



MEASUREMENT OF CHLORINATED HYDROCARBONS BY PID WITH A LONG LIFE 11.7 LAMP

J. N. Driscoll
PID Analyzers, LLC
780 Corporate Park Dr.
Pembroke, MA 02359

1.0 Introduction

The first commercial photoionization detector (PID) was introduced in 1974 (1,2) by HNU Systems. This PID used a sealed short wavelength (121 nm/10.2 eV) UV lamp. In 1979, we introduced an 11.7 lamp in response to the need for detecting chloroalkanes for the chemical industry (VCM production) and low molecular chloroalkanes for emergency response and hazardous waste field surveys (3,4). The 9.5 and 8.3 eV lamps were developed at about the same time.

HNU developed the sealed 11.7 lamp (LiF crystal) in 1979 and extended the lifetime of the lamp from a few hundred hours to > 500 hours through the use of a unique lamp design in 1989 (5). Long term lamp storage for our 11.7 lamp has never been a serious problem. Many of our customers have had 11.7 lamps for 3-5 years. Of course, the lifetime is 600-700 operating hours due to the yellowing of the lithium fluoride crystal (from patent). The Model 102 PID warms up quickly (15 sec), so turn on the analyzer just before the measurements and turn the analyzer off as soon as the measurements are through. Some choose to use just use an 11.7 lamp because of its uniform response to VOC's. Here, the lamp typically lasts about two years. One must keep liquid water away from the 11.7 Li F window since LiF is slightly soluble in water. During operation of the analyzer, there is no effect of humidity on the response.

There is a considerable difference in response for the 11.7, 10.6 & 9.5 lamps (> 20 fold). In our earlier design with the PI101, we used different probes with appropriate sensitivities to compensate for the difference in sensitivity. These probes used a common readout base for the three different probes. Note that the 9.5 PID has approximately the

same sensitivity as the FID (6) as shown in Table I.

Table I
Comparison of the Sensitivities of the Various Heads

Sensor	Sensitivity to Isobutylene
PID 10.6	100
PID 11.7	7
PID 9.5	5
FID	5

The process of ionization which occurs when a photon of sufficient energy is absorbed by a molecule and results in the formation of an ion plus and electron:



where:

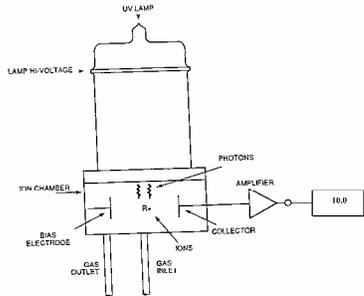
R = an ionizable species

hν= a photon with sufficient energy to ionize species R

In the ion chamber, the ions (R⁺) formed by absorption of the UV photons are collected by applying a positive potential to the accelerating electrode and measuring the current at the collection electrode. A PID consists of an ion chamber, a UV lamp with sufficient energy to ionize organic and inorganic compounds, a voltage source for the accelerating electrode, an amplifier and a readout. A schematic of a PID is shown in Fig. 1.

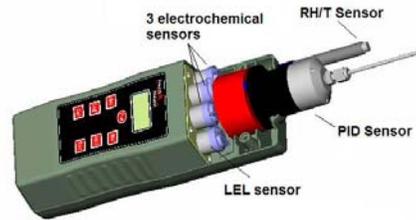
The Model 102 was introduced in 2002 as a single detector PID with Snap on 9.5 and 11.7 Heads. In 2006, the multisensor Model 102+ was introduced. It had > 7,000 points of datalogging. The new Model 102 uses

Fig. 1 Schematic of a PID



Snap-On heads in place of the old probes used with the PI101. One of the advantages

of these Heads is that there is no cable between the readout and the PID Head. The Head is simply snapped into place and the analyzer is turned on. The readout recognizes the type of head and the calibration is already stored in memory. The head has a complete PID with a HV board and an amplifier board. A library of response factors becomes available for the appropriate head that is snapped in place. The 102+ head has a 5 channel amplifier with a sensor board. New sensors (up to three) can be easily added to this Head. An additional advantage of the compact Head is that it can be easily detached and placed in a sealed plastic bag with a desiccant for storage. A fully loaded Snap-on Head/Readout is shown below.



Model 102+

Fig. 2 Model 102+ with Multiple Sensors

2. Applications

Chlorinated hydrocarbons are among the most common organic compounds found at **hazardous waste sites and landfills** (7). They pose serious long term problems because of their chemical stability (difficult to

break down by bacteria). In addition to trichloroethylene (TCE) and tetrachloroethylene (PERC), there are many breakdown products such as 1,1,1 trichloroethane (TCA), methylene chloride, chloroform and carbon tetrachloride present at these sites.

These chlorinated hydrocarbons are difficult to measure in the field at low ppm levels. An FID is sometimes used but the chlorinated hydrocarbons are converted to HCl in the reducing flame leading to instability and resulting in frequent electrode replacement because of the corrosive nature of wet HCl. If we examine some of the chlorinated organics in Table II, unsaturated hydrocarbons (VCM, TCE, PERC) can be detected with a 10.6 eV lamp in a PID but the saturated hydrocarbons have much higher ionization potentials and an 11.7 eV lamp is needed for detection. Although a PID can detect these low levels of chloroalkanes, one major difficulty with many 11.7 (sometimes called 11.8) PID's is that the lamp lifetimes maybe very short (< 30 days) so that the measurements can be very expensive and not always trustworthy.

