FID vs PID: The Great Debate

2017 Geotechnical, GeoEnvironmental, and Geophysical Technology Transfer

April 11, 2017

Raleigh, NC

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Why is it Important?

As consultants, we are expected to produce data that is

- Reliable
- Repeatable
- Representative
- Defensible

We can only meet these criteria if we understand the instruments we use and their limitations

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PID=Photo Ionization Detector

- Non-destructive to the sample
- Responds to functional groups
- Can operate in non-oxygen atmosphere

- Does not respond to methane
- Affected by high humidity

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FID=Flame Ionization Detector

- Destructive to the sample
- Responds to carbon chain length
- Must have oxygen to operate

- Responds to methane
- Not affected by high humidity

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Combination FID/PID

TVA 1000B

Main Concepts

Ionization Energy

- Minimum amount of energy required to remove an electron from an atom or molecule in a gaseous state

Response Factors

- The response factor is a calculated number provided by the instrument manufacturer for each compound, which is used to calculate the actual concentration of said compound in relation to the calibration gas.

Ionization Energy

- Basis for FID/PID operations and measurement
- Measurements are in electron volts (eV)

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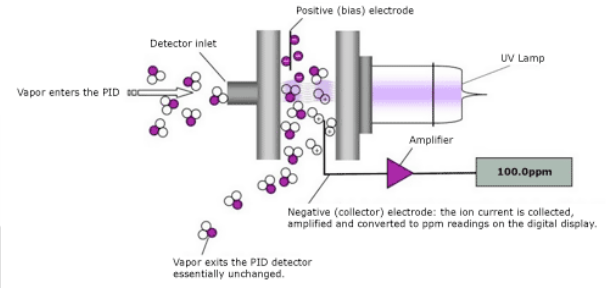
Ionization in a PID

Energy source for ionization with PID is an ultraviolet light



- Three UV lamp energies are used: 9.5 eV, 10.6 eV, and 11.7 eV
- The higher the lamp energy, the greater the number of chemicals that can be detected.
- Detection range of 0.1 to 10,000 ppm

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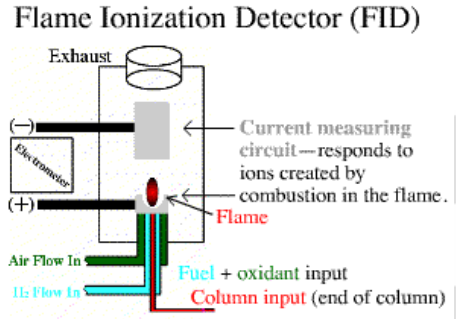
Ionization in a FID

Energy source for ionization with FID is a flame



- Flame energy roughly equivalent to 15 eV
- Detects organic compounds only (carbon counter)
- Detection range is 0.1 to 50,000 ppm

Calibration

FID most common calibration gas is methane (RF_{meth}=1; RF_{iso} = .65)

PID most common calibration gas is isobutylene (RF_{iso} = 1; RF_{meth} = NA)

Why calibrate daily? Instrument drift

The instrument reading is read as xx ppm as the calibration gas equivalent

Comparative Analysis

Compound	IE	FID	PID 9.5 eV	PID 10.6 eV	PID 11.7 eV
Methane (CH_4)	12.98	x			
Isobutylene (C_4H_8)	9.24	x	x	x	x
Hydrogen sulfide (H_2S)	10.46			x	x
Trichloroethylene (C_2HCl_3)	9.47	x	x	x	x
Ammonia (NH_3)	10.2			x	x
Benzene (C_6H_6)	9.25	x	x	x	x
Chloroform ($CHCl_3$)	11.37	x			x
Chrysene ($C_{18}H_{12}$)	7.59	x	x	x	x
Sulfur Dioxide (SO_2)	12.3				
Water (H_20)	12.59				

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Correlations?

