

Chapter 4

Photoionization

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Introduction

A photoionization detector (PID) is a non-specific chemical detector that can provide airborne concentration information for any chemical which may be ionized by a high energy ultraviolet (UV) light source. This type of detector has been used for quantitative field sampling in workplaces and hazardous waste sites, leak detection, work practice evaluations, decontamination screening, ventilation monitoring, and military preparedness. This chapter provides insight into the history of photoionization detectors, theory of PID operation, and examples of PID use to solve human exposure problems.

A PID signal is generated when a target analyte molecule in the gas phase absorbs UV energy and releases an electron to form a positively charged ion. Ion current generated this way is measured, and quantitative detection is possible as the number of ions produced is directly proportional to the airborne concentration of a target compound. Lamps with different UV light energy levels may be used, with 9.5, 10.6, and 11.7 eV being the most common. The amount of energy needed to strip an electron from any chemical substance is a unique property of that substance and thus different

target analytes will each have a specific ionization potential (IP) value. A user must know the IP value for an airborne chemical that is to be detected, as a PID will not be useful for compounds with IP values which exceed the energy level of the specific UV lamp that is used.

History of Photoionization

In the mid- to late-1960s, photoionization (PI) was investigated to provide a low-energy mass spectrometry (MS) ion source that would minimize fragmentation and produce simple mass spectra.⁽¹⁾ As discussed in Chapter 10, a conventional high energy (70 eV) electron ionization (EI) source imparts sufficient energy to a molecule so that considerable fragmentation and complex mass spectra result.⁽²⁾ Driscoll and Warneck experimented with PI-MS for more than 50 organic compounds and demonstrated that very simple mass spectra were produced for most of these.⁽³⁾ Figure 4.1 compares PI and EI mass spectra for benzene, and it can be seen that the PI spectrum shows ion current only related to the benzene molecular ion (M^{+}) with mass-to-charge ratio (m/z) of 78, while the EI spectrum shows ion current at this and numerous lower m/z values from fragmentation of M^{+} .

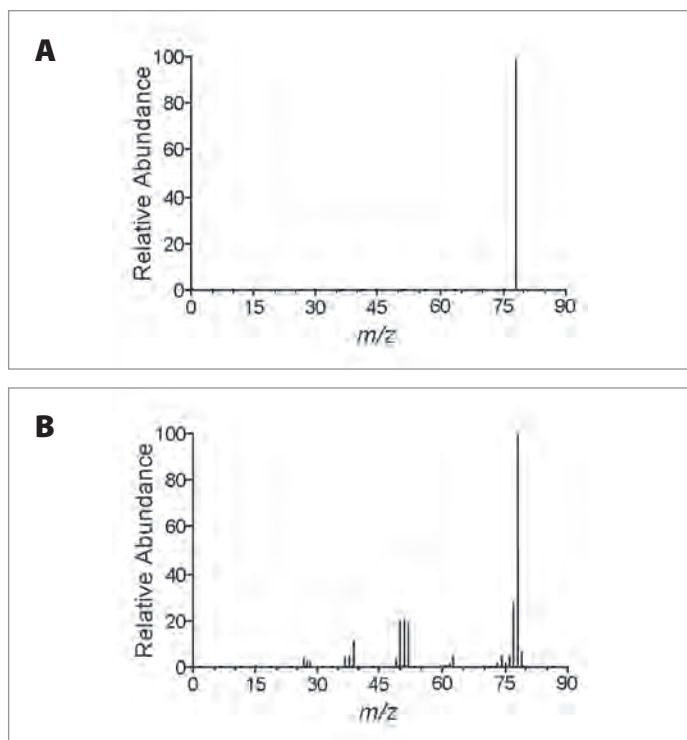


Figure 4.1 – A, PI mass spectrum for benzene; B, EI mass spectrum for benzene.

Detection limits using PI in early studies completed by Driscoll and Warneck were in the high ppm range⁽³⁾, and the mass spectrometer used was a large magnetic sector instrument that occupied an area of nearly 5 m² and weighed more than 180 kg. The ability to create simple mass spectra (often with only a single m/z value corresponding to M^{+} for a given analyte) would allow a mass spectrometer with a PI source to simultaneously measure a number of pollutant gases without the need for separation (e.g., by the use of a gas chromatographic inlet – see Chapter 9). However, the low sensitivity and large mass of the instrumentation package initially used limited the suitability of the method for ambient gas measurements.

The promising start of PI as an alternative to the traditional 70 eV EI-MS ion source was closing for a time by the early 1970s. Chemical ionization (CI, described in Chapter 10) had supplanted PI as a soft MS ionization method due to ease of use and the greater production of analyte ions with CI compared to the early PI source designs which relied on a monochromator that limited the intensity of transmitted UV light. However, a new application for PI was emerging. By connecting a sealed UV light source (a resonance lamp) to an ionization chamber, a compact detector could be created that would respond to many organic analytes at low ppm levels, while operating at atmospheric pressure.

Lower Occupational Exposure Limits Catalyze Acceptance of New PID Instrumentation

The first portable handheld PID was introduced in 1974 at the American Industrial Hygiene Conference & Exposition (AIHce) in Miami, FL. The HNU Model PI101 PID (see Figure 4.2) was battery operated, weighed 7.5 pounds and responded to many (but not all) volatile organic compounds (VOCs). A major discussion topic at the 1974 American Institute of Chemical Engineers meeting was the impending decrease in the U.S. Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for vinyl chloride monomer (VCM) from an interim 8-hour time weighted average (TWA) value of 50 ppm to a proposed value of 1 ppm. In a period of just over one year, the VCM PEL was reduced from 500 ppm to 1 ppm due mostly to a finding that exposure to VCM resulted in liver cancer.⁽⁴⁾



Figure 4.2 – HNU PI101 handheld PID instrument.

Portable combustible gas sensors had previously been used for monitoring VCM when the PEL was 500 ppm, and then when the PEL was reduced to 50 ppm the flame ionization detector (FID, see Chapter 7) became the instrumental method of choice. At 1 ppm concentrations however, neither a combustible gas sensor nor a FID could measure VCM exposure as background levels of methane are commonly 2–4 ppm (200–400% of the 1 ppm VCM PEL). Century Systems introduced the OVA instrument to overcome this FID limitation by adding a portable gas chromatography (GC) inlet and recorder to a FID. Once the background methane signal could be separated from that of VCM by the GC inlet (see Chapter 9), VCM and ethylene dichloride (EDC, an intermediate product) could be detected by FID, however this analyzer was more difficult to operate. A PID, with 10.6 eV lamp, proved to be an ideal instrument system for the detection of VCM as a PID does not respond to methane which has an IP value of 12.98 eV, nor to EDC (11.04 eV IP), allowing a PID detection limit of 0.1 ppm for VCM.

