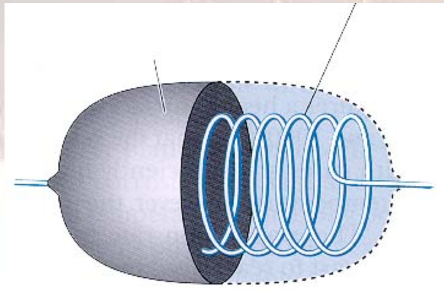
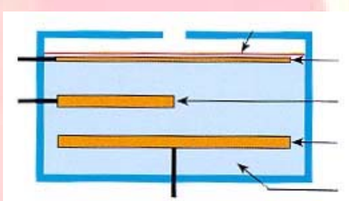
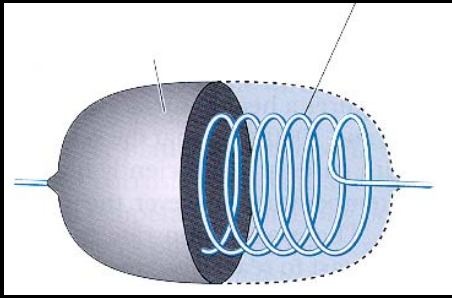


GAS ANALYSIS METHODS



Catalytic sensor



The catalytic sensor, also referred to as the catalytic bead sensor, is commonly used to detect and measure combustible gases from 0-100%LEL.

Example of Combustion

Methane (Natural Gas)

0%

100 %
by volume

AIR

Example of Combustion

Methane (Natural Gas)

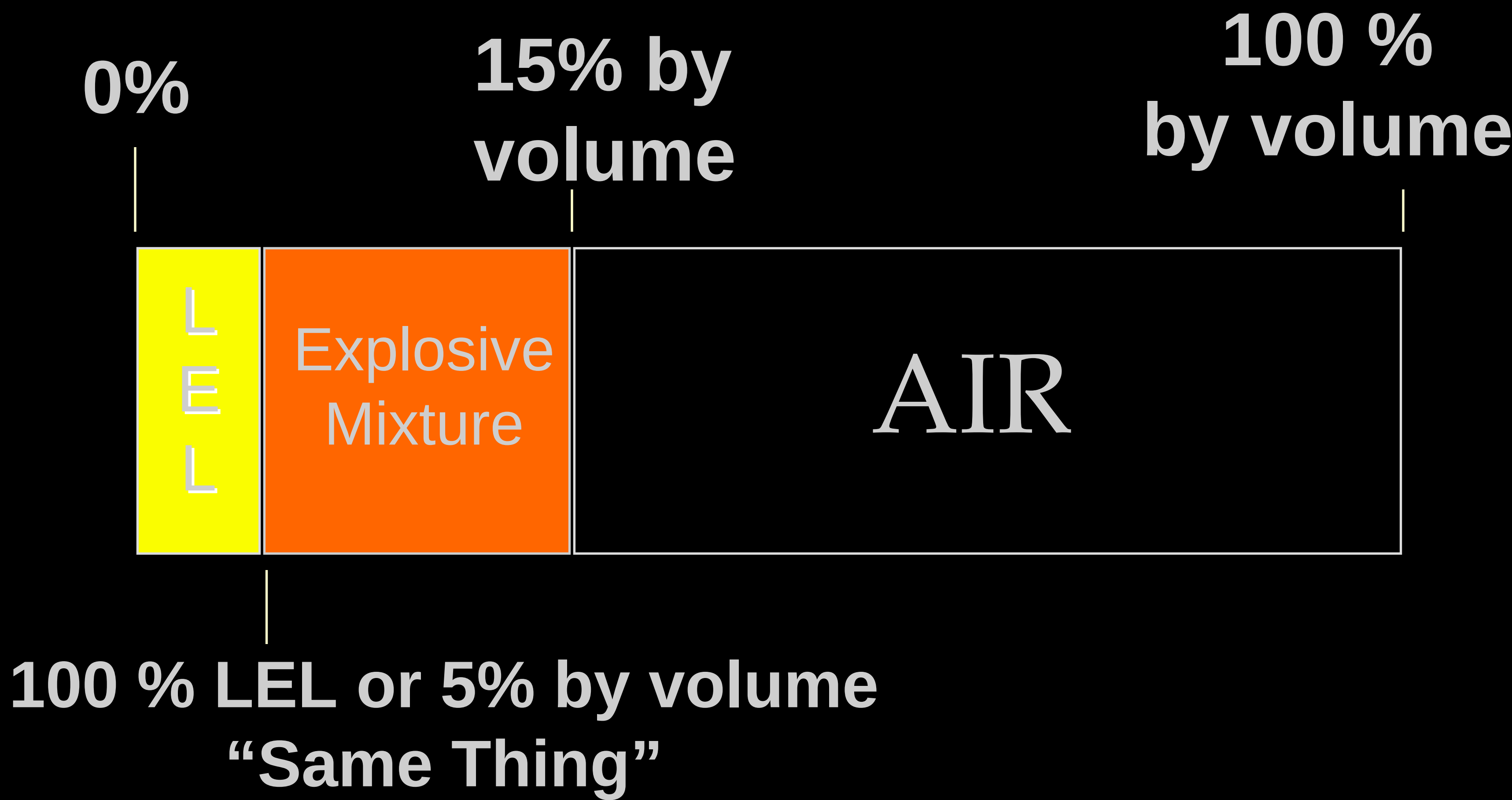
0%

100 %
by volume

100 % LEL or 5% by volume
“Same Thing”

