IH Chemistry

Gases and Vapors

Gas: **A state of matter characterized by very low density and viscosity…ability to diffuse readily into other gases, and ability to occupy with almost complete uniformity the whole of any container**

Vapor: **An air dispersion of <u>molecules</u> of a substance that is a liquid or solid in its normal state (i.e., at room temperature and 1 atm)**

Hawley's Condensed Chemical Dictionary

The Ideal Gas Law

$$pv = nRT$$

p = pressure (atm)
v = volume (liter)
n = mole
T = temperature (°K)
R = gas law constant, 0.0821 liter-atm/mole °K

Useful for calculating gas and vapor contaminant behavior

Conversion from ppm to mg/m^3 (& *vice versa*)

$$ppm = \frac{mg/m^3 \cdot 24.45}{mw}$$

$$mg/m^3 = \frac{ppm \cdot mw}{24.45}$$

Useful only for gas phase contaminants, 1 atm pressure, room temp.

Spectroscopy

Absorption

- **uv (Hg)**
- **IR**
- **AA**

Emission

- **ICP-OES**
- **FPD**
- **Fluorescence**
- **Chemiluminescence (O_3)**

Absorption spectroscopy follows Beer's law, and may be used in some instances for remote sensing (e.g. open path FTIR)

A photometer is used to detect either emission or absorption (e.g. a photomultiplier tube or photodiode array)

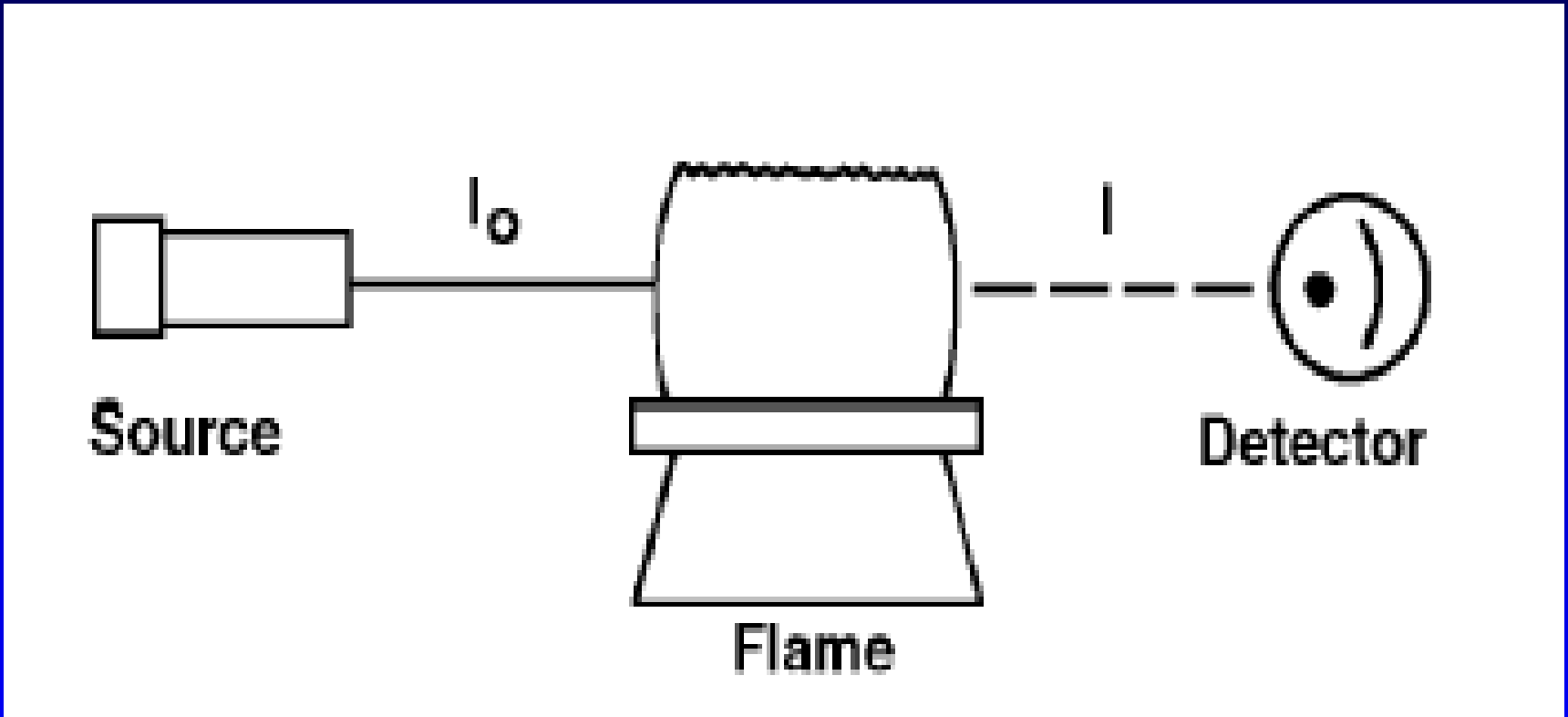
Mercury Vapor

Two Approaches:

