	4	0.85			0.57
Acrylonitrile	3	NR		NR	NR	Butane, iso-	4	~100			~67
Allyl alcohol	3	2.4			1.2	Butane, n-	4	NR		NR	NR
Allyl chloride	3	~4			~2	Butanol, n-	4	4.7			3.1
Aniline	6	3.0			3.0	Butanol, iso-	4	3.8			2.5

Technical Note TN-158 01/06/WH

Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)
Butyl mercaptan	4	0.52			0.35
Carbon tetrachloride	1	NR	0.08	NR	NR
Chlorobenzene	6	0.40	0.86	0.34	0.40
Chloroethane	2	NR		NR	NR
Chloroform	1	NR	0.10	NR	NR
Cumene	9	0.54			0.81
Cyclohexane	6	1.4			1.4
Dichlorobenzene, 1,2-	6	0.47			0.47
Dichlorobenzene, 1,4-	6	~0.5			~0.5
Dichloroethylene, 1,1-	2	~0.9	0.40		~0.3
Dichloroethylene,c-1-2-	2	~0.8			~0.3
Dichloropropane, 1, 2-	3	NR		NR	NR
Dimethylformamide, N-N-	3	~0.8			~0.4
Dioxane, 1,4-	4	~1.3			~0.9
Epichlorohydrin	2	8.5			2.8
Ethane	2	NR		NR	NR
Ethanol	2	12			4.0
Ethoxyethanol, 2- (Ethyl cellosolve)	4	~1.3			~0.9
Ethyl acetate	4	4.6	0.42	1.9	3.1
Ethyl acrylate	5	2.4			2.0
Ethylbenzene	8	0.52			0.69
Ethylene dibromide (1,2-Dibromoethane)	2	1.7			0.57
Ethylene dichloride (1,2-Dichloroethane)	2	NR	0.32	NR	NR
Gasoline	8	~1			~1.3
Heptane, n-	7	2.6			3.0
Hexane, n-	6	4.3	1.00	4.3	4.3
Isobutylene	4	1.0			0.67
Isoprene	5	0.6			0.53
Isopropanol	3	6.0	0.35	2.1	3.0
Methane	1	NR	0.21	NR	NR

Compound	C's	PID CF (10.6 eV)	Lab PID RF	PID- FID CF (Meas.)	PID-FID CF (C Atom Calc)
Methanol	1	NR	0.12	NR	NR
Methoxyethanol, 2- (Methyl cellosolve)	3	2.4			1.2
Methyl bromide	1	1.7			0.28
Methyl chloride	1	NR		NR	NR
Methyl ethyl ketone	4	0.86	0.48	0.41	0.57
Methyl isobutyl ketone	6	0.8			0.80
Methyl methacrylate	5	1.5			1.3
Methyl t-butyl ether	5	0.9	0.67	0.61	0.75
Methylene chloride	1	NR	0.20	NR	NR
Mineral Spirits	11	0.7			1.3
Nonane, n-	9	~1.4			~2
Octane (mix)	8	1.8			2.4
Pentane, n-	5	8.4			7.0
Prechloroethylene	2	0.57	0.29	0.16	0.19
Propane	3	NR		NR	NR
Propionaldehyde	3	~1.9			~0.95
Propylene oxide	3	6.5			3.3
Styrene	8	0.4			0.53
Tetrachloroethane, 1,1,2,2-	2	NR		NR	NR
Tetrahydrofuran	4	1.7	0.53	0.90	1.1
Toluene	7	0.5	1.1	0.55	0.58
Trichloroethane, 1,1,1-	2	NR	0.35	NR	NR
Trichloroethane, 1,1,2-	2	NR		NR	NR
Trichloroethylene	2	0.5			0.17
Trimethylbenzene, 1,2,4-	6	~0.35	0.22	~0.08	~0.35
Triethylamine	3	0.9			0.45
Vinyl acetate	4	1.2			0.80
Vinyl bromide	2	0.4			0.13
Vinyl chloride	2	2.0	0.43	0.86	0.67
Xylene, o-	8	0.59	0.76	0.45	0.79
Xylene, m-	8	0.43			0.57
Xylene, p-	8	0.45			0.60