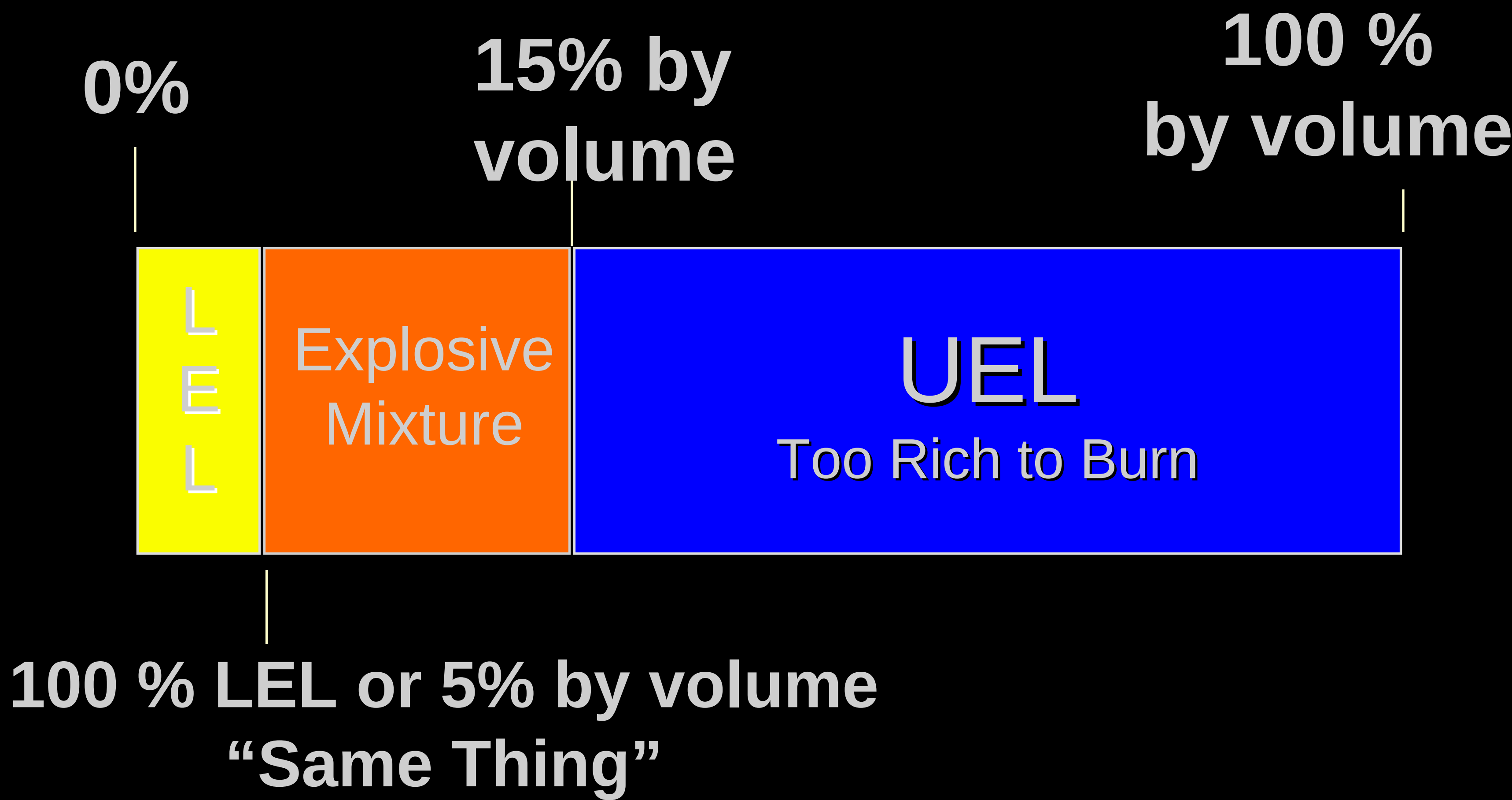
Example of Combustion

Methane (Natural Gas)



Example of Combustion

Methane (Natural Gas)

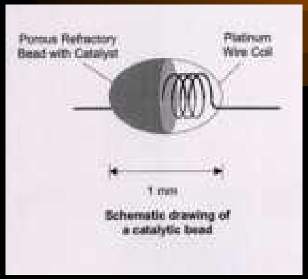


Common Combustibles

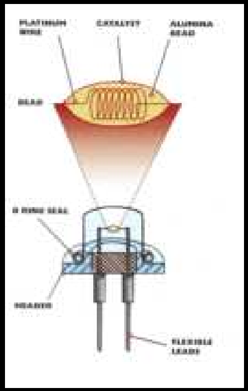
	LEL	UEL
Methane	5.0%	15% by volume
Hydrogen	4.0%	75%
Acetylene	2.5%	100%
Propane	2.1%	9.5%
Butane	1.9%	8.5%
Pentane	1.4%	7.8%
Hexane	1.2%	7.5%

