

REVIEW OF PID APPLICATIONS IN INDUSTRIAL HYGIENE

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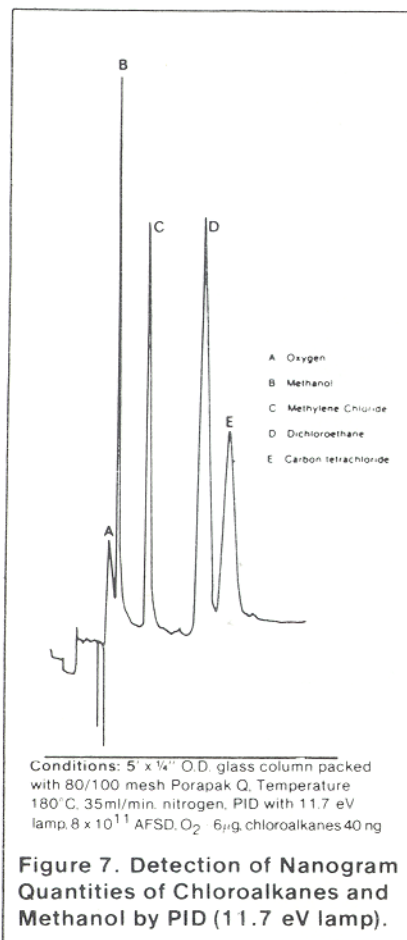
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The PID has been shown to be ideal for industrial hygiene applications because its sensitivity (with a 10.2 eV lamp) allows direct determination of many organic and inorganic vapors at ppb levels. If samples are collected on an absorbent such as charcoal, silica gel, ion exchange resin, etc., the chemicals can be desorbed with solvents such as acetonitrile, methanol and others which do not produce any solvent peak (positive response) on a PID with a 10.2 eV lamp. This feature allows the chromatography to be simplified. The PID can also be used in conjunction with an FID to allow the identification of hydrocarbon classes¹⁵ in complex mixtures.

These unique features of the PID make this detector an essential part of the arsenal of the industrial hygiene chemist.

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In order to assure compliance with OSHA regulations, companies can be required to determine the concentrations of gaseous organic vapors in work atmospheres. Initially, a preliminary plant survey should be conducted where the types and sources of solvents are located and identified (by inventory). Then a portable direct reading analyzer¹ could be used to locate the potential "hot spots" or high concentrations. At this point, the Federal Register should be consulted for the appropriate OSHA method and the criteria documents for those species should also be obtained. Another information source is the National Institute of Occupational Safety & Health (NIOSH) manual of analytical methods.²

Most analytical methods for vapor collection involve adsorption and concentration of the sample on a solid sorbent such as charcoal, silica gel, ion exchange resin, porous polymers, etc., enclosed in glass or metal tubes. The total volume of air (sample) drawn through the collection media is controlled by the flow-rate of a calibrated pump and the sampling time. Following sample collection, the tubes are capped and returned to a laboratory for analysis by gas chromatography.

The worker can wear the pump and collection tube to determine his actual exposure for an 8 hour work day or the pump and collection tube can be left in an area to determine a worker's exposure for that particular sampling point.

Once in the laboratory, the tube contents are placed in a container and desorbed either with a solvent or thermally. The sample is then injected into the gas chromatograph (GC) for subsequent analysis.

A flame ionization detector (FID) mounted on a GC is frequently used for analysis. While the sensitivity of this detector is sufficient for many compounds, it can be less than adequate for those compounds with low threshold limit values (TLV's) particularly if short sampling times are required. If one wanted to quickly screen an area by collection (with no concentration) of the sample in a Teflon bag and direct injection into the chromatograph, a detector with ppb sensitivity is required.

The photoionization detector (PID) clearly meets the additional sensitivity requirements since it has been shown³ to be 10-50 times more sensitive than an FID. In addition, the dynamic range of the detector is $>10^7$ so that the high levels can also be determined.