In 1974, more than 90% of world production of VCM occurred at a plant in Paducah, Ky. When the principal VCM manufacturer adopted the handheld PID as the method of choice for VCM monitoring at this location, plants all over the world adopted it for use in polymerization kettle entry protocols. The PID could also be used for finding leaks in valves, fittings, and process pipes. When these were found and corrected early, the levels of VCM around the plants were lowered and employee exposure to VCM was reduced. The PID was also used in conjunction with continuous GC air analyzers; if the VCM level was seen to increase in a particular area, a handheld PID could then be used to find the leak.

In the mid-1970s, the HNU Model PI101 photoionization analyzer and the Century OVA128 FID analyzer were widely used for leak detection and industrial hygiene measurements of hydrocarbons and other VOC compounds at ppm levels. Both were analog instruments with no data logging capability, but each could be used with an optional strip chart recorder. The PID approach offered several benefits compared to FID. While an FID requires a supply of hydrogen, a PID requires no auxiliary gases for operation. In addition, a PID may be used to detect airborne analytes at lower concentrations compared to a handheld FID (without GC separation), and a handheld PID has a faster response time than a GC-FID combination. When used for leak detection the latter two attributes resulted in the capability to quickly detect small leaks and correct them, resulting in lower exposures to personnel.

The first significant improvement to the handheld PID described in U.S. patent 4013913⁽⁵⁾ involved shielding of the collection electrode with a UV-opaque material to eliminate background current that occurs due to the photoelectric effect upon an unshielded electrode. The use of a sealed lamp window was relatively new, and this allowed a PID chamber to be operated at atmospheric pressure, improving stability and sensitivity. Also, shortly after the HNU PI101 was introduced, ion chamber geometry was optimized to provide greater field strength. These improvements resulted in a very stable PID with a wide dynamic range and low baseline noise. The PI101 detector provided a stable UV ionization source with low power requirements (< 1 watt) and high output intensity, was easy to use and very sensitive. As a result, more than 25,000 were sold and some are still in use in 2013. The PI101 used analog circuitry and can still be repaired nearly 40 years after it was introduced. A digital version, DL101 was introduced in 1989.

PID Use for Hazardous Waste Remediation and Spill Response

In the mid to late 1970s, Love Canal, near Buffalo, New York, became one of the first, and perhaps most infamous hazardous waste sites. Both handheld PID instruments (model PI101), and portable GC with PID (HNU model PI52 detector for GC) were used by the NY State Department of Health to survey homes, soil, and groundwater at the Love Canal site. In 1978, the U.S. Environmental Protection Agency (EPA) formed the Rapid Response Team located at Edison, New Jersey to respond to chemical release emergencies such as train derailments or other large chemical release incidents.⁽⁶⁾ This national group of responders became influential in analytical method development and for development of procedures to protect the health and safety of workers at hazardous material release or contamination sites.

Collaborative efforts between the U.S. National Institute for Occupational Safety and Health (NIOSH), Coast Guard, OSHA, and the EPA led to publication of the *Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities*⁽⁷⁾ in 1985, with both handheld PID and GC-FID instrumentation prominently mentioned in the air monitoring chapter of this manual. This interagency work has been credited with the eventual issuance of the OSHA hazardous waste operations and emergency response standard⁽⁸⁾ in 1989 to improve safety for workers at hazardous waste remediation sites, and for emergency responders to hazardous material releases. In 2005 Driscoll discussed the history of PID instrumentation as used for hazardous waste site responses, and described its role in field analysis methods for these locations.⁽⁹⁾

Widespread Adoption of PID Instrumentation

By the 1980s, additional manufacturers began to offer handheld PID instrumentation to meet a growing demand, digital control and data output became available, and the number of manufacturers increased further in the 1990s. Photovac (since acquired by Inficon Inc.) offered the handheld TIP PID instrument in the mid-1980s. The Foxboro Company (since acquired by Thermo Electron Inc.) entered the market with a combined PID/FID analyzer in the 1990s that weighed nearly 15 pounds, and employed a shoulder strap to allow for person-portability. RAE Systems Inc. began offering several small PID instruments in the mid-1990s and at about this time PID instruments combined with lower explosive limit detection and several electrochemical sensors (i.e., a four-gas meter) were introduced. Ion Science Ltd. began offering small PID instruments in the late 1990s.

While the handheld PID has gone on to become an important and widely-used stand-alone instrument for chemical detection, the use of PID technology for lab-based instrumentation and for field-portable GC instruments has also progressed. At the 1976 Pittsburgh Conference (Pittcon™) the first GC-PID instrument, the HNU Model 311, was introduced. For analytes such as aromatic compounds the detector used was reported to be up to 50 times more sensitive than conventional GC-FID instrumentation.⁽¹⁰⁾ In 1982, Bond and Dumas described the use of a PID-equipped Photovac 10A10 gas chromatograph to measure phosphine fumigant concentrations in the field at a grain elevator⁽¹¹⁾, and many additional examples of field-portable GC-PID instruments and their use have been described, including in the recent literature dealing with person-portable GC as reviewed by Smith.⁽¹²⁾

Returning to the early roots of PID development in the 1990s, the soundness of the early ideas put forward by Driscoll and Warneck to use PI as an MS ion source⁽³⁾ has been confirmed. Atmospheric pressure photoionization (APPI) began to grow in importance for the mass spectrometric detection of drugs and biomolecules following separation by high performance liquid chromatography (HPLC). When a modern APPI source is used the HPLC liquid stationary phase is vaporized after it elutes from the HPLC column, target analytes are ionized in the gas phase, and the ions are then introduced into the high vacuum region of a mass spectrometer for mass analysis.⁽¹³⁾ Based on advances in instrumentation design that have occurred since the early experiments completed by Driscoll and Warneck⁽³⁾, field-portable PI-MS instrumentation has also been introduced, for example an instrument package designed to detect dangerous chemicals in water as described by Syage *et al.* in 2006.⁽¹⁴⁾

Photoionization Detector Theory

A schematic of a PID is shown in Figure 4.3. A PID consists of a UV lamp which produces photons of several specific energies, an ion chamber, a voltage source for an accelerating electrode, an ion collection electrode, an amplifier, and a means to read the detector response. While the operating principles of a PID are fairly simple, a number of factors can influence the ionization and ion collection processes, and these are discussed below.