Catalytic sensors

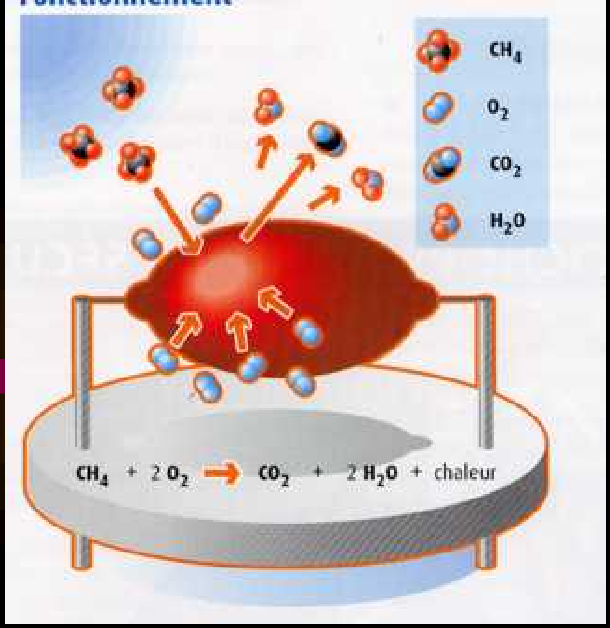
- *The sensor is composed by* two platinium spirals*, both plated with a ceramic coating (alumina)*
- *one of the pellistor is soaked with a special palladium catalyst that causes oxidation :* detector (sensing bead)
- *while the other one is not treated in order to forbid oxidation :* compensator (reference element).
- *Those two filaments and their* supports *are fixed in a* « flameproof » body *of cell.*