-uv

-Gold Film –resistivity change

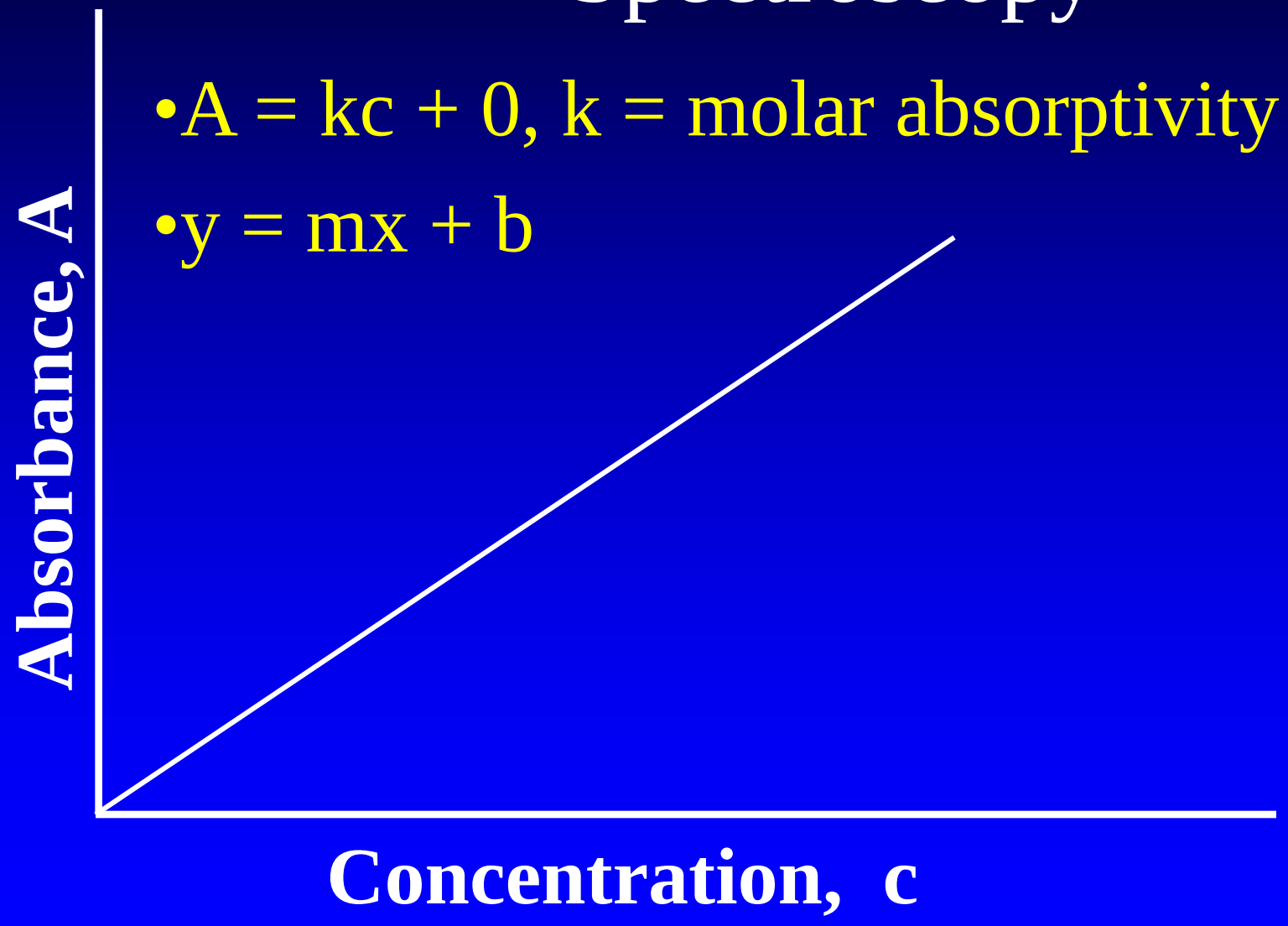
Atomic Absorption (AA) Spectroscopy



Transmittance = I/I_0

Beer's Law: Absorption Spectroscopy

- $A = kc + 0$, k = molar absorptivity constant
- $y = mx + b$



4-Gas Meter

O_2:	Electrochemical (redox)
LEL:	Catalytic bead (O_2 required)
CO:	Electrochemical (redox)
2nd "toxic":	Electrochemical