Photoionization Process

The photoionization process is initiated when a high energy UV photon is absorbed by a molecule. When the IP of the

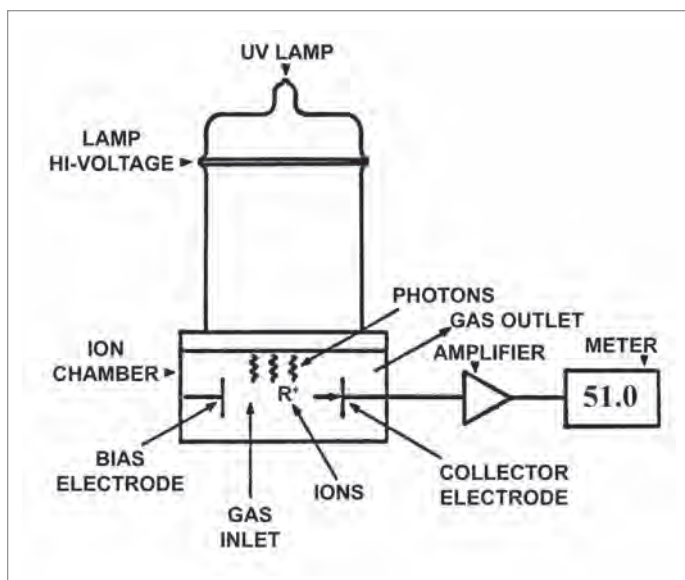


Figure 4.3 – PID schematic showing the major instrument components. Provided courtesy of PID Analyzers LLC, used with permission.

molecule allows, the photon energy causes an electron to be ejected and a positive molecular ion is formed. In the ion chamber, the ions formed by the UV photons are repelled away from an accelerating electrode by a positive potential (100–200 V), and arrive at a collector electrode. The ion current produced at the collector electrode is proportional to analyte concentration over a wide range. A stronger electric field between the accelerating and collector electrodes will result in collection of more ions and increased sensitivity. For a PID with axial geometry the strength of this field is described by Equation 4-1:

$$E = \frac{V}{2.3 r \log a/b} \quad (4-1)$$

In Equation 4-1, V is the applied voltage between the collector of radius a and the accelerating electrode of radius b , and E is the electric field strength at any point in distance r from the center of the accelerating electrode. The field strength increases rapidly as r approaches b .

The IP of a specific chemical discussed earlier is the amount of energy required to move an electron to an infinite distance from the nucleus thus creating a positive ion. As a general rule, the smaller the molecule, the tighter the electrons are bound resulting in a correspondingly higher IP value, while lower IP values are seen for larger molecules or molecules with increasing numbers of double bonds. As a lamp with lower energy is used, the detector will respond to fewer compounds and thus the detector selectivity will increase. The response for the photoionization analyzer is the sum of the chemical species in the sampled air that may be ionized

by the appropriate lamp (9.5 eV, 10.6 eV, or 11.7 eV). Table 4.1 lists IP values for the major constituents of air, and some representative contaminant compounds. Note that ionization of each major air component would require more than 12 eV, and while PID response will generally extend to compounds having IP values 0.1 to 0.3 eV higher than the lamp energy, the major air component IP values are all too high for ionization by any of the commonly used UV lamps.

Table 4.1 – Ionization potentials of major and minor components in air, and several volatile contaminants.

Substance	Ionization potential (eV)	PID Response
Nitrogen	14.54	—
Oxygen	13.61	—
Carbon Dioxide	13.79	—
Water Vapor	12.35	—
Methane	12.98	—
n-Hexane	10.13	+
1-Hexene	9.44	+
Benzene	9.25	+
1,1,1-Trichloroethane	11.00	A ⁺
Trichloroethylene	9.47	+

^ARequires 11.7 eV lamp

In contrast to a 9.5 eV lamp that responds selectively to analytes with low IP values, a lamp that operates at 11.7 eV may respond to more compounds and is more useful to warn of airborne analytes at hazardous waste sites and for first responders when the hazards are unknown. Due to the short life span of an 11.7 eV lamp, most PID work uses 10.6 eV lamp-equipped instrumentation. Driscoll has described fundamental aspects of the PID for use a GC detector⁽¹⁵⁾, and these are also relevant for its use as a stand-alone detector. The PID is a carbon counter (molar response increases with carbon number) like an FID, however there are several differences that often make the PID more suitable for use as previously discussed. Figure 4.4 provides a summary of the effect of UV energy on select chemical compounds.

PID Lamp

The use of a sealed lamp allows photoionization to occur at atmospheric pressure with high-energy short wavelength light from the vacuum UV region. Equation 4-2 describes the relationship between wavelength (λ) and photon energy (E):

$$\lambda = \frac{hc}{E} \quad (4-2)$$

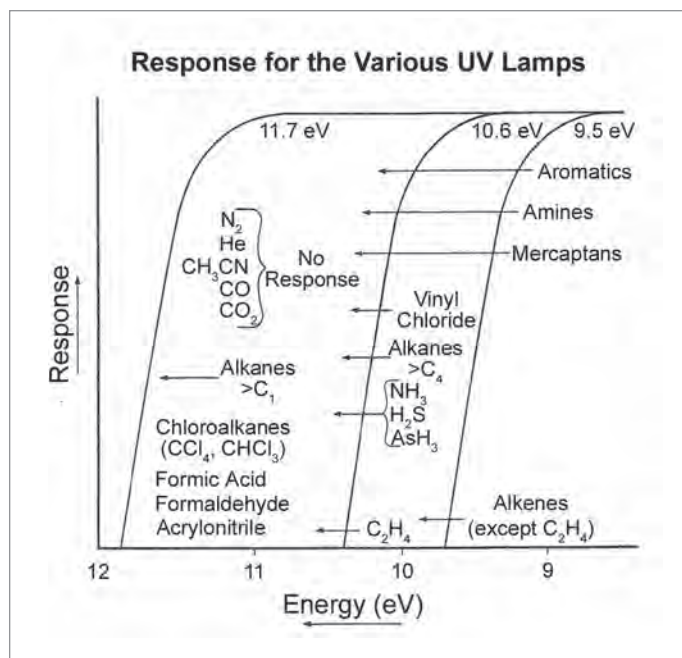


Figure 4.4 – Effect of UV lamp energy on PID response. Provided courtesy of PID Analyzers LLC, used with permission.

In this equation, h is Planck's constant and c is the speed of light in a vacuum. When the numeric values for these terms are included, Equation 4-3 results:

$$\lambda \text{ (nm)} = \frac{1,240}{E \text{ (eV)}} \quad (4-3)$$

The selection of gas to be used within the sealed lamp assembly determines the energy of a given lamp, and this is described by the most energetic photons produced by the specific gas used. For example, when krypton gas is subjected to resonant excitation it emits at several discrete wavelengths, with an intense line at 123.6 nm (10.0 eV), but with the highest energy level (10.6 eV) due to a less intense emission line at 116.5 nm. The lamp gases used for 9.5 and 11.7 eV lamps are xenon and argon with 129.6 and 104.8 nm emission lines respectively providing the highest energy levels in each.