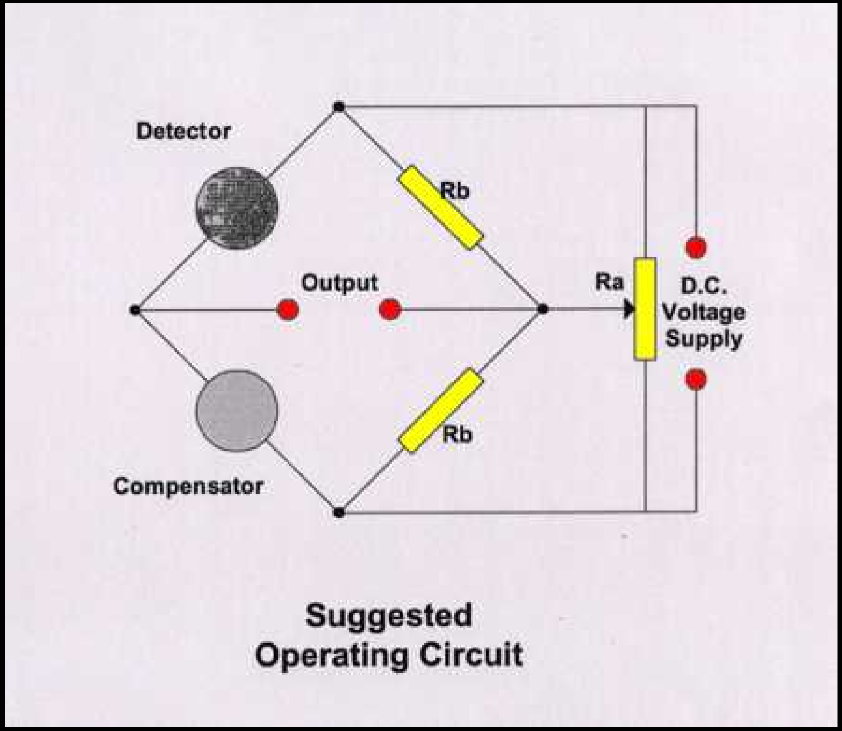
Flame arrestor



Physical principle : **Wheatstone** *bridge*

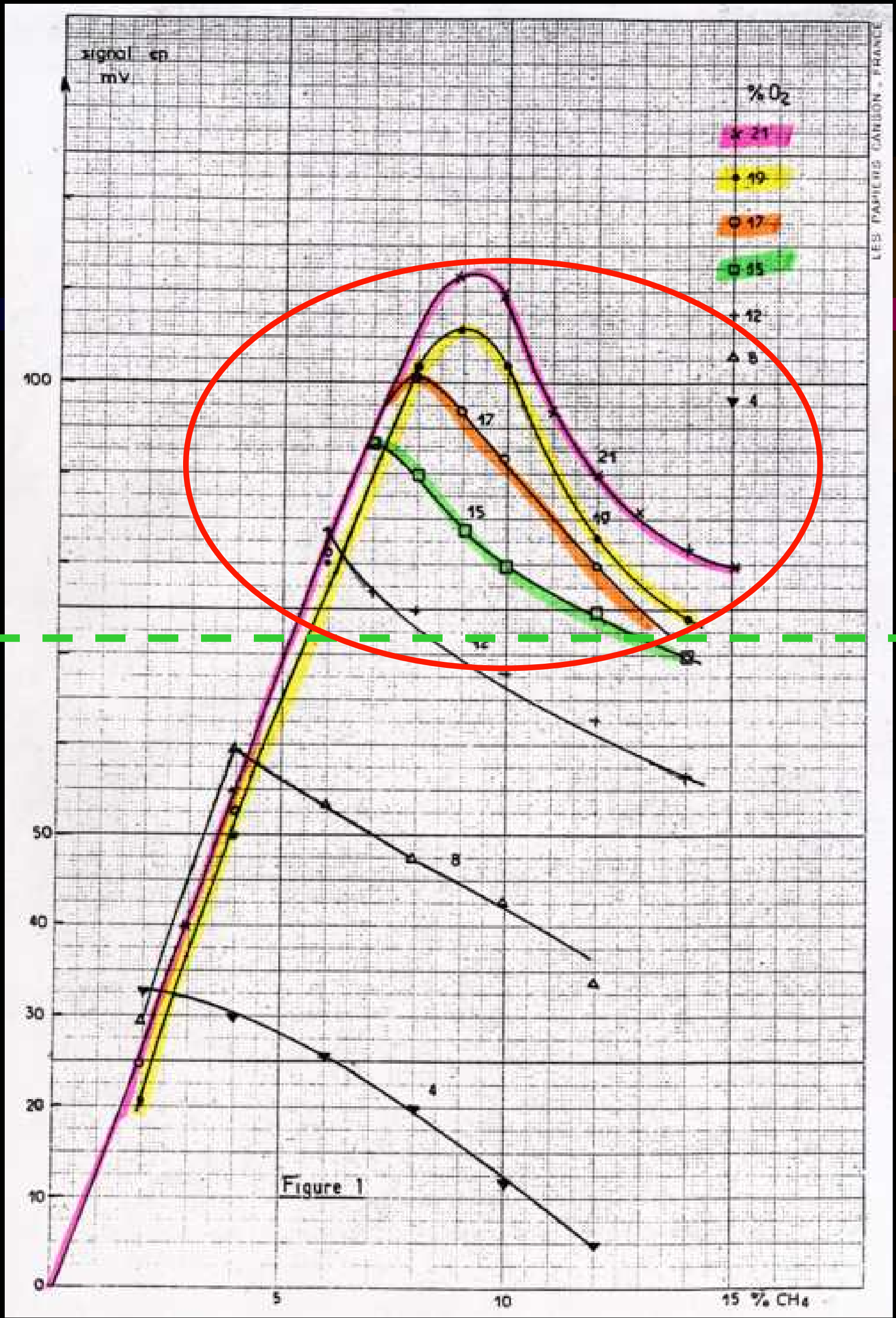


- *The working principle of these sensors is based on flammable gas* oxidation *on the surface of a catalytic element with electric heating*
- *The current passes through the spirals in order to reach* 450°C *temperature that allows* gas oxidation
- *when fuel gas has burned in the detector, oxydation causes a temperature increase only in the treated pellistor and not in the non-treated one (reference), causing* unbalance in the bridge circuit.



Suggested Operating Circuit

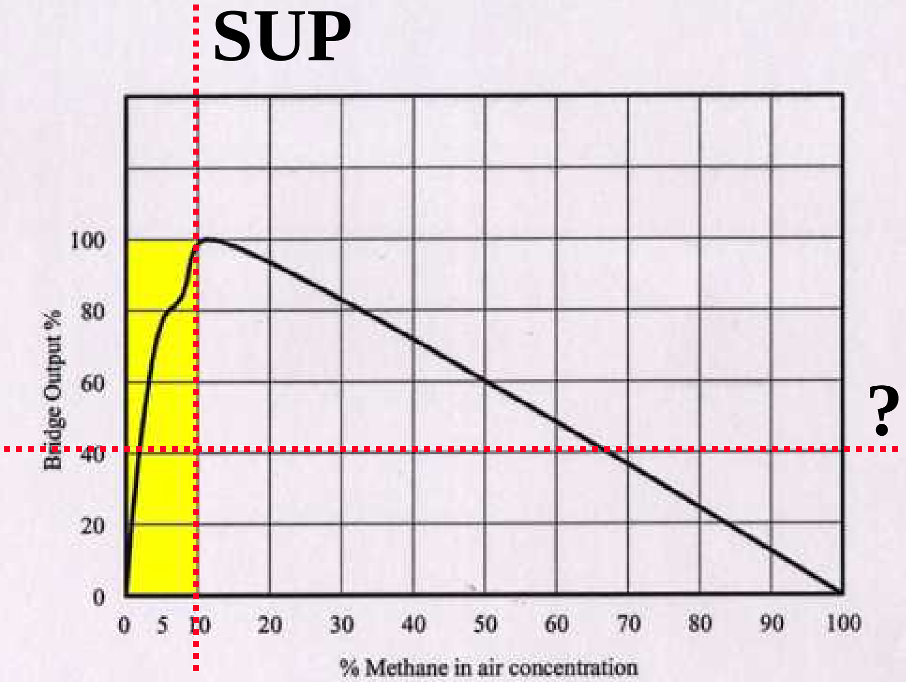
mV


signal en mV
% O_2
21
19
17
15
12
8
4
100
50
40
30
20
10
0
5
10
15 % CH_4
Figure 1
LES PAPIERS CANSON - FRANCE

15 % O2 mini

Catalytic sensors : typical response curve

The bridge exit is substantially linear up to 3-5% vol. of methane, while it decreases for oxygen insufficiency at concentrations higher than 10% vol., to have a correct oxidation, causing an ambiguity in the instrument.

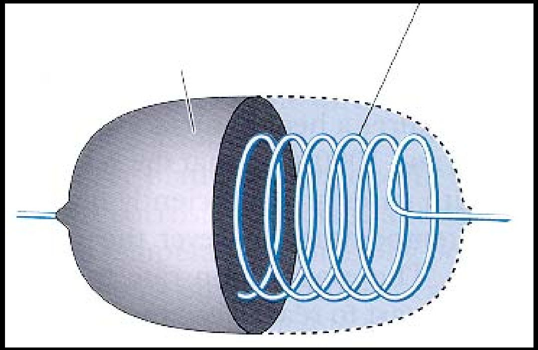


CATALYSE : note

- Flammable gas oxidation: *must be used in environments containing*

a concentration of oxygene (O2) >

15% .

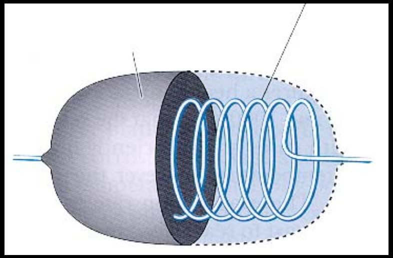


Catalytic Gas Sensors: ... Note !

