



Whitepaper Article

A Basic Guide To Photo-Ionisation Detectors

What Is A PID?

PID stands for “Photo-Ionisation Detector”. A PID is a sensor that can be incorporated into a hand-held, personal, or fixed detector for detecting a broad range of volatile organic compounds (VOCs) and some inorganic compounds from parts-per-billion (ppb) to thousands of parts-per-million (ppm).

They are able to give a continuous read-out and can be programmed to signal an alarm when concentrations exceed set-points.

PIDs are most commonly used for industrial hygiene measurements to ensure that workers are not overexposed to toxic compounds, along with numerous applications in these sectors:

- Oil and Gas
- Pharmaceutical and medical
- Food and Beverage
- Government and Defence
- Manufacturing
- Semiconductor manufacturing
- Construction
- Aerospace
- Water
- Power generation
- Laboratories
- Education

In this whitepaper, we discuss the facts and common questions asked regarding PIDs. We also highlight which lamp is best to use when detecting VOCs within your industries.

Key Topics:

- What is a PID?
- How does a PID work?
- Which lamp to use?
- Patented fence electrode prevents humidity problems
- Matrix effect false negative: CH₄ & H₂S
- What is a VOC and what makes a volatile detectable by PID?
- PIDs and Oxygen
- What Compounds can a PID Measure?
- What a PID Does Not Measure
- Using Response Factors (RFs)
- Programmed Response Factors
- Compound Mixtures
- Pre-Programmed Response Factors
- Concentration measurements of ppm vs mg/m³

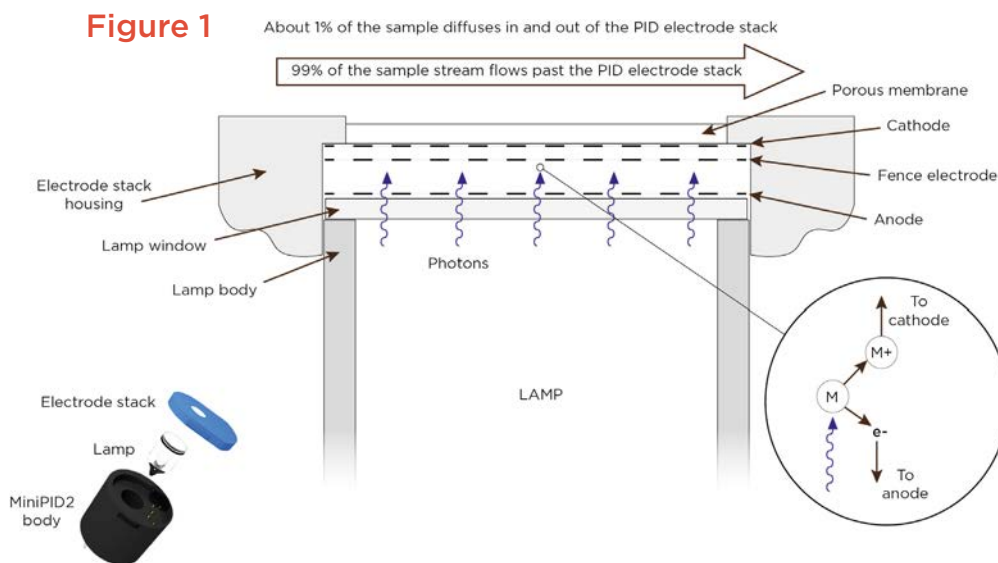




How Does a PID Work?

Figure 1 shows how an ION Science PID sensor system works. A UV lamp generates high-energy photons, which pass through the lamp window into the sensor chamber. The sample gas passes over the sensor and about 1% of it diffuses through a membrane filter into the sensor chamber.

The inset on the lower right shows what happens on a molecular level. When a photon with enough energy, strikes a molecule M, an electron e^- is ejected. The M^+ ion travels to the cathode and the electron e^- travels to the anode, resulting in a current. This current is proportional to the gas concentration. The electrical current can be displayed as a ppm or ppb concentration. Not all molecules can be ionized and the major components of air, i.e., nitrogen, oxygen, carbon dioxide, argon, etc., do not cause a response, but most VOCs do give a response.