The gas pressure in a lamp is selected to avoid difficulty in lamp starting, and self-absorption of photons by the lamp gas. Lamp window material is selected to allow transmission of UV photons and a reasonable life span where possible. Materials commonly used for 9.5, 10.6, and 11.7 eV lamp windows are magnesium fluoride (9.5 and 10.6 eV), and lithium fluoride (11.7 eV). The relatively short lifetime for an 11.7 eV lamp is related to the properties of the LiF window used with this lamp, as it is subject to discoloration caused by interaction with UV photons. Resonant lamp gas excitation may be accomplished with direct current (DC) discharge, or by the

use of a radiofrequency (RF) coil. The DC discharge approach requires electrodes embedded within the glass lamp body, and the lamp gas is in direct contact with these electrodes. The RF coil approach allows for easier lamp manufacturing, as the coil is simply wrapped around a glass lamp and no metal components penetrate into the lamp interior.

Effect of Non-Ionizable Chemicals on Photoionization

While a gas with a high IP value (e.g., oxygen, IP = 13.61 eV) is not detected by a PID equipped with a lamp of lower energy, the atmospheric concentration of such a gas can affect PID response. In 1977, Driscoll described a negative GC-PID peak that was attributed to electron capture by oxygen eluting at the detector from the GC column. The O_2^- created through electron capture was thought to react with and neutralize background ions formed in the detector that otherwise provided a nearly constant baseline response in the absence of eluting analytes.⁽¹⁰⁾ Senum explored this phenomenon by completing GC-PID analyses of oxygen and several additional gases, and produced negative peaks with oxygen, nitrous oxide, carbon dioxide, and methane.⁽¹⁶⁾ The reductions in PID signal resulting from oxygen and carbon dioxide were attributed to the electron capture mechanism first described by Driscoll, as these molecules have very low absorption coefficient values for the relevant UV photons. Nitrous oxide and methane are not only electron absorbing species but are also known to have high absorption coefficients, and thus these affected the chromatographic baseline both by attenuating the UV photon excitation energy, and through electron capture ion quenching.

As with nitrous oxide and methane, water vapor also has a high absorption coefficient value for UV wavelengths relevant to a PID lamp⁽¹⁷⁾, and the effect of water vapor on PID readings is well known. Chelton *et al.*⁽¹⁸⁾ described a loss of PID sensitivity when sampling high humidity air compared to dry air in 1983, and Barsky *et al.*⁽¹⁹⁾ described similar results in 1985. In 2007, Smith *et al.* reported the use of two types of PID instruments to detect sarin vapor in both dry and humid air, with the airborne analyte concentrations confirmed by sorbent tube sampling and GC-MS analysis.⁽²⁰⁾ The PID instruments produced linear data when sampling from both dry and humid air, but as with earlier results^(18,19) the calculated sarin response factors were much higher for the humid air measurements as a result of decreased sensitivity.

In line with the GC-PID data reported by Senum⁽¹⁶⁾, Nyquist *et al.*⁽²¹⁾ described a decrease in the sensitivity of a handheld PID instrument to toluene and gasoline vapors related to the

presence of elevated methane concentrations in sampled air. At concentrations of 0.5% (5000 ppm) and 5% (50,000 ppm) methane, the expected readings produced by a 10.6 eV PID instrument fell by 30% and 90% respectively. In 1994, Mouradin and Flannery reported on the use of different calibration gases stated to contain the same VOC concentrations, that produced different readings when analyzed by a portable VOC detector.⁽²²⁾ To investigate, the contents of each calibration gas cylinder were analyzed by laboratory GC-FID instrumentation, and while the manufacturer's stated VOC calibrant concentrations were found to be accurate, the oxygen concentrations of the two cylinders were eventually found to be different. The use of a handheld PID to detect 350 ppm isobutylene in gas mixtures with varied oxygen content demonstrated that the response varied substantially with oxygen concentration (See Figure 4.5), and the authors showed similar results for an FID instrument. Based on these results Mouradin and Flannery noted that "calibration of a portable PID or FID with a span gas that contains oxygen levels different from normal ambient air could lead to significant measurement errors." The PID results obtained by Mouradin and Flannery are consistent with the observations of Driscoll⁽¹⁰⁾ and Senum⁽¹⁶⁾ where electron capture by oxygen results in production of O_2^- that quenches analyte ions before they can produce ion current at the collector electrode. While the effect of water vapor and oxygen content on PID response has been the subject of PID design modifications by several instrument manufacturers, the user of a handheld PID should be aware of the potential for deviation from expected results when a PID is calibrated at an oxygen or water vapor concentration different than in the atmosphere to be sampled.

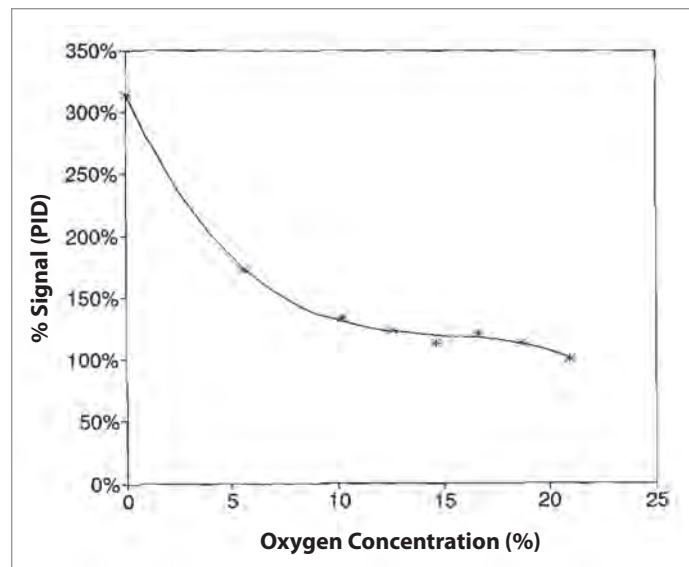


Figure 4.5 – Effect of oxygen concentration on handheld PID response to isobutylene. From Mouradin and Flannery.⁽²²⁾

PID Measurement of VOC Analytes

PID Calibration

Calibration of a handheld detector is necessary to verify instrument performance and to allow collection of quantitative data with a reasonable degree of confidence, and calibration gas mixtures which have had calibrant concentrations verified through careful analysis may be purchased from a variety of suppliers. The handheld PID is often calibrated using isobutylene in air, dispensed from a small compressed gas bottle. When a PID calibrated this way is subsequently used to detect other gases or vapors without further data handling, the response will be read in isobutylene equivalent units. If a target airborne analyte provides the same relative response as isobutylene, then the corresponding response factor will be 1. If two different target analytes respond exactly twice and one-half as strongly as isobutylene at the same concentration they would each have response factors of 0.5 and 2 respectively. This relationship can be described mathematically for a PID calibrated using isobutylene that is then used to measure different concentrations of a target analyte to determine relative response:

$$RF = \frac{1}{m} \quad (4-3)$$

Where RF is the response factor for that airborne analyte, and m is the slope of the PID response for that analyte in isobutylene units plotted against the actual analyte concentration sampled. The RF may also be calculated as follows for a single point comparison:

$$RF = \frac{R_s}{R_A} \quad (4-4)$$

In Equation 4-4 R_s is the PID response for the calibration standard (e.g., isobutylene), and R_A is the response for analysis of the same concentration of the target analyte. This single point RF determination assumes that a constant RF value exists across a range of varied and equal concentrations of both isobutylene and the target analyte.