PID may also be included for VOCs

FID vs. PID

The biggest difference is variability in sensitivity from one organic substance to another (for PID), also humidity effects

Amount of energy (or ionization potential) necessary to dislodge an electron to create a charged fragment determines sensitivity of PID for a specific molecule

IP varies widely from one substance to the next

For these reasons sensitivity of PID detector also varies widely between compounds: response factors (inverse of response slope) are used –a large response factor = relatively weak response relative to isobutylene

PID

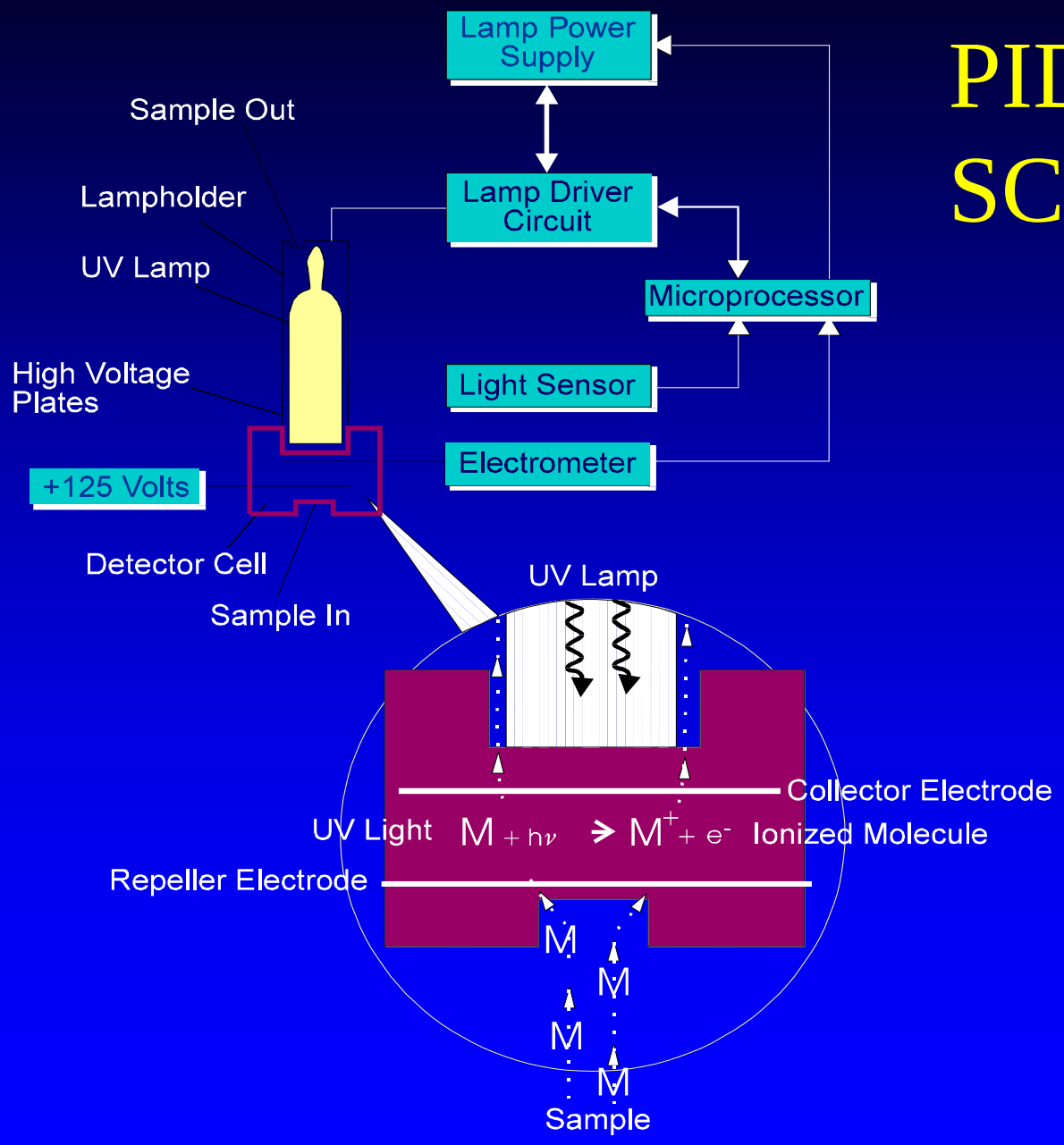
PIDs use uv light as a source of energy to remove an electron from neutrally charged target molecules creating electrically charged fragments (ions)