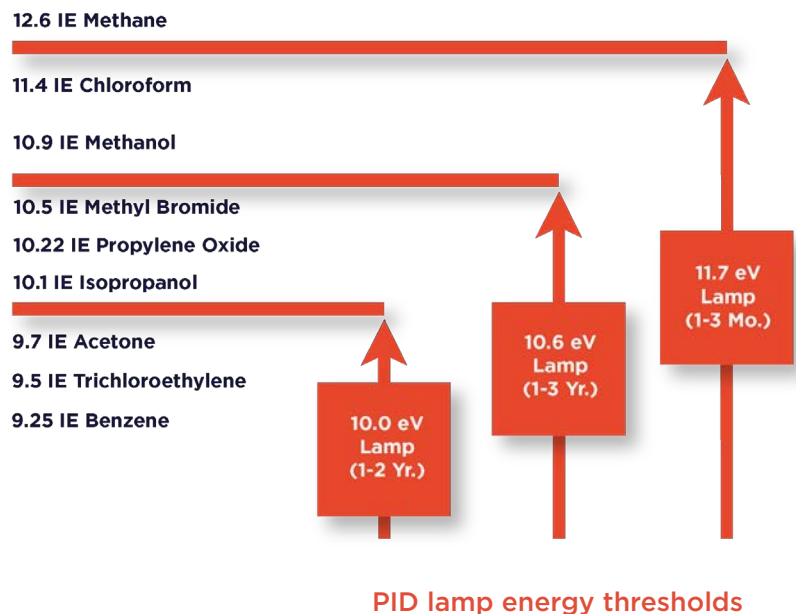




Which Lamp To Use

Three PID lamps are available from ION Science with photon energies of 10.0 eV, 10.6 eV, and 11.7 eV. **Figure 2** shows a lamp can only detect compounds with ionization energies (IE) equal to or below that of the lamp energy. So, a 10.6 eV lamp can measure methyl bromide with IE of 10.5 eV and all compounds with lower ionization energy, but cannot detect methanol or compounds with higher IE. The choice of lamp depends on the application, but the standard 10.6 eV lamp which is the lowest cost and has the longest working life of up to a few years is usually recommended. For high IE compounds like

Figure 2



Patented Fence Electrode Prevents Humidity Problems

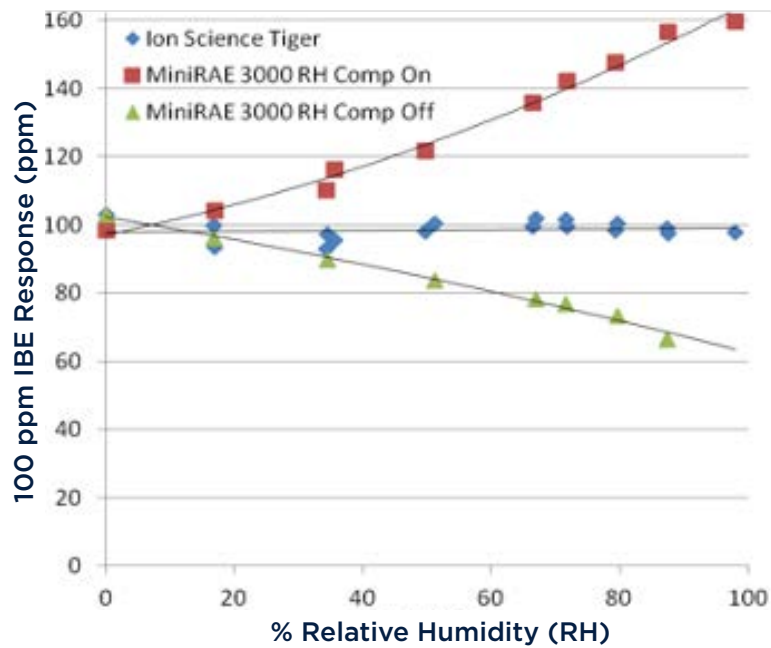
Most PIDs suffer from low readings when humidity is high, due to quenching by water vapour, and most PID manufactures use humidity compensators to alleviate this issue, both of which are demonstrated in **Figure 3**. The opposite, i.e., drifting high readings at high RH, can also occur when the sensor becomes contaminated, see **Figure 3**.



By contrast, the ION Science Tiger instrument (blue diamonds in **Figure 3** below) is not affected by humidity and requires no artificial compensation, and thus is much more reliable and accurate in normal humid air.

This feature makes ION Science PIDs especially useful for such applications as soil headspace analysis during environmental clean-ups, where the samples are both highly humid and prone to dirt and dust contamination, which creates severe problems for other PIDs.