Following calibration with isobutylene, when the identity of a target analyte with a pre-determined RF value is known, the actual analyte concentration measured by the PID is obtained when the reading in isobutylene units is multiplied by the RF value for that analyte. While this RF correction may be completed manually, a modern handheld PID calibrated with isobutylene may also be programmed to measure a known target analyte selected by the user. When used this way the



Figure 4.6 – Model 102+ handheld PID (right), with an interchangeable head (left) that may be used to quickly switch between UV lamps of different energy levels. Provided courtesy of PID Analyzers, used with permission.

RF correction is completed by the instrument and the actual target analyte concentration is displayed on the instrument readout. It must be emphasized that designation of the target analyte assumes that the PID is responding only to that analyte, and the user must verify that this analyte is actually present, and that other ionizable species are not present. Gas mixtures with other calibrant gas or vapor compounds may also be purchased for calibration of a PID instrument, and PID control firmware of some manufacturers allows calibration with any gas or vapor that has an entry in the onboard RF library. For example, the Model 102 or 102+ PID manufactured by PID Analyzers (Figure 4.6) may be calibrated this way.

Static Calibration using a Large Volume Syringe

When an RF value is not available for a fairly volatile solvent but a sample of the solvent is available, quantitative standards may be created using a two liter gas-tight syringe. In general, ppm levels can be prepared with little difficulty using a 10 μ L liquid syringe to deliver a precise solvent volume for evaporation within the larger syringe after it has been filled with a suitable gas.

$$\text{ppm} = 10^6 \frac{(V_L) \times (SG) \times (V_G)}{(MW) \times (V_S)} \quad (4-5)$$

In Equation 4-5, V_L is the volume of liquid solvent delivered (mL), SG is the specific gravity of the solvent (g/mL), V_G is the molar volume of an ideal gas at the prevalent temperature and pressure conditions (L/mole), MW is the solvent molecular weight (g/mole), and V_S is the volume of gas held within the large syringe. Using this equation, preparation of a calibration curve is a relatively easy task that can be accomplished using incremental volumes to cover the desired concentration range, while recording the resulting PID readings in isobutylene units. The samples prepared in the large syringe can be diluted with room air or with zero air depending on the ultimate PID analysis needs, and the resulting solvent vapor concentrations should be within 5–10% of expected values, with the largest source of error being the accurate delivery of the liquid solvent material into the gas within the large syringe. This procedure works best with volatile liquids, but the syringe can be mildly heated with a hair dryer to assist with evaporation of less volatile liquids.

Calibration using Pressurized Cylinders

A cylinder equipped with an accurate pressure gauge and inlet and outlet shutoff valves may be filled at atmospheric pressure (14.7 psi) with a known concentration calibration gas mixture. If the cylinder is subsequently pressurized to a higher pressure (without exceeding the rated safe pressure of the vessel) using clean gas with no calibrant, the resulting concentration of the calibrant is described by Equation 4-6:

$$C_f = \frac{C_i \times 14.7 \text{ psi}}{P_f} \quad (4-6)$$

where C_i is the initial calibrant concentration, C_f is the final calibrant concentration and P_f is the final pressure in the cylinder after addition of the clean gas diluent.

Dynamic Flow Permeation Tube Calibration

A dynamic calibration method may also be employed with a measured volumetric airflow through a system where a target analyte is introduced at a constant rate. Permeation tubes are very useful for generating low ppm or ppb levels of VOC analytes, and are commercially available for more than 300 different chemicals. The manufacturer-supplied permeation rates are determined by measuring the constant temperature weight loss of a tube loaded with the target analyte over time (typically several months). The temperature-dependent

permeation rate is provided by the manufacturer as mass of analyte loss/unit time, and while in use a permeation tube is maintained at a stable temperature in an oven to maintain a constant diffusion rate. Diffusion through a membrane is driven by the concentration gradient between the inside of the tube and the external environment, and when a permeation tube is swept with clean air or another gas at a constant rate the mass of calibration analyte/volume of diluent gas is easily calculated to provide the final analyte concentration. This dynamic calibrant generation method may be used with diluent gases that contain different amounts of water vapor, and since the standard generating system is dynamic with continual input from the permeation tube it may be assumed that adsorption of analyte to surfaces in the standard generating system will equilibrate with volatilization from such surfaces to provide a stable and accurate airborne analyte concentration.

PID Use in the Field

Handheld PID instrumentation is commonly used for the detection of VOC analytes at low ppm levels. In addition to many “typical” hydrocarbon-based VOC compounds, a PID responds to a number of other compounds such as CS_2 , tetraethyl lead (and other metal alkyls), and halogen gases such as I_2 and Br_2 (10.6 eV lamp) and Cl_2 (11.7 eV lamp). Hydrides of nitrogen (e.g., ammonia), sulfur (hydrogen sulfide), selenium, phosphorus, arsenic, and antimony may also be detected by PID. Many of these analytes are quite toxic, and where they are commonly used or found a handheld PID is a good candidate for routine detection and measurement for health protection. The early PI101 PID instrument shown in Figure 4.2 was used in 1975 to detect the infiltration of solvents into homes in the Love Canal area, and to protect the health of the workers establishing the extent of the problem. Nearly forty years later, handheld PID instruments are still being used to complete this type of field detection mission, and in many other ways as describe below.

First Responders

While first responders such as firefighters routinely use four-gas meters to test for oxygen and explosibility, a need exists beyond that capability for rapid detection of a wide range of dangerous airborne chemicals or contamination in emergency situations. As first responders are not air sampling/chemical detection specialists, an ideal detector to address this need must be easy to operate, must not require special gases for operation, nor extensive maintenance. Patel *et al.* studied the use of handheld instrumentation by minimally-trained firefighters in a simulated chemical

contamination triage scenario, and described advantages of PID instrumentation for contamination detection.⁽²³⁾

The device could be used as a tool which would improve current decontamination protocol and enhance the safety of emergency personnel. The practice of mass decontamination could be refined by the ability to pinpoint and prioritize victims who are actually contaminated. This has the practical effect of reducing the number of people requiring full decontamination and allowing for the prioritization of those most affected. Emergency personnel may benefit from the ability to better identify casualties that present a potential inhalational hazard through secondary “off-gassing.”⁽²³⁾

The need for simple contamination detection capabilities for first responders and emergency medical personnel became evident in 1995 due to the well-known release of the chemical warfare agent sarin in the Tokyo subway system. Emergency response and medical personnel were overwhelmed by this terrorist attack, which resulted in 10 deaths and over 5,000 individuals reporting to local medical facilities.⁽²⁴⁾ Substantial secondary contamination was documented among first responders and emergency medical staff. For example, most of the doctors treating patients in the Keio University School of Medicine emergency department showed symptoms of organophosphorous nerve agent poisoning.⁽²⁵⁾ and the benefits of PID screening described by Patel *et al.* may have helped to deal with the emergency situation more effectively.