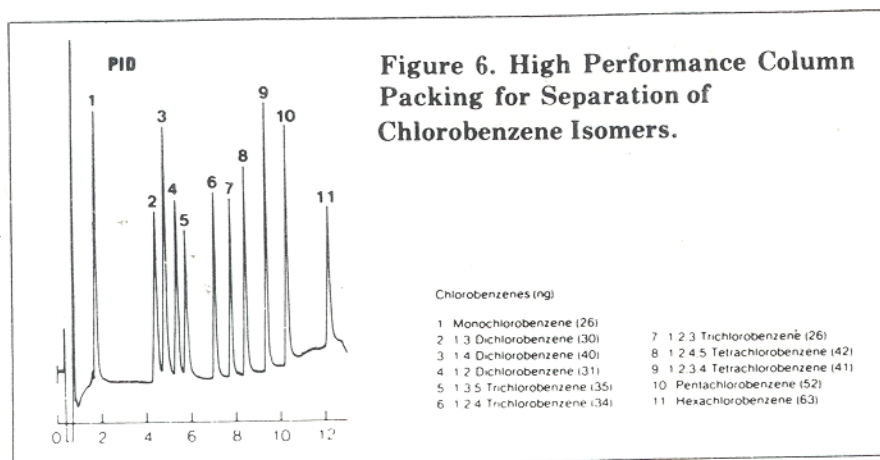
The following sections describe the PID and a number of applications and methods for this detector in industrial hygiene.

Instrument Description

These results were obtained with an HNU Systems Model PI-52-02 photoionization detector with a 10.2 or 11.7 eV lamp installed. A photograph of the PID is shown in Figure 1. An HNU model 401 gas chromatograph⁴ with an appropriate column was used for the separations. The chromatograms were recorded on a Linear Instruments Model 261 recorder.

The carrier gases were either high purity nitrogen or helium. A molecular sieve/charcoal trap was maintained in the carrier gas line to prevent buildup of hydrocarbons and maintain low backgrounds.

The solvent used was acetonitrile (Resi-Analyzed from J. T. Baker Co.) and samples were injected with Hamilton Model 701 syringes. Gas samples were injected with Hamilton 1000 series gas tight syringes.



A method for collection of amines on silica gel and elution with a methanol/water mixture was evaluated by Woods et al.¹¹ The sensitivity of the PID versus the FID was determined for a variety of primary amines. The PID was found to be from 15-66 times more sensitive than the FID. The major difficulty was found to be with the chromatography on the column (10% Carbowax 20M treated with 2% KOH on 80/100 mesh Chromosorb WAW). Tailing and asymmetric peaks were obtained for the underivatized primary amines. The final procedure involved the formation of benzylidene derivatives to eliminate the excessive tailing. A recent development in gas chromatography column technology¹² should provide a support inert enough to allow the direct determination of amines without derivitization.

A method for the determination of chlorobenzene (monochloro through hexachlorobenzene) isomers in air at ppb levels using the PID was described by Langhorst and Nestruck.¹³ The procedure involves collection/concentration of the chlorobenzenes on Amberlite XAD-2 resin followed by desorption with carbon tetrachloride and analysis by gas chromatography with a PID. The separation of 11 different chlorobenzene isomers (Figure 6) was achieved on a specially prepared column (Synerg CTM coated with PEG 40M, available from HNU Systems). Collection and desorption efficiencies were found to be $95 \pm 12\%$ (2σ) between 5 ppb and 15 ppm. The detector was found to be linear for chlorobenzenes over more than

five orders of magnitude. Another interesting feature found¹³ was that the relative molar response in the PID for chlorobenzene isomers was the same regardless of the degree of chlorination.

Moeckel et. al.¹⁴ evaluated the PID for industrial hygiene monitoring in the pharmaceutical industry. They were interested in a single detector which would respond to nitrogen and sulfur compounds as well as hydrocarbons. They found increased sensitivity and linearity for sulfur compounds analyzed by the PID rather than the FPD. In addition, nitrogen compounds (methyl amine) could also be determined at low levels. Their use of the PID included direct analysis of low ppm levels and analysis of pollutants desorbed from silica gel or charcoal tubes. A further use of the non-destructive characteristic of the PID involved collection of unknowns from the PID effluent for mass spectral identification.

Although the majority of the applications previously discussed have employed the 10.2 eV lamp, other interchangeable lamps are also available for use with the PID. The 9.5 eV lamp will provide more selectivity but an order of magnitude less sensitivity. The 11.7 eV lamp, again less sensitive than the 10.2 eV lamp in a PID provides response to low nanogram levels of small chlorinated hydrocarbons such as CCl₄, which have high ionization potentials (IP 11.47 eV). The chromatogram in Figure 7 depicts the separation and detection by PID (11.7 eV) of some low molecular weight chlorinated hydrocarbons which do not respond to the PID with a 10.2 eV lamp.



