

# Photoionization Detector

## Introduction

The reason to use more than one kind of detector for gas chromatography is to achieve selective and/or highly sensitive detection of specific compounds encountered in particular chromatographic analyses. The selective determination of aromatic hydrocarbons or organo-heteroatom species is the job of the photoionization detector (PID). This device uses ultraviolet light as a means of ionizing an analyte exiting from a GC column. The ions produced by this process are collected by electrodes. The current generated is therefore a measure of the analyte concentration.

## Theory

If the energy of an incoming photon is high enough (and the molecule is quantum mechanically “allowed” to absorb the photon) photo-excitation can occur to such an extent that an electron is completely removed from its molecular orbital, i.e. ionization.

## A photoionization reaction:



If the amount of ionization is reproducible for a given compound, pressure, and light source then the current collected at the PID's reaction cell electrodes is reproducibly proportional to the amount of that compound entering the cell. The reason why the compounds that are routinely analyzed are either aromatic hydrocarbons or heteroatom containing compounds (like organosulfur or organophosphorus species) is because these species have ionization potentials (IP) that are within reach of commercially available UV lamps. The available lamp energies range from 8.3 to 11.7 eV, that is,  $\lambda_{\max}$  ranging from 150 nm to 106 nm. Although most PIDs have only one lamp, lamps in the PID are exchanged depending on the compound selectivity required in the analysis.

## Selective detection using a PID

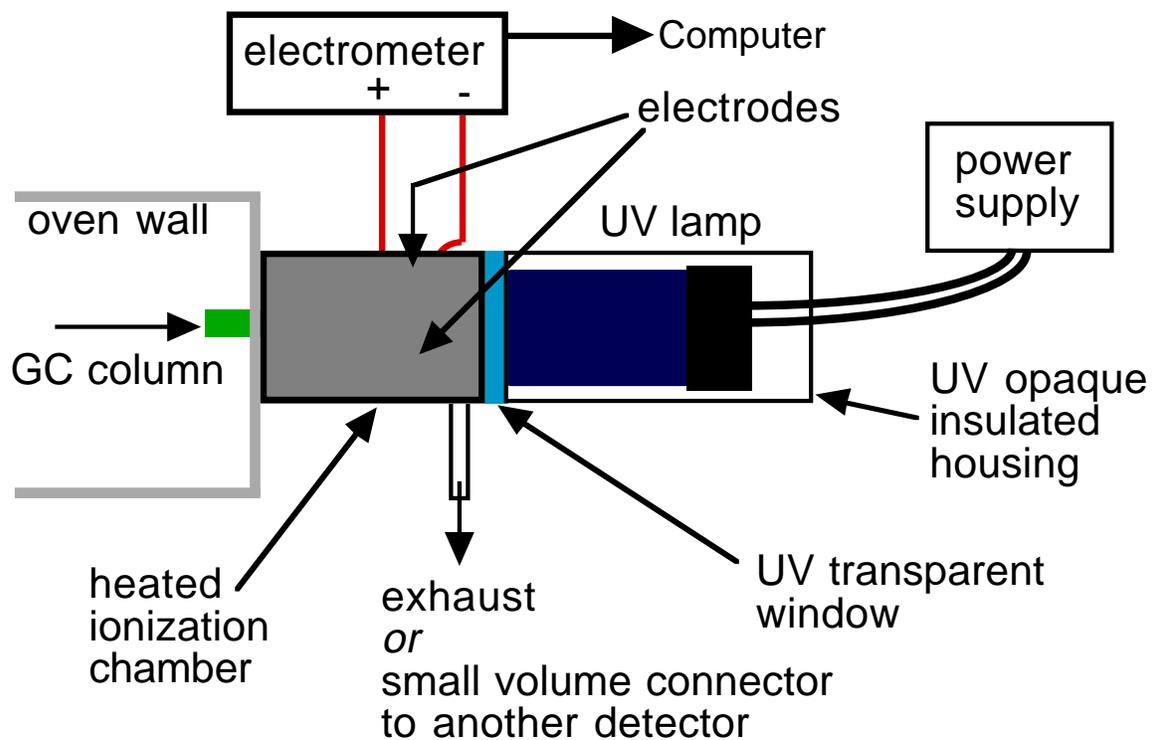
Here is an example of selective PID detection: Benzene's boiling point is 80.1 degrees C and its IP is 9.24 eV. (Check the CRC Handbook 56th ed. page E-74 for IPs of common molecules.) This compound would respond in a PID with a UV lamp of 9.5 eV (commercially available) because this energy is higher than benzene's IP (9.24). Isopropyl alcohol has a similar boiling point (82.5 degrees C) and these two compounds

might elute relatively close together in normal temperature programmed gas chromatography, especially if a fast temperature ramp were used. However, since isopropyl alcohol's IP is 10.15 eV this compound would be invisible or show very poor response in that PID, and therefore the detector would respond to one compound but not the other.

### Instrumentation

Since only a small (but basically unknown) fraction of the analyte molecules are actually ionized in the PID chamber, this is considered to be a nondestructive GC detector. Therefore, the exhaust port of the PID *can* be connected to another detector in series with the PID. In this way data from two different detectors can be taken simultaneously, and selective detection of PID responsive compounds augmented by response from, say, a flame ionization detector (FID) or an electron capture detector (ECD). The major challenge here is to make the design of the ionization chamber and the downstream connections to the second detector as low volume as possible (read small diameter) so that peaks that have been separated by the GC column do not broaden out before detection.

### Schematic of a gas chromatographic photoionization detector



These notes were written by Dr. Thomas G. Chasteen at Sam Houston State University, Huntsville, Texas.