Figure 3

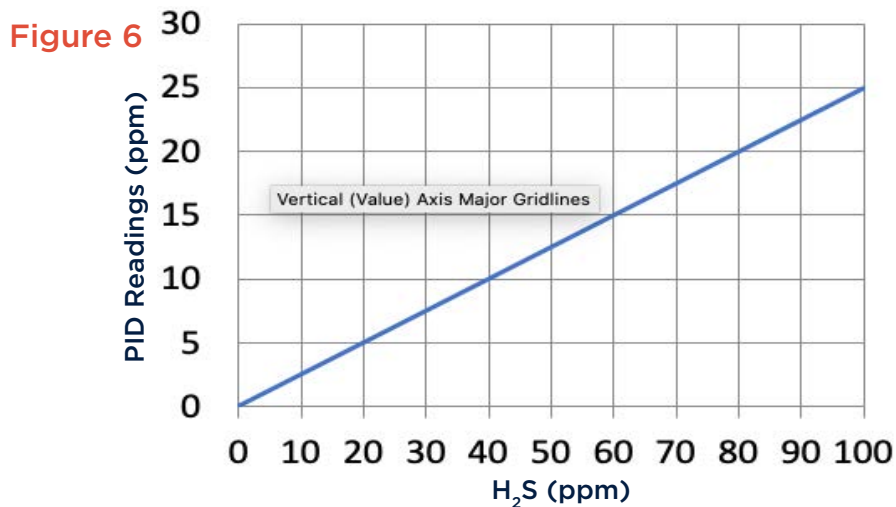
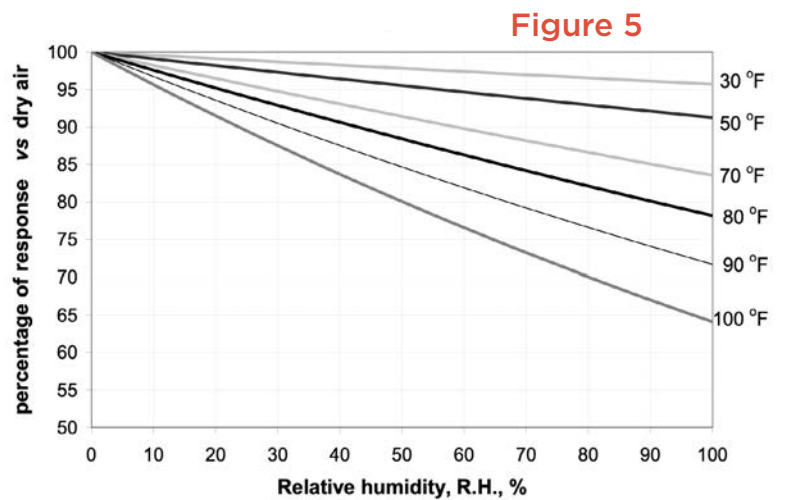
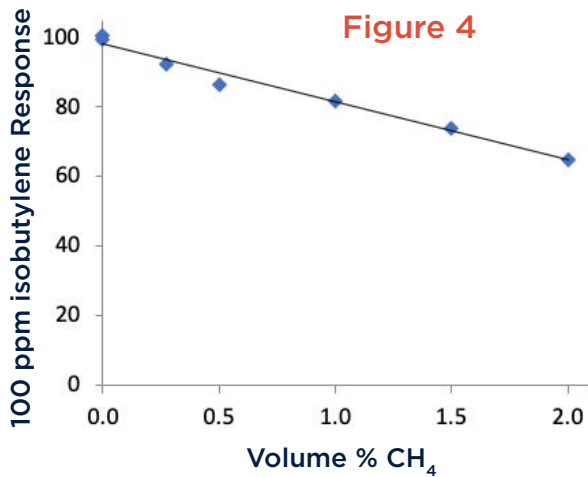


Effect of RH on Tiger and MiniRAE 3000 PIDs



Matrix Effect False Negative: Methane (CH₄) & Hydrogen Sulphide (H₂S)

While most compounds with IEs higher do not interfere with PID readings, methane can cause quenching within a sensor. While the methane molecule isn't ionised, it does absorb some of the energy, and the response is suppressed, even at concentrations as low as 2% of methane, the response can be compromised which is demonstrated in **Figure 4** and **Figure 5**. This effect is also seen with high concentrations of Carbon Dioxide (CO₂) and demonstrated in **Figure 6** with Hydrogen Sulphide (H₂S). However, if Hydrogen Sulphide is present in your environment, you can remove the effect by using a lower energy lamp (10.0 eV) to mitigate any false negative caused by H₂S.





What Is A VOC And What Makes It A Volatile Detectable By PID?