Figure 1. Model PI-52-02 Photoionization Detector

PID Operation and Description

The principle of operation, termed photoionization, results from absorption of a photon of ultraviolet radiation by a molecule (R) and subsequent ionization via the following process:



Where $h\nu$ is a photon with an energy \geq the ionization potential (IP) is Species R.

The detector shown in Figure 2 consists of a sealed interchangeable UV lamp that emits a photon with a specific energy (9.5, 10.2, 10.9, or 11.7 eV depending on the UV lamp). Photons in this energy range are

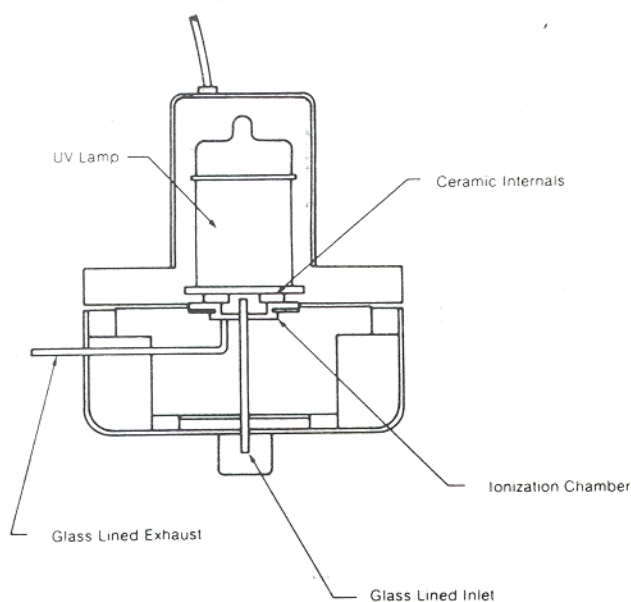


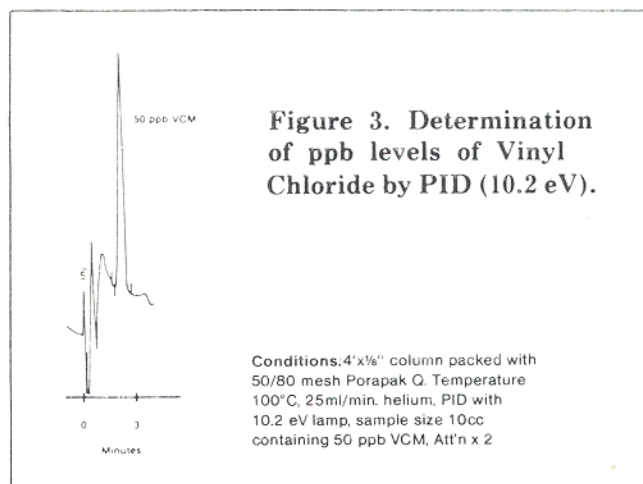
Figure 2. Schematic Drawing of PID.

energetic enough to ionize many organic and some inorganic species but do not ionize compounds such as N_2 , CO, CO_2 , H_2O , or He. An ionization chamber adjacent to the UV source contains a pair of electrodes for acceleration and collection of ionized species. The current measured at the collection electrode is directly proportional to the concentration of the species being measured and linear over a wide range ($>10^7$ with a 10.2 eV lamp).

Any compound with an IP lower than the lamp energy will respond in the PID. Molecules with IP's up to 0.3 eV higher than a given lamp energy will also respond although with a lower efficiency. A short list of IP's for a series of compounds was given in reference 1 but a more detailed list is also available in reference 5.

Applications

One of the earliest environmental applications for the PID was its sensitivity to ppb levels of vinyl chloride monomer.⁶ With the threshold limit value (TLV) of vinyl chloride reduced to 1 ppm, a sensitive detector was needed to allow direct injection and detection of ppb levels without sample concentration. The PID was found to be 40 times more sensitive than the FID for vinyl chloride.³ A typical chromatogram of VCM at the 50 ppb level is shown in Figure 3.