Figure 4.7 demonstrates the speed with which a handheld PID responded to organophosphorus contamination on cloth material compared to a widely-used handheld ion mobility spectrometry (IMS, see Chapter 6) instrument which is used by numerous military organizations for detection of volatile chemical warfare agent compounds. Not only did Smith *et al.* show that the PID instrument responded much more quickly to the contaminant than the IMS detector, but it also cleared down much more quickly when it was moved away from the source of contamination.⁽²⁰⁾ The primary reason for the differences observed is the use of a polymer membrane inlet in the IMS-based instrument, while a PID employs a direct ion chamber inlet. One potential problem with the direct PID inlet is the possibility that the PID lamp window may be contaminated, resulting in the need for cleaning, and while the IMS instrument responds more slowly the membrane inlet used in the IMS detector does eliminate this maintenance requirement.

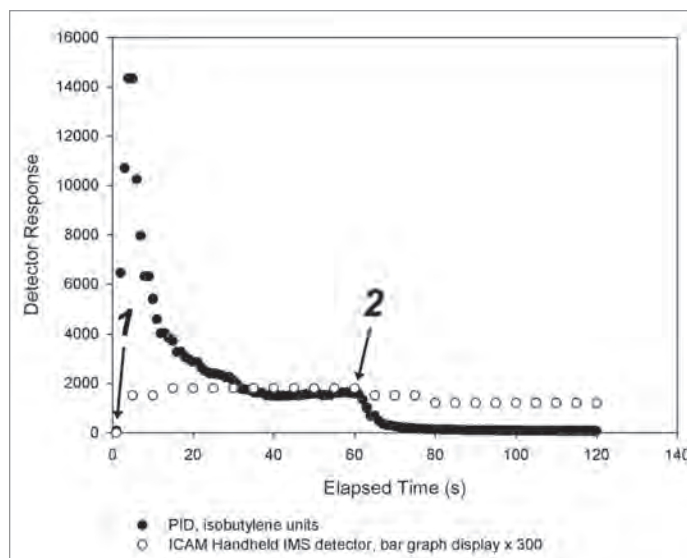


Figure 4.7 – Comparison of response and recovery time difference between PID and a hand-held ion mobility spectrometer; **1** two μL dimethyl methylphosphonate placed on cloth material within 1 cm of inlet for both instruments at time = 0 s, **2** both instrument inlets removed away from contamination at 60 s elapsed time. From Smith *et al.*⁽²⁰⁾

Leak Detection and Process Hazard Mapping

As described previously, an important factor that drove early development and commercialization efforts for handheld PID instruments was the need to measure airborne VCM in near real-time at newly lowered PEL concentrations. The HNU PI101 was well-suited for this task, and could also be used to detect VCM leaks and releases. Handheld instruments (often PIDs) are commonly used for process leak and emission detection⁽²⁶⁾, and Rao *et al.*⁽²⁷⁾ described the use of a PID instrument to determine VOC concentration maps for a refinery.

Industrial Hygiene Measurements

In order to use a handheld PID instrument quantitatively in an industrial hygiene survey, it is necessary to have advance knowledge of any VOC materials in use to verify that IP values for specific chemicals will allow detection. The goals of an industrial hygiene program typically include protection of workers based on acceptable exposures to both long duration (e.g., 8-hour TWA) and short duration concentration profiles. As discussed in Chapter 2, a small detector with datalogging capabilities is well suited for task-exposure investigations, where timed video recording or careful note taking may be used to correlate worker activities with short-duration periods of relatively high exposure. Earnest described the use of PID instrumentation in a dry cleaning shop, combined with video recording to “analyze tasks, code data, and determine which worker activities and movements

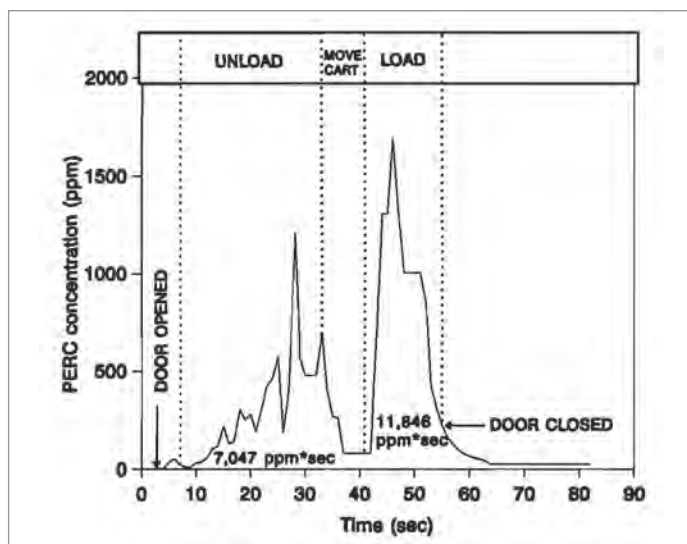


Figure 4.8 – Operator exposure during dry cleaning machine loading/unloading.⁽²⁸⁾

resulted in the highest exposures.⁽²⁸⁾ Figure 4.8 shows PID data reported by Earnest for elevated worker exposures to perchloroethylene associated with loading items into a dry cleaning machine, and unloading of cleaned items.

Handheld PID instrumentation may also be used as an industrial hygiene survey tool to locate areas in a worksite with the highest concentration profiles for airborne contaminants to guide further sampling for analyses using laboratory-based methods. This approach was described by Goyer, who used a PI101 instrument equipped with an 11.7 eV lamp to determine the best locations for area air samples to be collected in a pulp mill.⁽²⁹⁾ Goyer found that the handheld PID allowed unanticipated emissions from pipe joints and valves to be identified and corrected, and that PID area concentration readings were highly correlated to airborne pinene concentrations determined by charcoal tube sampling and laboratory GC analysis.

Hazardous Waste Sites

The OSHA hazardous waste operations and emergency response (HAZWOPER) standard was developed during the major Superfund activities of the nineteen eighties to improve worker protection at these sites.⁽⁸⁾ One of the more important uses of PID instrumentation at a hazardous waste site is monitoring of airborne contaminant concentrations for worker protection, but a broad-response handheld detector also provides important capabilities for site characterization. A few years after the promulgation of the HAZWOPER standard Wesolowski and Alwan described a field analysis approach for environmental remediation activities

where a handheld PID was used to rapidly scan a site to identify contaminated areas.⁽³⁰⁾ Other more sophisticated field-portable detection gear or laboratory-based analysis methods could then be selected as required. Karl *et al.*⁽³¹⁾ used handheld PID instrumentation to locate areas where large diameter core samples would be collected at a site where trichloroethylene had contaminated groundwater. They obtained small diameter (~1.6 cm) core samples from the large diameter soil core samples and the small core samples were immediately transferred to sealed vials for laboratory GC-based analysis. To expedite the analysis process and improve the resulting data quality the sampling probe of a handheld PID instrument was inserted into a hole in the larger core sample material near the location of the sample to be analyzed by GC, and a PID reading was obtained. The PID results were used to estimate the dilution solvent volume needed so that GC analysis results would fall within the linear calibration range of the laboratory GC instrumentation used. This eliminated the need to handle the samples repeatedly or to re-analyze samples with trichloroethylene concentrations outside the bounds of the laboratory GC instrument calibration.