This produces a flow of electrical current at an electrometer proportional to the concentration of contaminant

The amount of energy needed to remove an electron from a particular molecule is the ionization potential (or IP)

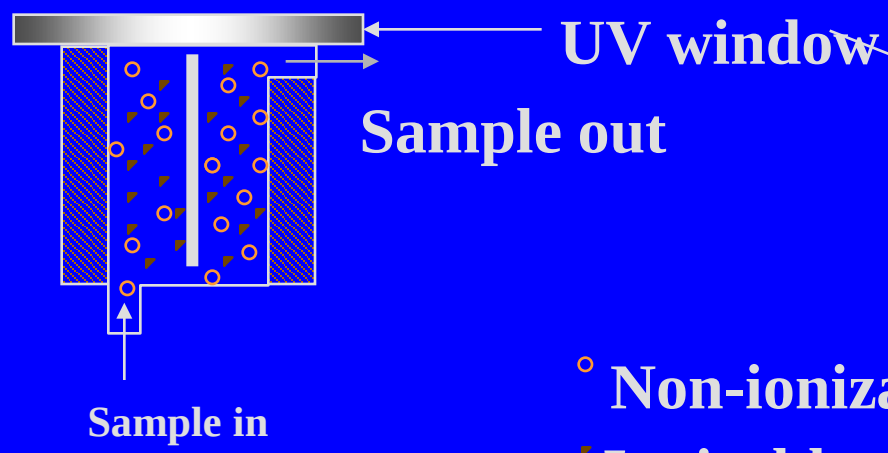
The uv light energy available must be > IP in order for a PID to be able to detect a particular substance

PID SCHEMATIC

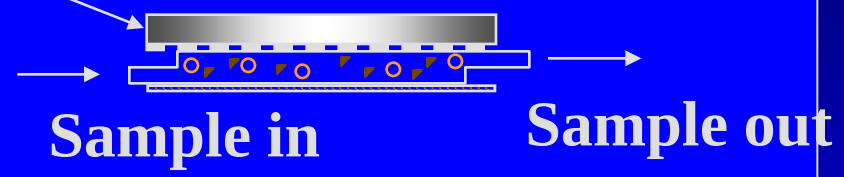


Gas Flow in Ionization Chamber

Perpendicular flow



Laminar, parallel flow



- Non-ionizable molecule
- Ionizable molecule

Shorter path length for UV light
Less interference from humidity
Less interference for methane
Less quenching
Inert construction - Teflon™
& stainless steel