- *The sensor can be poisoned so that it cannot respond to a flammable gas if exposed to lead, silicone or certain other gases…*
- *The presence of inhibitors or poisons is the most common cause of problems in gas detection systems and, for this reason, it 's necessary to pay attention in order to avoid any contamination.*

Catalytic Gas Sensor Poisons/Inhibitors

- Inhibitors (H_2S, SO_2, halogenated compounds) *causes a temporary sensitivity loss of the sensor*
- Poisons *affect catalytic sensor response & longevity and cause a permanent reduction of the sensor sensitivity that may be completely damaged*
- *Erosion, impervious covering, or plugging active sites*
- *Impact depends on poison type, level, time of exposure*
- *Known catalytic sensor poisons:*
  - *silicone oils, greases, resins (RTV adhesive)*
  - *halogens (halon, chlorine, fluorine, bromine, freon)*
  - *phosphate esters*
  - *tetraethyl lead, trichlorobenzene*
  - *acid and pvc vapors, other corrosive materials …*



ADVANTAGES

- The principle is simple, it uses a real phenomenon
- valid for all flammable gases
- very short response time (<15s.)
- very good repeatability
- very good reproducibility
- low cost

The thermal conductivity sensor

Has been used in instruments for measuring gases above the %LEL range and for leak detection.

INDUSTRIAL SCIENTIFIC

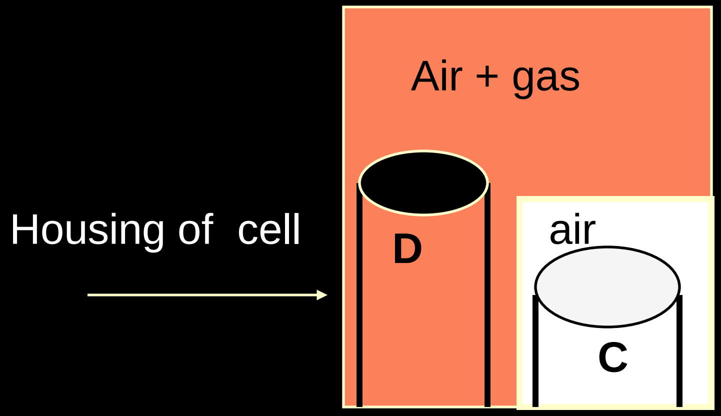
OLDHAM

Thermal conductivity

- *Measuring the* thermal conductivity *of gases was one of the earliest forms of gas detection and it 's suitable for* % volume *levels of certain binary mixtures : two different gases, one of which can be air .*
- TC *gas detectors operate by comparing the thermal conductivity of the sample with that of a reference gas (usually air)*
- *this principle of detection , without chemical reaction, can be used in an atmosphere with or without oxygene.*

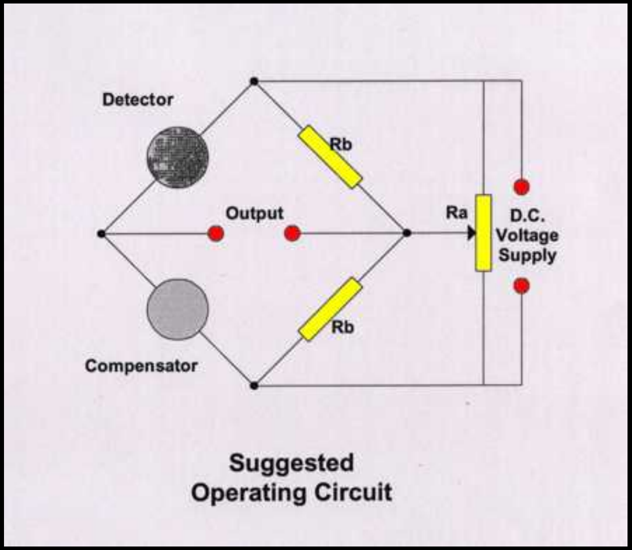
Thermal conductivity : ***principle***

- The sensor consists of two elements, both comprised of a wire coil.One element (detector) is exposed to the atmosphere, whereas the other element (reference) is sealed in a standard gas atmosphere such as nitrogen or air.



Thermal conductivity : ***principle***

- The reference element compensates for changes in temperature.
- The elements are heated to an operating t° of approximately 250°C.



ADVANTAGES

- High concentrations measurement (100% v/v)
- With or without oxygene
- possibility of detection: helium ….
- No poisonning
- long life time
- resistant filaments.

INDUSTRIAL SCIENTIFIC

OLDHAM

Limitations of use

- *This technique is only suitable for gases and vapours whose thermal conductivity is significantly different from air !*
- *Thermal conductivity sensors are used primarily in portable gas leak detectors.*