Volatile organic compounds (VOCs) are a wide range of naturally and synthetically occurring chemicals. They are described as volatile because they evaporate in conditions found on earth, releasing molecules into the atmosphere. VOCs are also extremely useful as they form the building blocks of many synthetic materials (plastics, rubbers, glues, paints etc.). VOCs also play a key part in pharmaceutical manufacturing and are a great fuel for transport and heating.

For successful detection of a VOC by PID the following 3 general criteria must be met:

1. Have less than 10 Carbon atoms
2. Have a boiling point of less than 250 °C. A boiling point between 250 and 300 °C is only marginally detectable by PID and a boiling point over 300 °C is not volatile enough for detection
3. Have a vapour pressure greater than 0.00004 (4.0×10^{-5}) mbar or 0.00005 (5.0×10^{-5}) mm Hg at 25 °C

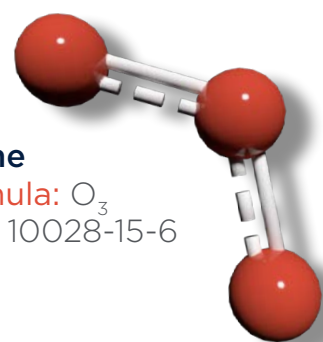
PIDs And Oxygen

PIDs are fully functional in applications where it is necessary to measure toxic compounds without oxygen present. This is useful as most electrochemical sensors and pellistor-type LEL sensors require oxygen to function.

Even though workers use breathing apparatus in such situations, it may still be necessary to measure VOCs.

VOCs are not only harmful through breathing but can be a hazard through skin exposure, or even have the potential for an explosion should air and oxygen suddenly intrude. Some chemical processes are also run in oxygen free atmospheres (inert atmospheres typically with N_2 present) and PID can be used to monitor for VOCs in these applications. However, if you are using a PID in an oxygen free environment, it should also be zeroed and calibrated on oxygen free gas.

Oxygen is also incredibly useful when using PID, as a very small amount is ionised to create ozone (O_3) which helps clean any residual contaminants from within the sensor chamber.



Ozone

Formula: O_3

CAS: 10028-15-6



What Compounds Can A PID Measure?

PIDs can detect many thousands of VOCs. The sensitivity is roughly in the following decreasing order:

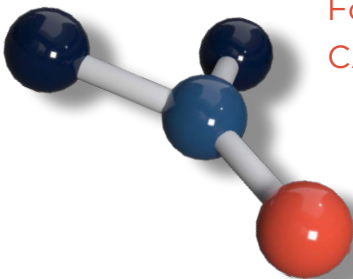
- **Aromatics**, like benzene, toluene, xylene, pyridine, phenol, aniline, naphthalene...
- **Olefins**, like butadiene, cyclohexene, trichloroethylene, vinyl chloride, turpentine, limonene cleaner...
- **Bromides & Iodides**, like methyl bromide fumigant, n-bromopropane degreaser, iodine disinfectant...
- **Sulfides & Mercaptans**, like methyl mercaptan natural gas odorant...
- **Organic Amines**, like methylamine, trimethylamine... **(prone to an unstable response)**
- **Ketones**, like acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK)...
- **Ethers**, like ethyl ether solvent, methyl-t-butyl ether gasoline additive, ethyl cellosolve...
- **Esters & Acrylates**, like ethyl acetate solvent, methyl methacrylate glues, PGMEA...
- **Aldehydes**, like glutaraldehyde sterilant, acetaldehyde, formaldehyde...
- **Alcohols**, like butanol, isopropanol, ethanol, propylene glycol...
- **Alkanes**, like hexane & Isopar solvents, octane & diesel fuels...
- **Some Inorganics**, like ammonia (NH₃), hydrogen sulfide (H₂S), and phosphine fumigant (PH₃)...

In addition, there is a varying response to chlorinated compounds, organic acids, silicate-, borate-, & phosphate- esters, isocyanates, and many others. Fuels like automotive gasoline (petrol), diesel, kerosene and jet fuels are mixtures of aromatics, olefins and alkanes, giving a good strong response.