Compounds not detectable by PID

Air

- N_2
- O_2
- CO_2
- H_2O
- *Argon*

Toxics

- *CO*
- *HCN*
- SO_2

Natural gas

- *Methane* CH_4
- *Ethane* C_2H_6

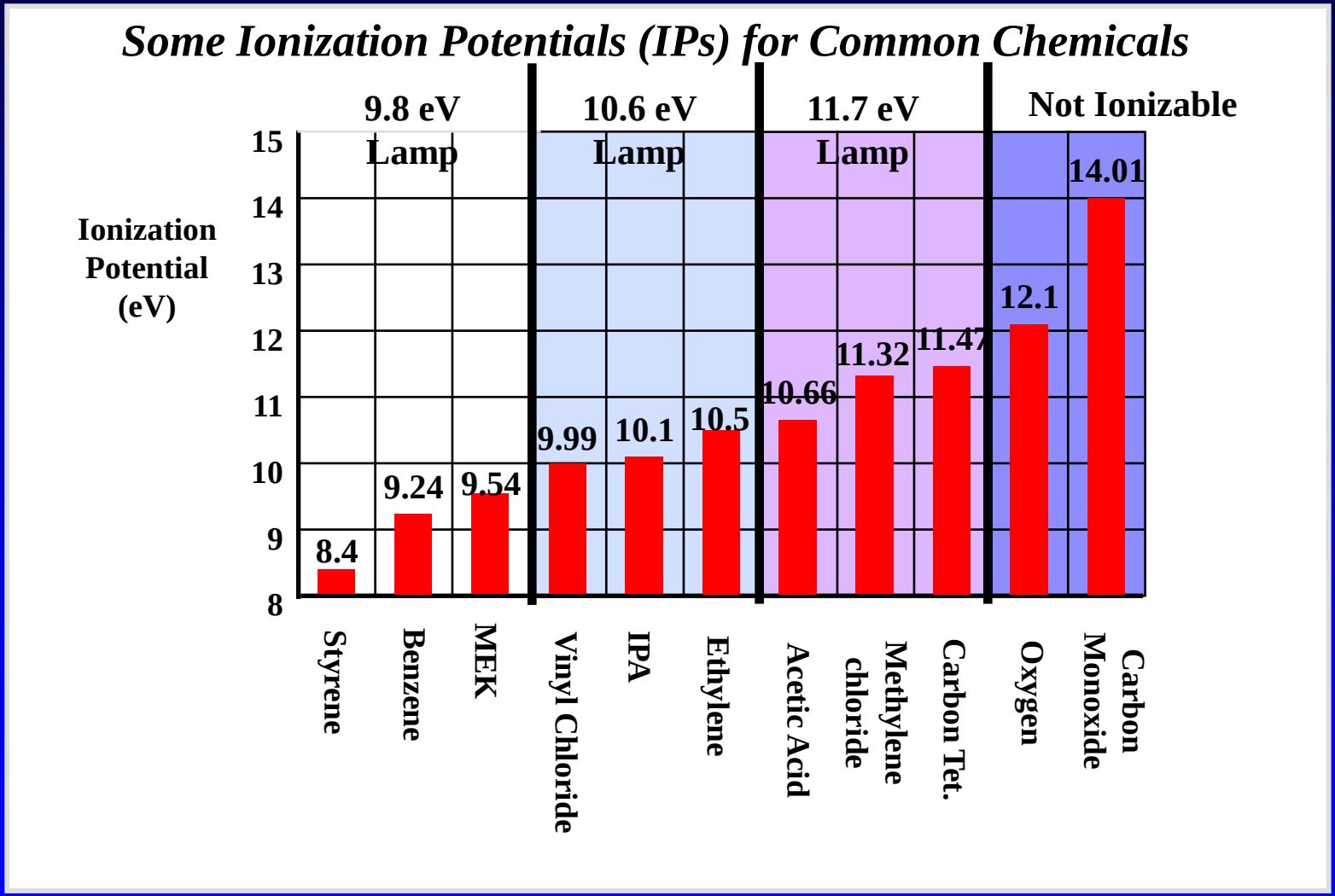
Acids

- *HCl*
- *HF*
- HNO_3

Others

- *Freons*
- *Ozone* O_3

PID Selectivity



Low Correction Factor = High PID Sensitivity to a Gas or Vapor

PID correction factors are scaling factors, they do not make a PID specific to a chemical, they only correct the scale to that chemical

Correction Factors allow calibration on cheap, non-toxic "surrogate" gas (e.g., 100 ppm isobutylene)

Correction Factor Example: Toluene

Toluene CF with 10.6eV lamp is 0.5, so PID is relatively more sensitive to toluene than to isobutylene

If PID reads 100 ppm of isobutylene units in a toluene atmosphere

Then the actual concentration is 50 ppm toluene units

$$0.5_{CF} \times 100\ ppm_{iso} = 50\ ppm_{toluene}$$

Correction Factor Example: NH_3

Ammonia CF with 10.6eV lamp is 9.7 so PID is less sensitive to ammonia

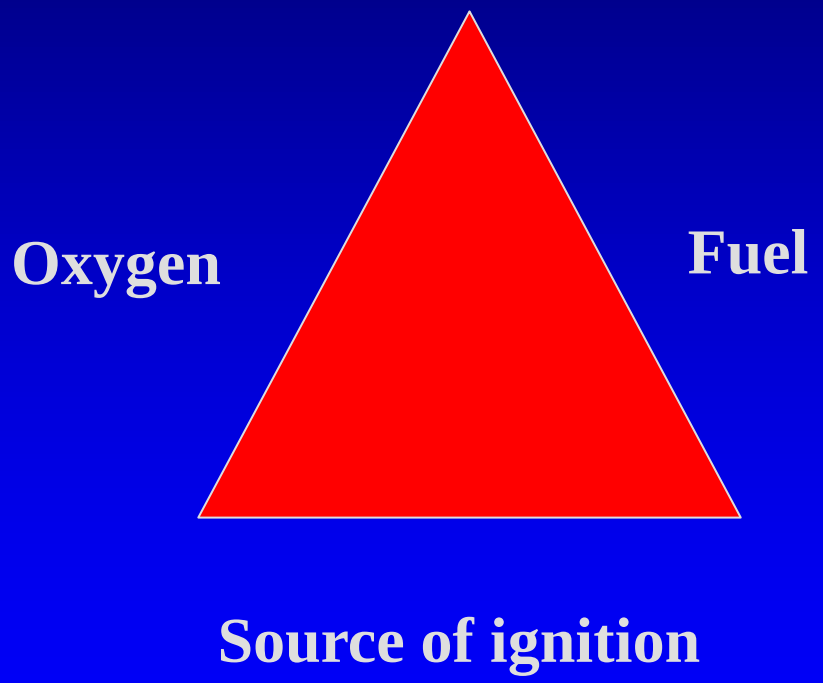
If PID reads 100 ppm of isobutylene units in an ammonia atmosphere