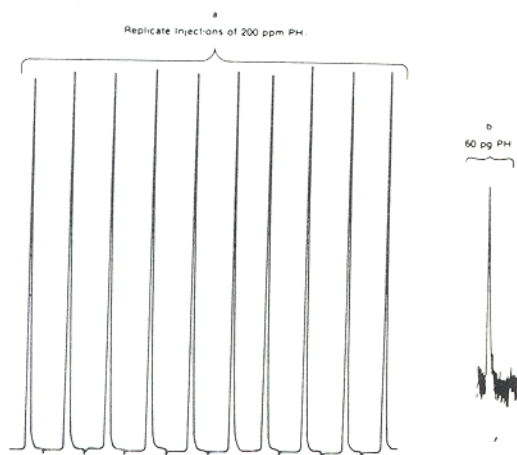


The PID also responds to many inorganic species and provides lower limits of detection (LLD's) that match or exceed those obtainable with other detectors. A few of the LLD's for some inorganic compounds are shown in Table I. The wide dynamic range ($>10^7$) of the PID allows the detector to be used for analyzing ambient (TLV's), trace levels, or high concentrations.

TABLE I
LLD's For Selected Inorganic Compounds
with the PID

Compound	LLD (pg)
H ₂ S	15
PH ₃	20
I ₂	25
NO	52
NH ₃	200
AsH ₃	25

The sensitivity and LLD for phosphine was about five times better than the flame photometric detector (FPD). Figure 4 demonstrates the reproducibility of measurements made with the PID; the relative standard deviation (RSD) for the ten replicates in Figure 4 was $\pm 0.15\%$. The chromatogram (4b) obtained by injecting 60 pg PH₃ clearly demonstrates the sensitivity of the PID to PH₃.



Conditions: 1.5m x 4mm glass column packed with Porapak P, Temperature 90°C, 30ml/min. nitrogen, PID with 10.2 eV lamp.

Figure 4. Analysis of Phosphine by PID (10.2 eV).

The PID is one of the most sensitive GC detectors available for sulfur compounds. The data in Table II demonstrates the sensitivity obtained for some low molecular weight sulfur compounds. Typically, the PID is an order of magnitude more sensitive to these

TABLE II
LLD's for Low MW Sulfur Compounds by PID

Compound	LLD (pg)
H ₂ S	15
(CH ₃) ₂ S	20
(CH ₃) ₂ S ₂	22
CH ₃ SH	20
CS ₂	30

sulfur compounds than the FPD. A typical chromatogram for picogram levels of H₂S is shown in Figure 5. The PID has a linear response over its entire range⁷ rather than the square root response observed with the FPD.⁸ Kramer et al⁷ found the PID response to be linear from 0.1 to 1000 ppm for H₂S and a number of the other sulfur compounds investigated.

Smith and Krause⁹ developed a procedure employing the PID/GC (with a Porapak QS Column) for analysis of charcoal tube samples containing CS₂. The desorption of CS₂ from charcoal with acetonitrile was found to be nearly 100%. Acetonitrile is a particularly good solvent for the PID because it does not produce a positive response. The advantages of the PID were found to be ease of operation, wide dynamic range, linear response and sensitivity. The latter feature allows shorter sampling times. The relative standard deviation (RSD) for 100 replicate samples was found to be $\pm 2\%$.⁹

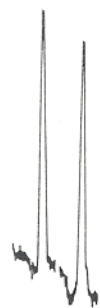


Figure 5. Detection of Picogram Quantities of Hydrogen Sulfide by PID (10.2 eV).

Conditions: 4.5' x 4mm i.d. glass column packed with 80/100 mesh Poropak P, Temperature 150°C, 40ml/min. helium, PID with 10.2 eV lamp, 1x10¹² AFSD, 100 pg H₂S

A procedure for tetraethyl lead (TEL) analysis was developed by A. D. Little, Inc.¹⁰ which involved collection on Amberlite (XAD-2 resin), desorption with pentane and analysis by PID/GC. The lower limit of detection found for TEL with the PID was 150 pg with a 10 by 5% Carbowax® 20M column used for separation. For a TEL concentration of 0.5 TLV (~ 0.038 mg/m³), a two hour sample was found to yield 200 times the detection limit for the PID. The RSD for multiple TEL samples was $\pm 2.5\%$.