The early availability of field-portable GC-PID instrumentation that operated without additional detector gases resulted in the use of this hyphenated technology to complete on-site analyses at numerous hazardous waste sites, and this type of instrumentation will be discussed below.

Indoor Air Pollution

The energy crisis of the early 1970s resulted in efforts to lower energy use for heating and cooling in buildings. This was typically accomplished by significantly reducing the number of ventilation air exchanges per hour in occupied spaces. The type of information provided by a handheld PID instrument (response to total airborne VOCs) is useful in determining ventilation effectiveness, problems with outgassing of solvents from construction materials, or identification of a source of indoor air contamination, such as a copying machine.

In 2000, Stefaniak described the use of pocket PID instruments and sorbent tube sampling to provide an estimate of average total VOC exposure and exposure variability during workshifts in several university copy centers where thousands of copies per day were made.⁽³²⁾ The PID data were useful to determine the minute-to-minute fluctuations in total sub-ppm VOC concentrations which were not measurable from analysis of the sorbent tube samples. In 2001, Lee *et al.* reported the use of PID instrumentation to

measure total VOC emissions from various computer printers in an emission testing chamber.⁽³³⁾

In some cases, poor indoor air quality is related to external contamination sources, such as a material release or a leaking underground storage tank. Kullman and Hill used a PID instrument to determine the location of gasoline vapor intrusion into a public office building in Morgantown, WV. Traditional sorbent tube samples were subjected to laboratory GC analysis to identify the hydrocarbon air contaminants that were ultimately found to be leaking from abandoned underground gasoline storage tanks that the building owner did not realize were present on the property.⁽³⁴⁾ Moseley and Meyer used a PI101 instrument to create a three dimensional map of total hydrocarbon readings in soil around a school that had been evacuated due to flammability readings taken there that approached the lower explosive limit. A metal rod was used to create small diameter holes in the soil into which a 0.5" diameter hollow steel tube was inserted, and total ionizable hydrocarbon readings were taken with the PID from air pulled through the steel tube. The information obtained is shown in Figure 4.9, along with the location of a nearby home and the leaking gasoline storage tank that caused the problem.⁽³⁵⁾

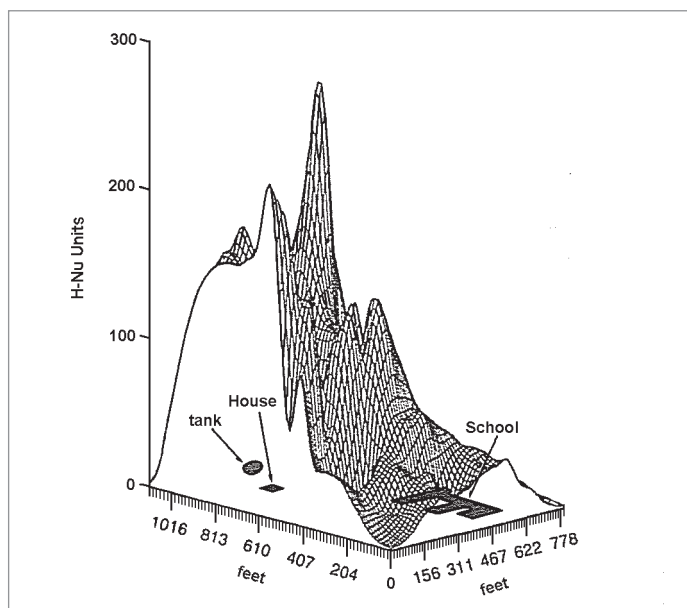


Figure 4.9 –Peak soil total ionizable hydrocarbon readings relative to the locations of a leaking gasoline storage tank, and nearby home and school. Reprinted with permission from From Moseley and Meyer.⁽³⁵⁾ Copyright (1992) American Chemical Society.

Field-Portable GC-PID

A GC-PID instrument is classified as a dual or hyphenated analytical technology that merges two separate techniques to produce a new configuration that takes advantage of their individual capabilities. Chapter 9 of this book deals with field-portable GC, and the general usefulness of GC to separate multiple analyte signals in time is discussed there. Separation occurs on the GC column, and the analyte signal must be produced by a detector situated at the end of the column. Numerous GC detectors are discussed in Chapter 9, including PID, but the use of a PI-based GC detector is especially important for field-portable GC instruments since it is the only widely-used high-sensitivity, broad response GC detector that does not require an auxiliary gas for operation. The FID is also a widely-used GC detector that responds to virtually all hydrocarbon analytes, but it requires a supply of pure hydrogen to produce a flame. Coupling compatible GC and PID analytical methods in tandem (GC-PID) has provided improved trace chemical detection with low detection limits and improved quantitative response. The simple operating principles of a PID, and the ability to operate without an auxiliary detector gas has made GC-PID attractive for field detection and quantitation studies, for which the PID has been used since the 1970s. In addition to the individual GC and PID components, a GC-PID system requires a GC carrier gas supply and a computer data system which may be built into onboard GC-PID electronic circuitry. In a GC-PID instrument, GC column effluent is introduced into the PID over a period of minutes. Since a PID is a non-destructive detector, it is possible to run this detector in-series with many other types of detectors to identify hydrocarbons (FID), nitrogen compounds (nitrogen/phosphorous detector), halogen compounds (electron capture detector), sulfur or phosphorous compounds (flame photometric detector), etc. Target analyte compounds may be quantitated by either the more selective detector or the PID.

The separation provided by the GC column simplifies the chemistry within the ionization region, ideally by eluting one compound at a time into the detector. Thus, product ions can be formed without competitive ionization interferences or unexpected UV photon absorption, eliminating the effect that high humidity, high background methane, or high or low oxygen in ambient air may have if a handheld PID is used.⁽¹⁸⁻²²⁾ Figure 4.10 shows a characteristic two-axis chromatogram from the analysis of VCM in air with a field-portable GC-PID instrument. In this chromatogram the x-axis denotes a GC retention time and the y-axis denotes PID signal intensity.