Table II
Chlorinated Organic Compounds at Superfund Sites & Landfills

Compound	Ionization Potential (eV)	Head
TCE	9.45	10.6 or 11.7
PERC	9.32	10.6 or 11.7
Vinyl chloride	10.0	10.6 or 11.7
Dichloromethane	11.35	11.7
Ethylene dichloride	11.0	11.7
Carbon tetrachloride	11.47	11.7
Chloroform	11.42	11.7
1,1,1 Trichloroethane	11.25	11.7
Methane	12.98	None
Oxygen	13.61	None
Water	12.35	None

The PID is an ideal tool for **IH surveys** where chlorinated solvents are used. These compounds are heavier than air because of the embedded chlorine atoms and the highest concentrations are found near the ground. The PID can be used to find the problem areas, then charcoal tubes can be collected and analyzed in the lab in order to define the compounds present and their concentrations. This is the approach taken by OSHA industrial hygienists.

First Responders go to a site where little is known initially about the actual chemicals spilled so an analyzer with the broadest response & greatest flexibility is required. Here, the 11.7 lamp is ideal since it responds to chlorine, low molecular weight chlorinated organics and other VOCs. The 102+ PID can also have 3 electrochemical sensors (Cl₂, HCl & NH₃). In addition, the 102+ has snap on heads so that a 10.6 head can replace the 11.7 head. The readout unit recognizes the head and sensors and retains the PID calibrations.

Leak Detection- A required application for chemical manufacturing is leak detection and repair of valves, pumps etc to minimize leaks of monomers such as VCM (PEL = 1 ppm), EDC (PEL= 1 ppm). The VC is

detected with a 10.6 eV lamp but the intermediate material is ethylene dichloride that requires an 11.7 eV lamp. An advantage of the PID is that a 10.6 and 11.7 Head can be used for the measurements in place of two instruments (PID & FID) and the portable FID can be eliminated. One additional advantage is that the ambient methane (3-5 ppm) is not detected by the 11.7 PID.

Headspace Samples- The measurement of low concentrations (ppm levels) of organics in water or soil can be performed through the application of Henry's Law which states that, at equilibrium, the solubility of a gas in a liquid or solid is proportional to the partial pressure of a gas in contact with a liquid or solid as given below:

$$TCA (aq) = K P_{TCA}$$

where TCA (aq) is the concentration of TCA in the liquid phase, K is the Henry's Law constant which governs the solubility of gases in water or soil, and P_{TCA} is the partial pressure of TCA in the gas phase.

As a result of the above equation, it can be seen that if the concentration of TCA in the gas phase and at equilibrium is measured, this is related to the concentration of TCA in the dilute aqueous solution by a proportionality constant (K) that can be determined by calibration.

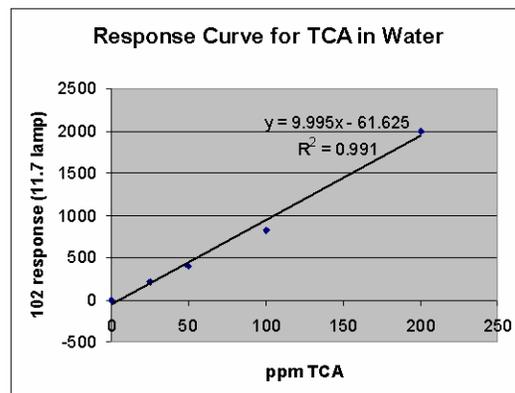


Fig. 3 Response Curve for 1,1,1 TCA in Water (headspace)

The headspace method is easy to perform, requires a minimum of equipment, and requires only that the sample and standards be at equilibrium to obtain accurate results. A typical procedure involves weighing (or measuring) 1 g of soil into a weighing boat which is placed in a container of about 40 (VOA vial) -100 cc volume which can be sealed placed in an oven at 60 °C for 15 minutes, cooled to room temperature (8). The sample can also be left at ambient (in a trailer on site, for example) for a specified period of time (approximately 1 hour). Standards bracketing the samples should be run at the same time and under exactly the same conditions. For a total hydrocarbon measurement, the vessel top is removed and a headspace reading is taken. With the Model 102, the headspace method is incorporated in the 102 software. Go to the headspace mode and press ENT, the peak height (maximum value) is measured automatically and displayed on the screen until the next reading is taken. This eliminates any operator error in the measurements. The concentration can then

be determined by comparison to a calibration curve generated from standards. A typical calibration curve for 1,1,1 trichloroethane (TCA) in water is shown in Fig. 8. Note the linear response and sensitivity of this method. Robbins (9) described a headspace method using a polyethylene bag where samples are collected in a modified one quart bag. Twenty five grams of soil are added to the bag and the bag is inflated until taut. After three or four minutes of agitation, the bag is ready to be sampled. This method will also work with water samples.

3. Summary

A stable 11.7 lamp is a key component for a PID since chloroalkanes are present in many environmental samples and cannot be detected with a 10.6 lamp. The Snap-on heads improve the flexibility of the analyzer and minimize the equipment needed for field applications. With the expansion capabilities of the 102+, there are now nearly 40

different sensors that can be added to the multisensor head.

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