Formaldehyde

Formula: CH₂O

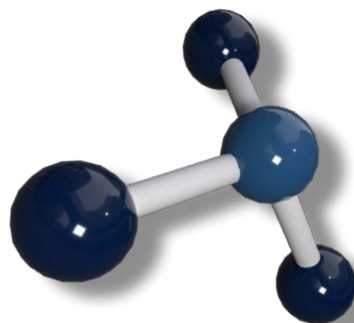
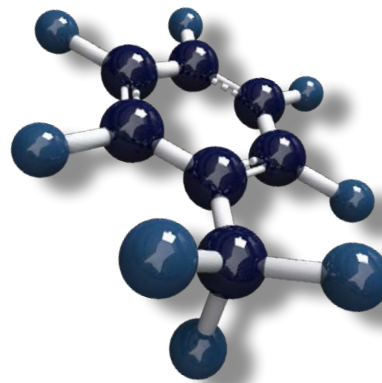
CAS: 50-00-0



Toluene

Formula: C₇H₈

CAS: 108-88-3



Ammonia

Formula: NH₃

CAS: 7664-41-7



What A PID Does Not Measure

PID will not respond to:

- **Components of Clean Air**, like nitrogen, oxygen, carbon dioxide, water vapour, argon...
- **Noble Gases**, like helium, xenon, krypton, argon...
- **Most Small Molecules**, like hydrogen, carbon monoxide, HCN, ozone, hydrogen peroxide, sulfur dioxide...
- **Natural Gas**, including methane and ethane...
- **Mineral Acids**, like hydrochloric acid, nitric acid, sulfuric acid...
- **Fluorinated Compounds**, like Freon® refrigerants, aesthetic gases, sulfur hexafluoride...
- **Non-Volatiles**, like PCBs, PAHs, MDI, greases, waxes...
- **Radioactives**, like uranium, plutonium, radon...

Using Response Factors (RFs)

When a PID is calibrated with isobutylene, the readings of other compounds need to be converted, as follows:

True concentration = PID Reading x RF

Most instruments that use PID technology will do this calculation for you if the correct RF is selected.

Table 1 gives some RF values for a few chemicals. For example, if a PID calibrated with isobutylene is used to measure benzene with a 10.6 eV lamp and the reading is 10 ppm, the true concentration is:

Benzene concentration = 10 ppm x 0.5 = 5.0 ppm benzene

If the same result is obtained with ethanol, the true concentration is:

Ethanol concentration = 10 ppm x 11 = 110 ppm Ethanol



Programmed Response Factors

TA-02 (ION Science PID Response Factors) quantitates the sensitivity of over 900 compounds in the form of response factors (RFs) relative to the response of isobutylene. While this list is extensive, it is not exclusive. It is most accurate to calibrate with your targeted VOC however it's not always readily available, making calibration with standard isobutylene gas very convenient.

Table 1: Response Factors of Example Compounds with PID Lamps

Chemical name	Alternative name	Formula	CAS no.	IE, eV	Lamp Type (RF)			notes
					11.7 eV	10.6 eV	10 eV	
Acetone	2-propanone	C3H6O	67-64-1	9.69	1.7	1.17	1.20	
Ammonia	R717	NH3	7664-41-7	10.18	5.7	8.5	NA	
Anisole		C7H8O	100-66-3	8.21	0.57	0.59	0.59	
Benzene		C6H6	71-43-2	9.24	0.53	0.50	0.54	
Camphene		C10H16	565-00-4	8.86	0.46	0.35	0.6	
Carbon dioxide		CO2	124-38-9	13.77	ZR	ZR	ZR	
Carbon disulfide		CS2	75-15-0	10.08	0.3	1.4	1.3	
Chloroform	R20	CHCl3	67-66-3	11.42	0.8	ZR	ZR	
Cyclobutanone		C4H6O	1191-95-3	9.35	1.6	1.12	1.10	
Dibromomethane	methylene dibromide	CH2Br2	74-95-3	10.41	0.70	1.9	ZR	
Ethanol	alcohol, ethyl alcohol	C2H6O	64-17-5	10.43	3	11	ZR	
Ethanolamine		C2H7NO	141-43-5	10.47	NA	3	ZR	V X
Ethylbenzene		C8H10	100-41-4	8.76	0.54	0.56	0.6	
Gasoline			8006-61-9	~9.9	NA	0.9	1	
Hydrogen sulfide		H2S	7783-06-4	10.46	1.5	4	ZR	
Iodobenzene		C6H5I	591-50-4	8.73	0.3	0.20	0.2	
Isobutylene		C4H8	115-11-7	9.24	1	1	1	
Kerosene	C10-C16		8008-20-6	~8	NA	0.8	0.7	
Methyl ethyl ketone	MEK, Butan-2-one	C4H8O	78-93-3	9.51	1.2	0.96	2	
Methyl mercaptan		CH4S	74-93-1	9.44	1	0.7	0.6	
Naphthalene		C10H8	91-20-3	8.14	0.8	0.63	0.67	
Propane-1,2-diol	propylene glycol	C3H8O2	57-55-6	10.00	5	3	16	
Propyl mercaptan		C3H8S	107-03-9	9.15	0.8	1.0	0.9	
Propylbenzene	includes cumene	C9H12	103-65-1	8.72	0.47	0.5	0.55	
Pyridine		C5H5N	110-86-1	9.25	0.9	0.7	0.87	
Styrene		C8H8	100-42-5	8.40	0.50	0.45	0.52	
TAC	Total Aromatic Hydrocarbons			~9	NA	NA	0.5	
Tetramethyldisiloxane, 1,1,3,3-	dimethylsilylether	C4H14OSi2	3277-26-7	~9	0.5	0.7	1.1	
Toluene		C7H8	108-88-3	8.82	0.55	0.56	0.60	
Toluene-2,4-diisocyanate	TDI	C9H6N2O2	584-84-9	8.82	2	1.6	NA	
Trichloropropane, 1,2,3-		C3H5Cl3	96-18-4	~11	0.64	ZR	ZR	
TVOC	Total Volatile Organic Compounds			~10	1	1	1	
Xylene mixed isomers	dimethylbenzenes	C8H10	1330-20-7	8.56	0.49	0.54	0.59	