INDUSTRIAL SCIENTIFIC
OLDHAM

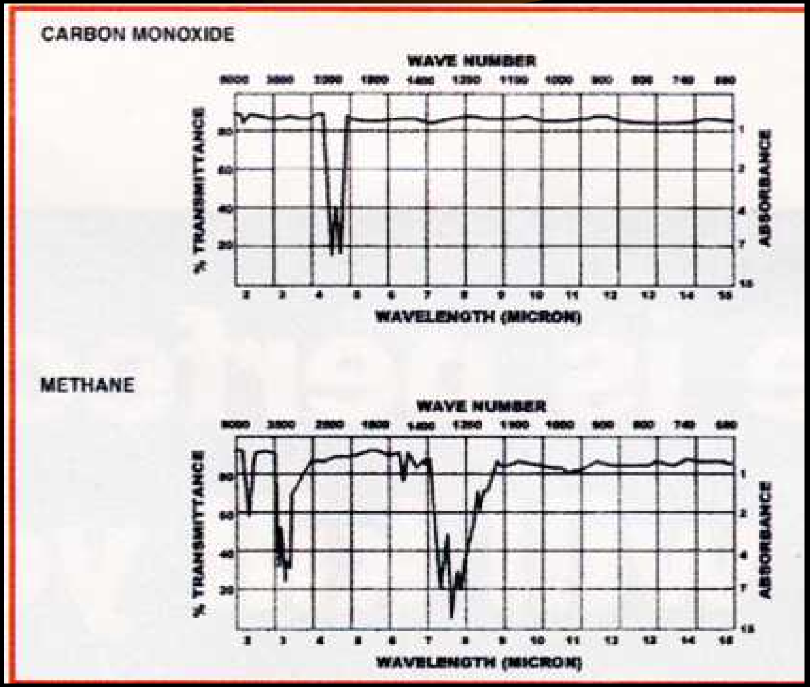
TCOD IR *(CO2)*

OLCT IR

INFRARED ABSORPTION

INFRARED SENSORS :

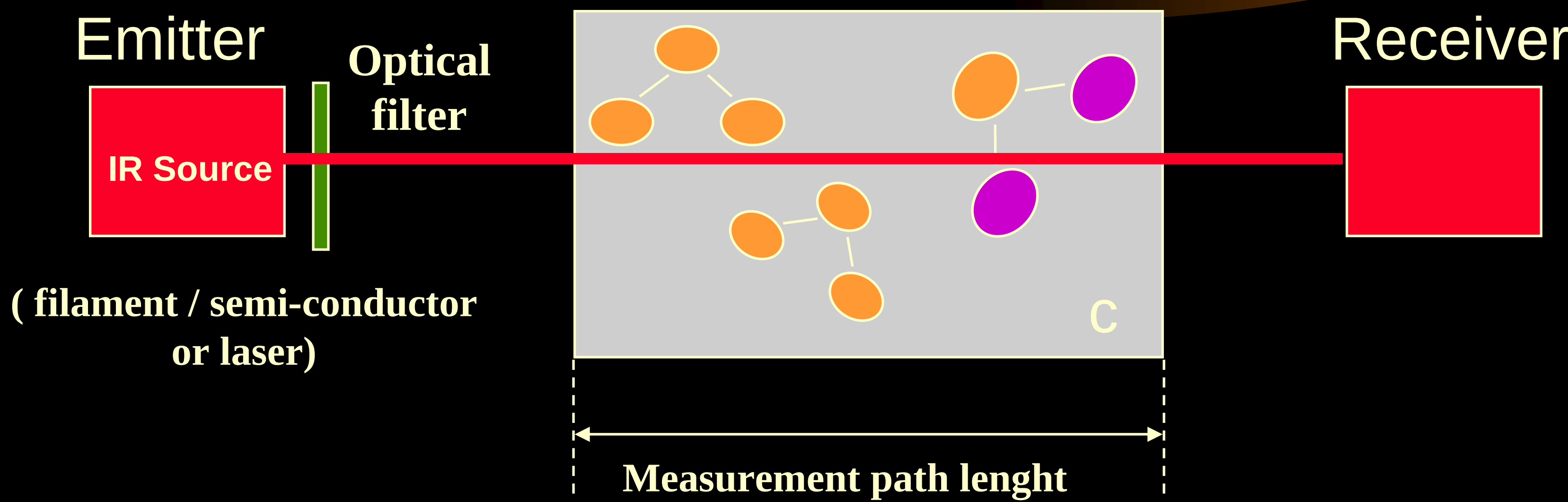
- The non-dispersive infrared sensor, commonly referred as the infrared sensor, is based on the principle that gases absorb light energy at a specific wavelength, typically in the infrared range.



INFRARED SENSORS

- *Gases that contain more than one type of atom absorb infrared radiation.*
- *Gases such as carbon dioxide (**CO2**), carbon monoxide (**CO**), methane (**CH4**) and sulphur dioxide (**SO2**) can be detected by this means …*
- *But gases such as oxygen (**O2**), hydrogen (**H2**), helium and chlorine (**CL2**) cannot.*

INFRARED ABSORPTION



•*When flammable gas passes between the source and detector, the gas absorbs* infrared radiation *and a lower intensity is registered at the detector*

•*The gas concentration is directly proportional to the amount of energy absorbed and this absorption is illustrated by the BEER LAMBERT formula.*

ADVANTAGES in summary

- Instantaneous response time
- no poisoning
- no need of oxygen
- no interferent gases

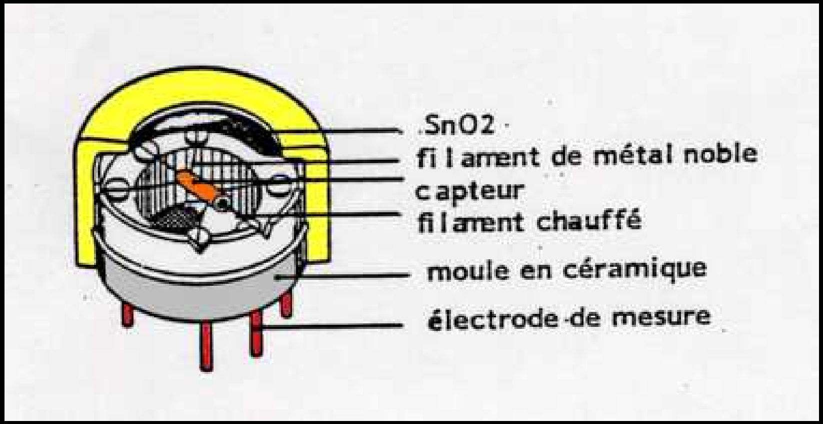
Limitations of use

- *Exposure* to high concentrations *may* saturate *the instrument for a finite time.*
- *Cannot detect* monatomic *or* diatomic *homonuclear molecules : mercury, chlorine and other halogens ...*