Headspace vs Soil

Sample	Location	FID	PID	DRO	GRO
SS-1-1	Greenville, NC	--	5.8	<6.1	--
SS-2-3	Greenville, NC	--	1.0	25.9	--
SS-4-1	Greenville, NC	--	13.6	1260	--
1-2-1	Greenville, NC	4.9	40	686	--
3-1	Greenville, NC	10	6.6	654	--
SB-1	Rowan County, NC	90,800	--	3440	5170
SB-2	Rowan County, NC	26,400	--	3220	5230
SB-7	Rowan County, NC	70,200	--	528	5360
61-3	Piedmont	--	312	4005	1106
61-5	Piedmont	--	701	149.5	<1.1

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Controllable Factors Affecting Field Screening

- Incorrect calibration
- Length of time allowed for volatilization
- Inconsistency in the amount of time allowed for volatilization
- Temperature of sample at time of screening
- Filters
- Probe clogged
- Contaminated soil remaining in probe influencing reading
- Incorrect Response Factor

Response Factors

- The response factor is a calculated number provided by the instrument manufacturer for each compound, which is used to calculate the actual concentration of said compound in relation to the calibration gas.

$$\text{Response Factor (RF)} = \frac{\text{Actual Concentration}}{\text{Instrument Response}}$$

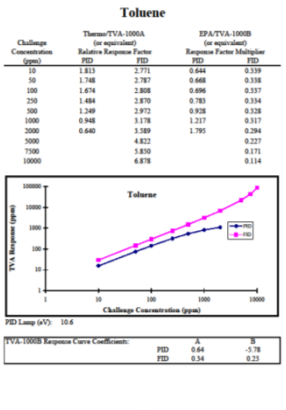
Actual Concentration = Instrument Response x Response Factor

Response Factors are more relevant to industrial hygiene/health and safety than for field screening

Response Factor

What affects the RF?

- Instrument
- Manufacturer
- Calibration gas
- Compound of interest concentration
- Linearity


Toluene

Challenge Concentration (ppm)	Thermo/TVA-1000A (or equivalent) Relative Response Factor PID	FID	EPA/TVA-1000B (or equivalent) Response Factor Multiplier PID	FID
10	1.813	2.771	0.644	0.339
50	1.748	2.787	0.668	0.338
100	1.674	2.808	0.696	0.337
250	1.484	2.870	0.783	0.334
500	1.349	2.972	0.928	0.328
1000	0.948	3.178	1.217	0.317
2000	0.640	3.589	1.795	0.294
5000		4.822		0.227
7500		5.830		0.171
10000		6.878		0.114

PID Lamp (eV): 10.6

TVA-1000B Response Curve Coefficient:

	A	B
PID	0.64	-5.78
FID	0.34	0.23

2-62

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Single Gas RF

Compound	IE	FID	9.5eV	10.6eV	11.7eV
Benzene	9.25	0.7	0.55	0.47	0.60
TCE	9.47	2.8	0.62	0.54	0.43

Benzene

FID: 100 ppm x 0.7 = 70 ppm actual
PID: 100 ppm x 0.47 = 47 ppm actual

FID the better instrument

TCE

FID: 100 ppm x 2.8 = 280 ppm actual
PID: 100 ppm x .54 = 54 ppm actual

PID with a 9.5 eV lamp the better instrument

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Multiple Gas Mixture RF

$$RF_{MIX} = \frac{1}{\frac{\%A}{RF_A} + \frac{\%B}{RF_B} + \frac{\%C}{RF_C} + \frac{\%D}{RF_D} + ...}$$

Actual Concentration = Instrument Reading x RF_{MIX}

Multiple Gas Mixture RF

Compound	FID	9.5eV	10.6eV	11.7eV
Benzene	0.7	0.55	0.47	0.6
Ethylbenzene	1.0	0.52	0.65	0.51
Toluene	0.9	0.54	0.45	0.51
Xylenes	1.2	0.5	0.43	0.4

Benzene = 20%
Ethylbenzene = 10%
Toluene = 30%
Xylenes = 40%

Multiple Gas Mixture RF

FID RF_{MIX} = 0.95

PID RF_{MIX} = 0.45

For an instrument reading of 100 ppm (calibration gas equivalent):