ZR = No Response

NA = that the value is not available, because the PID response is insignificant at toxic concentrations of the volatile, or its RF is difficult to predict or measure.

V = Variable response. The response is susceptible to small changes in ambient conditions, particularly humidity.

X = Temporarily contaminating. PID responsivity may be suppressed for at least 30 min after 100 ppm-min exposure.

** Note that RFs are inverse to sensitivity, i.e., the lower the RF, the more sensitive the compound. It takes 110 ppm of ethanol to give the same 10 ppm response as 5.0 ppm benzene.*



Compound Mixtures

PID is non selective, non-discriminatory, and non-quantitative so will respond to all detectable volatiles present so it's not possible to measure the concentration of each individual VOC. When we know what is in a mixture of VOCs, the overall response factor for the mixture can be calculated as follows:

$$RF = \frac{1}{\left[\left(\frac{X_1}{RF_1} \right) + \left(\frac{X_2}{RF_2} \right) + \left(\frac{X_3}{RF_3} \right) \dots \right]}$$

where X_1 , X_2 , and X_3 are the percentages of the components within the mix of VOCs. For example, if a mixture consisted of 20% anisole (RF = 0.59), 30% acetone (RF = 1.17) and 50% ethanol (RF = 11), the overall RF would be:

$$RF = \frac{1}{\left[\left(\frac{0.2}{0.59} \right) + \left(\frac{0.3}{1.17} \right) + \left(\frac{0.5}{11} \right) \right]}$$

$$RF = \frac{1}{[(0.34)+(0.26)+ (0.05)]} = \frac{1}{0.05} = 1.56$$

This factor can then be used to reconstruct the concentration of each component. For example, to measure worker exposure near a vat generating the volatile mixture used in the above example, the PID is calibrated with isobutylene and the response factor is set to 1.56. If the overall reading is 100 ppm, then the concentration of anisole is 20 ppm, acetone is 30 ppm, and ethanol is 50 ppm.

Pre-Programmed Response Factors

Most ION Science PID instruments come pre-loaded with 900+ RFs that can be called up by the user. In that case, the display gives the concentration of the chemical directly and no extra calculations need to be done. But it should be noted that calling up an RF from the memory does not make the PID more selective for that particular chemical - it still responds to all detectable chemicals present if there is a mixture.



Concentration Measurements Of ppm vs mg/m³

PID instruments are typically configured to display measurement in ppm. ION Science detectors have the capability to also display concentrations in mg/m³. The following equation is used for the conversion (this is based on 25 °C and 1012 mbar pressure).

$$\text{Concentration} \left(\frac{\text{mg}}{\text{m}^3} \right) = \frac{\text{Concentration (ppm)} \times \text{molecular weight (g/mole)}}{24.5}$$

When an ION Science instrument is selected to display mg/m³, the instrument uses the above conversion internally and the user does not need to make any adjustments. However, the user should make sure to enter or adjust all High, Low, STEL and TWA alarm limits in the appropriate units if these are not provided by the instrument database.

For further information about RFs, see TA-02 which has an extensive list of chemicals and response factors. If you can't find the compound you require, please email info@ionscience.com with the chemical name and CAS number as we will endeavor to assist you with further details.

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