C1100

Typical measurement tasks

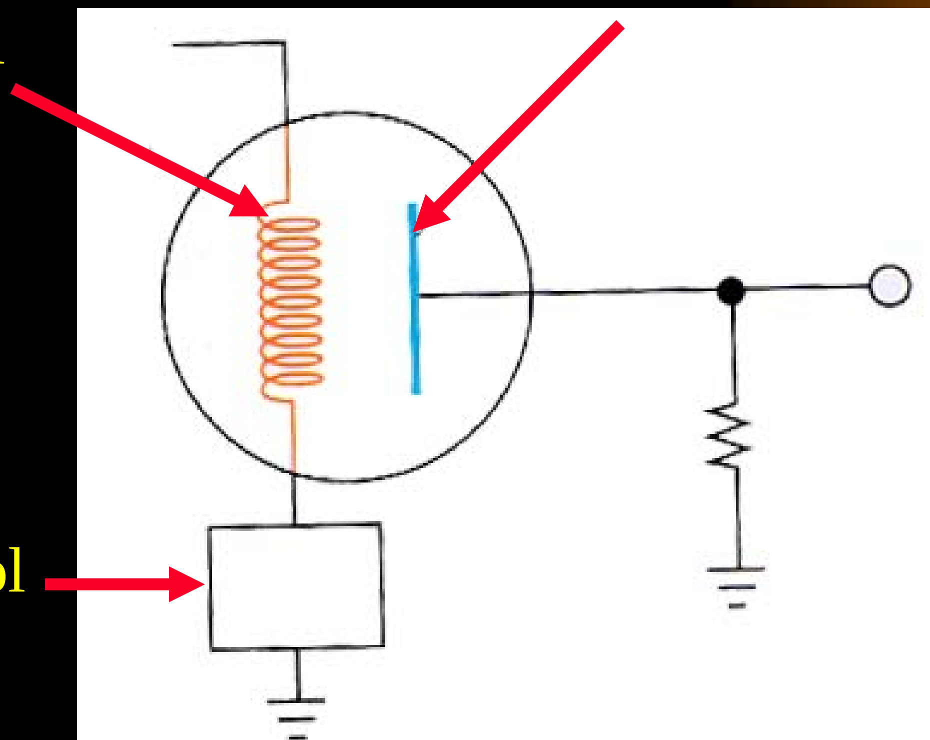
- Combustion efficiency monitoring : CO/CO_2
- Continous Emission monitoring systems: *$CO/CO_2/SO_2$ and helium*
- *Process control: CO/CO_2 and total hydrocarbons*
- *Landfill gas monitoring : CH_4/CO_2*
- *Plant protection: $CH_4/C_3H_8/C_4H_{10}$*
- *Distilleries and breweries : CO_2*
- *Personnal protection : CO_2*
- *Automotive emissions.*



SEMI-CONDUCTORS

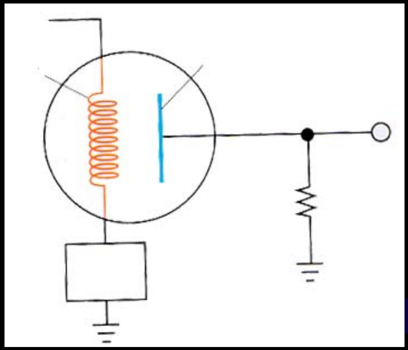
INDUSTRIAL SCIENTIFIC
OLDHAM

SEMI-CONDUCTORS



Schematic Diagram of a Bead-type Sensor

•This semi-conductor (SNO2 for example) is placed on the surface of a substratum (tube or plate).



PRINCIPLE

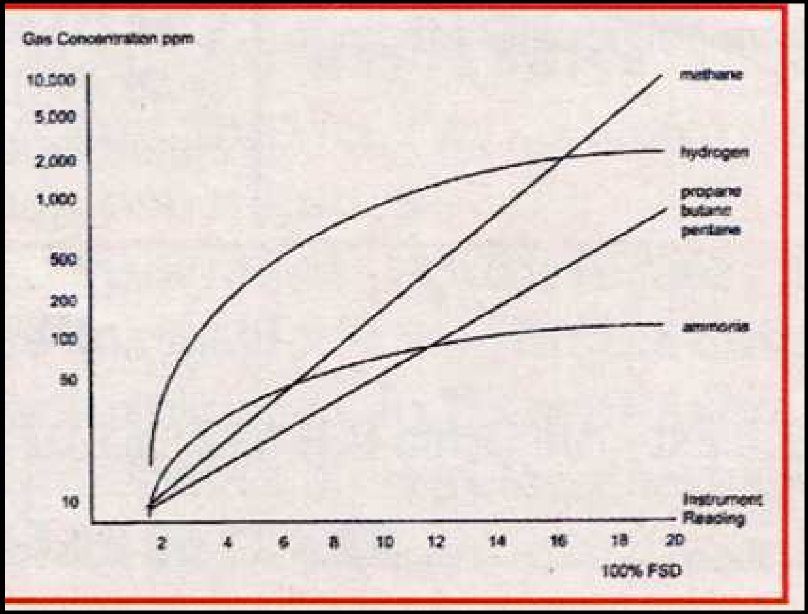
- A filament is heated by an electric current,
- the substratum increases its temperature until it reaches 300 to 500 °C.
- The sensitivity of **SnO2** to different gases varies with the temperature.
- This temperature will be chosen to work with the maximum operation sensitivity.