FID Actual = 95 ppm

Benzene = 19 ppm
Toluene = 28.5 ppm
Ethylbenzene = 8.5 ppm
Xylenes = 39 ppm

PID Actual = 45 ppm

Benzene = 9 ppm
Toluene = 13.5 ppm
Ethylbenzene = 4 ppm
Xylenes = 18.5 ppm

The FID is the better instrument to use in this situation

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Cecil Field

Compound	Concentration (µg/L)	% of Mix	OEL (ppm)	RF_{FID}	$RF_{PID(10.6eV)}$
1,4-Dichlorobenzene	216	17.7	75	0.7	0.64
3&4-Methylphenol	5.7	0.5	2.3	4.8	1.1
Naphthalene	76.2	6.2	10	0.9	0.42
Cis-1,2-Dichloroethene	246	20.1	200	2.6	0.8
Vinyl Chloride	4.1	0.3	1	2.57	2.0
TCE	534	43.6	100	2.8	0.54
1,1-Dichloroethene	126	10.3	NA	1.23	1.0
PCE	15.6	1.3	100	1.79	0.7

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Multiple Gas Mixture RF

FID RF_{MIX} = 1.54

PID RF_{MIX} = 0.62

For an instrument reading of 100 ppm (calibration gas equivalent):

FID Actual = 154 ppm

1,4-Dichlorobenzene = 27 ppm
3&4-Methylphenol = 0.77 ppm
Naphthalene = 10 ppm
Cis-1,2-Dichloroethene = 31 ppm
Vinyl Chloride = 0.46 ppm
TCE = 67 ppm
1,1-Dichloroethene = 16 ppm
PCE = 2 ppm

PID Actual = 62 ppm

1,4-Dichlorobenzene = 11ppm
3&4-Methylphenol = 0.29 ppm
Naphthalene = 4 ppm
Cis-1,2-Dichloroethene = 12 ppm
Vinyl Chloride = 0.2 ppm
TCE = 27 ppm
1,1-Dichloroethene = 6 ppm
PCE = 1 ppm

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Multiple Gas Mixture RF

	FID RF_{MIX} = 1.54	PID RF_{MIX} = 0.62
Vinyl Chloride OEL = 1 ppm	1 ppm = 0.46 x 2.17	1 ppm = 0.2 x 5
TCE OEL = 100 ppm	100 ppm = 67 x 1.5	100 ppm = 27 x 3.7

Actual Concentration = Instrument Reading x RF_{MIX}

$$\text{Instrument Reading} = \frac{\text{Actual Concentration}}{RF_{MIX}}$$

Actual FID = 154 x 2.17= **334 ppm**

Actual FID = 154 x 1.5 = **231 ppm**

Inst FID = 334/1.54 = **217 ppm**

Inst FID = 231/1.54 = **150 ppm**

Actual PID = 62 x 5 = **310 ppm**

Actual PID = 62 x 3.7 = **229 ppm**

Inst PID = 310/.62 = **500 ppm**

Inst PID = 229/.62 = **370 ppm**

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PID/FID Comparison

Parameter	PID	FID
Ease of Use; Size and Weight	Handheld, lightweight	Bulky, heavy, requires hydrogen cartridges
Linearity	Better at lower concentrations	Good linearity throughout range
Range	0.1 to 10,000ppm	0.1 to 50,000 ppm
Compound Detection	Organic vapors and gases; some inorganic gases	Organic vapors and gases
Compound Selectivity	Increases with low energy lamps and decreases with high energy lamp, responds to functional groups	Broad sensitivity, responds to carbon chain length
Inert Matrix Gas	Measures directly in inert gas matrix	Requires oxygen presence
Sample Collection	Non-destructive	Destructive
Use	Personnel monitoring and fugitive emissions	Fugitive emissions
Reliability	Reliable, low cost, long lamp life	"Flame out" issues
Intrinsic Safety	Intrinsically safe with cold operation	Explosion-proof using a flame arrestor to isolate hot flame

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Conclusion

The appropriate use of either a PID or FID is dependent on:

- the purpose of the screening
- the compound(s) of interest
- the site conceptual model

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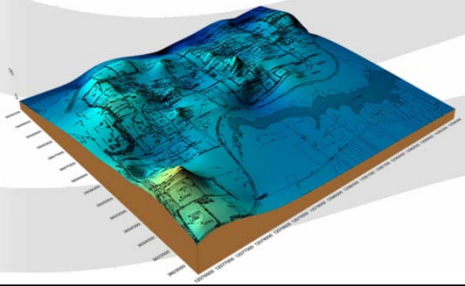

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