Then the actual concentration is 970 ppm ammonia units

$$9.7_{CF} \times 100\ ppm_{iso} = 970\ ppm_{ammonia}$$

Catalytic Bead LEL Sensors

"Fire Triangle"

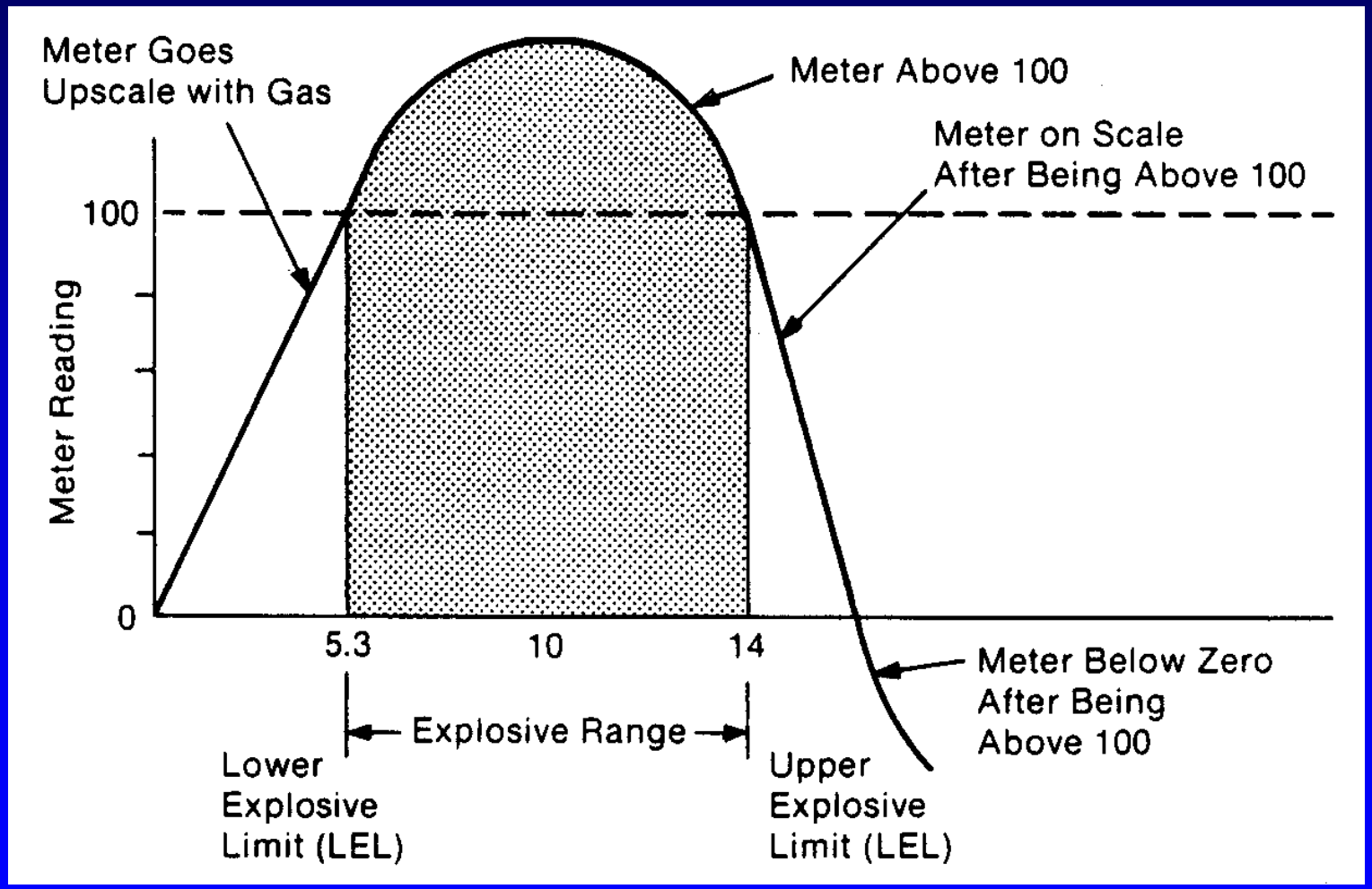


LEL Sensors

Example Flammability Ranges

	LEL		UEL	
	%	ppm	%	ppm
Methane	5 %	50,000	15 %	150,000
Propane	2.2 %	22,000	9.5 %	95,000
Acetone	2.6 %	26,000	12.8 %	128,000
Ammonia	16 %	16,000	25 %	250,000
Carbon monoxide	12.5 %	12,500	74 %	740,000
Ethylene oxide	3 %	3,000	100 %	10^6
Hydrogen sulfide	4.3 %	4,300	46 %	460,000