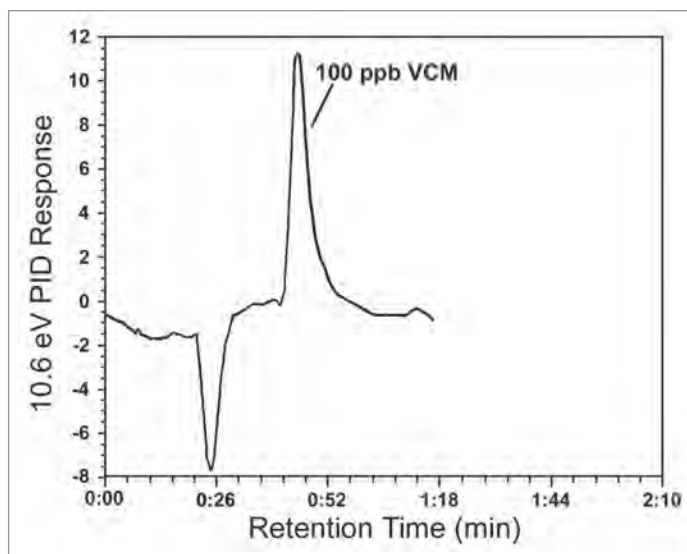


Figure 4.10 – GC-PID chromatogram obtained from analysis of 100 ppb vinyl chloride monomer (VCM) in air. Open tubular fused silica column (7.5 m x 0.32 mm i.d., 10 μ m methylsilicone film).

The negative peak prior to the elution of VCM is due to signal quenching from the presence of O_2 in the sampled air as previously discussed^(10,16), and this graphically demonstrates how the use of a separation method prior to detection provides a signal for a target analyte that is not influenced by other components present in the gas sample analyzed.

Some of the early person-portable GC instruments in the 1970's used short packed columns and no temperature control⁽¹¹⁾ but with < 50 theoretical plates, only simple separations were possible. With 6' packed columns, one can achieve separations representing about 500–1,000 theoretical plates. In the early 1980s Dandeneau and Zerenner⁽³⁶⁾ described the benefits of fused silica as the basis for an extremely inert capillary column. When an open tubular thin walled fused silica column with small diameter (e.g., 0.32 mm i.d.) is coated with a protective material on the exterior (polyimide), the result is a strong flexible high-performance column that is considerably easier to use in a GC instrument. This revolutionized capillary column GC and greatly expanded the potential for its use in field-portable instrumentation.

A properly made capillary column of 5 m length will have resolving power of about 12,000–15,000 theoretical plates, more than 30 times the resolving power of a short packed column that occupies a similar volume within a GC instrument. Before the advent of high performance capillary columns the separation of gases such as VCM or ethylene required columns packed with porous polymers or heavily loaded liquid phase on a solid support. With thick film

capillary columns available now (3–10 micron stationary phase film thickness), the separation of a light analyte such as VCM is now easily accomplished with a capillary column as shown in Figure 4.10.

GC-PID Instruments and Applications

Many of the examples provided in Chapter 9 involve GC-PID instrumentation. Bond and Dumas (1982)⁽¹¹⁾, Wesolowski and Alwan (1992)⁽³⁰⁾, Tang *et al.* (1995)⁽³⁷⁾, and Sweet *et al.* (2004)⁽³⁸⁾, described the use of various GC-PID instruments for field analysis, and two NIOSH analytical methods are based on the use of field-portable GC-PID instrumentation.^(39,40)

As an example of a commercially-available GC-PID instrument the Model 312 (Figure 4.11) is enclosed in a heavy duty suitcase, weighs about 25 pounds and may operate on battery power for 5-6 hours, or indefinitely if an automotive power source (i.e., a cigarette lighter outlet) is available. This instrument uses an internal pressurized cylinder that contains about 30 liters of carrier gas to provide 15–25 hours of operation depending on whether a packed or capillary column is used. A high pressure refill adapter is used to charge the cylinder through a quick disconnect fitting. Onboard digital data acquisition and data handling are provided by an integrated computer and a proprietary software package. Two sample introduction methods are possible: (1) a syringe (liquid or gas sample) injection port, or (2) an automatic injection that employs a 6 or 10 port valve



Figure 4.11 – Model 312 person-portable GC, equipped with PID.

for introduction of external gas and vapor samples. Other detectors are available in addition to a PID, including a FID, or a far UV detector⁽⁴¹⁾ which responds to nearly any analyte that elutes from the column. The chromatogram shown in Figure 4.10 was produced by a PID-equipped Model 312 instrument. A widely-recognized GC-PID instrument was manufactured in the past by Photovac (since acquired by Inficon). The Voyager™ was commercially-available until recently, and it could be equipped with a PID and an electron capture detector.

Although one can establish the identity of target analytes and relative concentrations in the field by collection of air samples on a solid sorbent and sending samples to a laboratory for detailed analysis, it is possible to perform this analysis in the field “in real-time” with a portable GC instrument and not wait 2–3 weeks for the laboratory analysis results. A portable GC-PID instrument can provide on-site detection at low (ppb) levels and identification as far as possible (by retention time only), of specific components present. This instrument can be used in conjunction with a handheld PID for site characterization as discussed by Wesolowski and Alwan⁽³⁰⁾ to identify the hot spots, with portable GC analysis completed where the faster, simpler instrument indicates the most contamination exists. The use of direct reading instruments in the field is convenient and allows the industrial hygienist to confront and solve problems concerning worker safety in near real-time. The array of PID and other handheld detectors found in level 2 of Figure 1.5, combined with field-portable GC instrumentation (level 3) provide a useful supplement for laboratory tests, help obtain better quality data, ensure proper worker protection, and help solve difficult problems more quickly.

Conclusion

The historical details related to development of the PID as both a stand-alone and GC detector, the early use of PID technology, and the eventual widespread adoption of PID instrumentation for measurement of airborne contaminants parallel important historical milestones in occupational safety and health and environmental protection. The PID has been used to minimize worker exposure to hazardous materials in chemical, petrochemical, and pharmaceutical plants, and many manufacturing processes that use solvents. Its sensitivity and rapid response time enable a PID user to quickly find the source of a potential problem and fix it. These instruments have proven to be a very useful for monitoring total VOC compounds in the workplace, and

in other locations where indoor air quality measurement is necessary. In the hands of a skilled industrial hygienist, a PID can be used to monitor intake air on a continuous basis, improve ventilation rates in a plant or building, provide an instantaneous readout of total hydrocarbon concentration in a work environment, measure the total concentration profiles over time in a selected area in conjunction with sorbent tube sampling, and to identify contamination sources and work practices that lead to elevated exposures for even brief periods. Additional sensors are available on some PID instruments to provide multi-pollutant detection capabilities for analytes such as carbon dioxide, carbon monoxide, hydrogen cyanide, and others that a PID alone will not detect. Hyphenated GC-PID field-portable instrumentation can allow laboratory-quality results to be obtained in the field, eliminating site characterization or worker protection delays, reducing costs, and solving problems in “real time.”

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