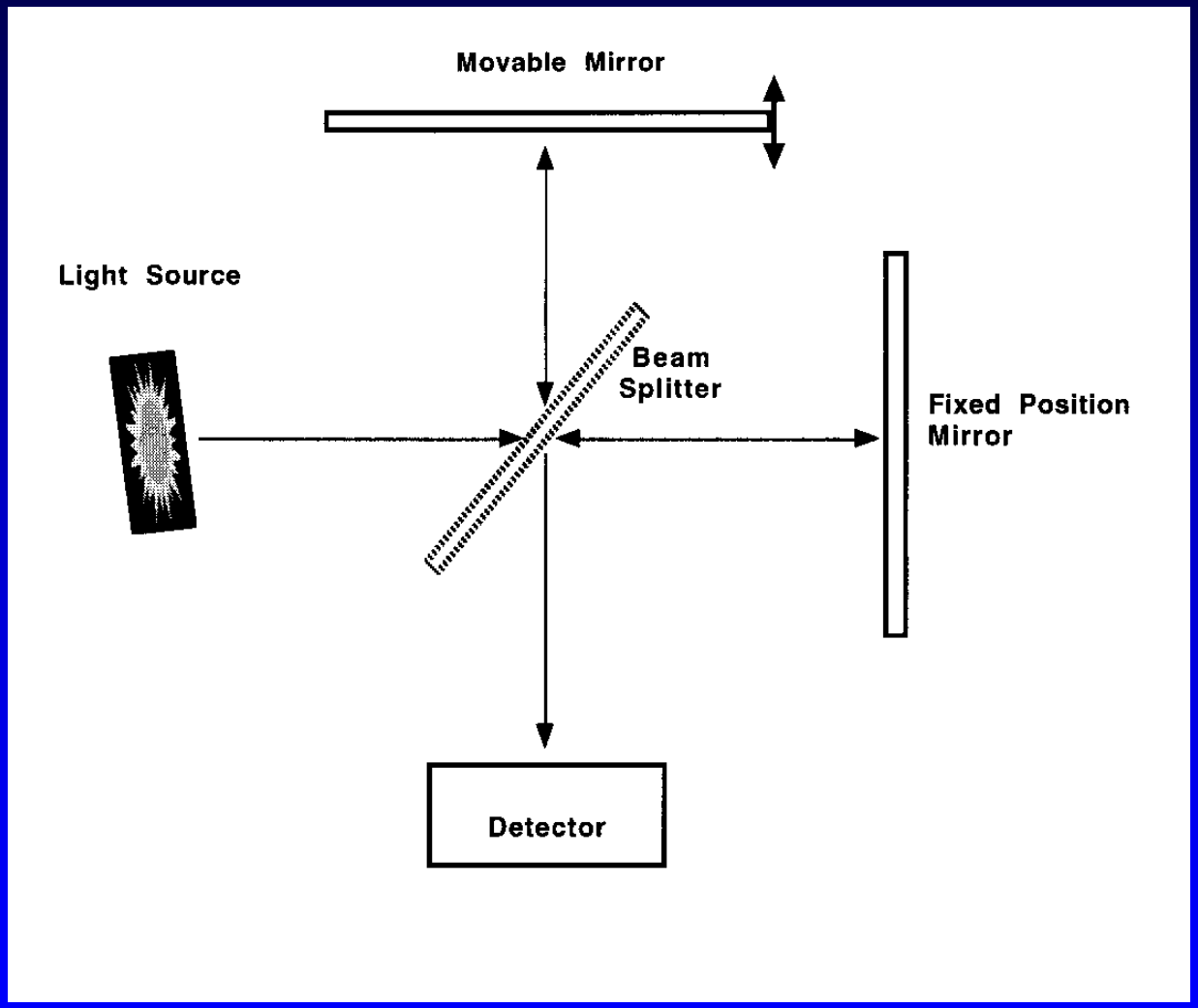
Catalytic Bead LEL Sensors



Dispersive IR

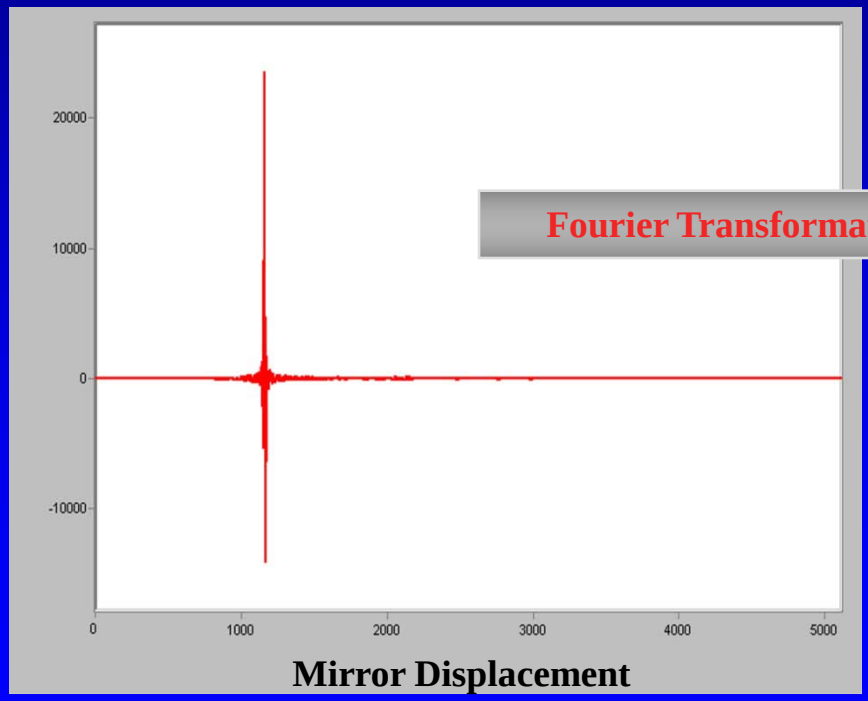
Uses diffraction grating (disperses IR light into frequency bands) to scan a range of frequencies sequentially to obtain a spectrum (slow), or can monitor pre-set frequencies for a known target analyte (faster)

FTIR

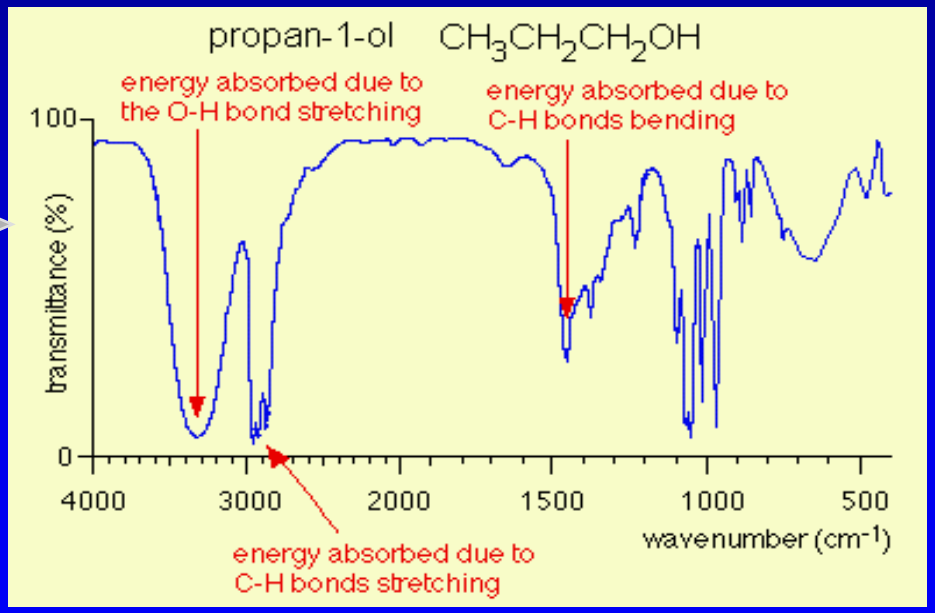

Movable Mirror
Light Source
Beam
Splitter
Fixed Position
Mirror
Detector

FTIR

Uses moving mirrors to simultaneously scan an entire range of frequencies to obtain a spectrum (fast), no need to restrict monitoring to pre-set frequencies for a known target analyte



Fourier Transformation



IR Analytes

Depends on molecular bonds absorbing IR radiation -molecule detected must have a bond and a dipole

Not detectable: diatomic molecules (O_2, N_2, etc.)
noble gases (He, Ar, etc.)
metals