PRINCIPLE

- Signal= induced variations of electric conductivity,

by absorption of gas, on the surface of a metallic oxide.

When gas enters the sensor it reacts with the oxide coating which causes a decrease in resistance between the two electrodes.



Detected GASES

- **Toxic and flammable gases**: **VOC** , hydrocarbures (toluène,xylène …), vapors of hydrocarbures (essence,kérosène…), cétones (2-butanone…), esters, (acétate of méthyle, éthyle éther…), alcools (méthanol…)
- **FREONS**.
- example : toxic products with low concentrations,

ADVANTAGES

- High sensitivity
- very good stability of the signal
- long life time (~ 5 years)
- low cost
  - used to measure a wide range of gases and vapours.
  - Commonly used in low cost, hard-wired gas detection systems

Limitations of use

- *Wide range of sensitivity (interference) to different gases*
- *after exposure to high gas concentrations the sensor may need a recovery time of several hours and may have irreversible changes to its zero gas reading and sensitivity*
- *exposure to basic or acidic compounds, silicones, organo-lead, sulphur compounds and halogenated compounds may have a significant effect on sensitivity*
- *Oxygen concentration,humidity and temperature may have a significant effect on sensitivity.*

Electrochemical gas sensors

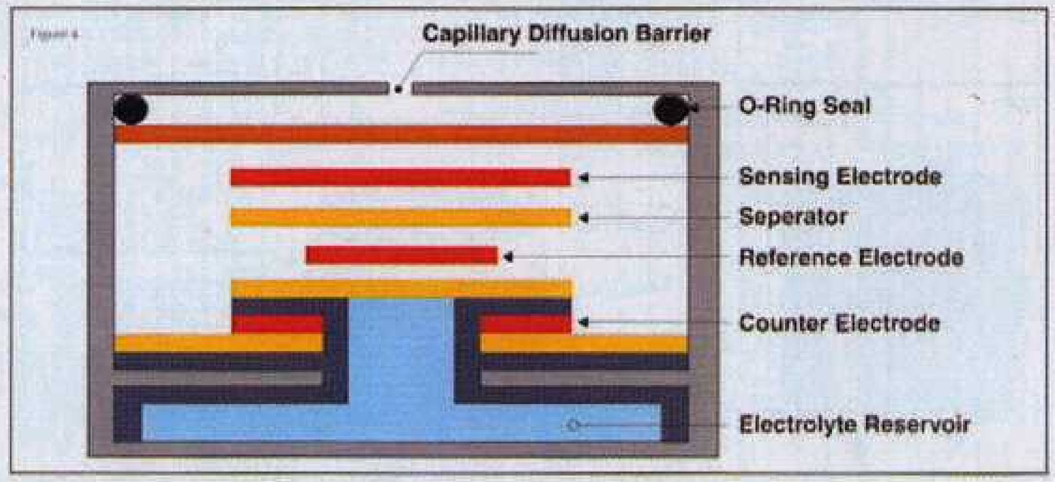
with liquid or gelled electrolyte.

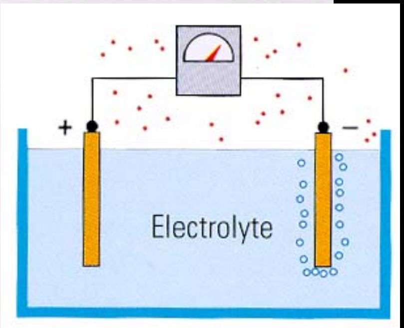
Electrochemical gas sensors

- Are widely used for the gas detection of toxic gases at the ppm level and for oxygen in levels of % of volume .

Toxic electrochemical sensors

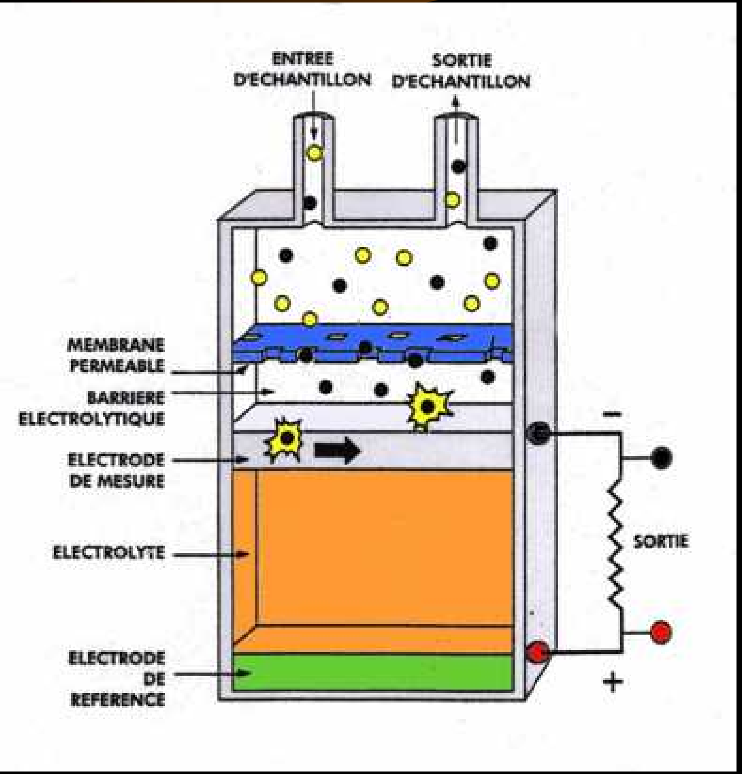
In its most simple form, the electrochemical sensor has two electrodes, "Sensing" and "Counter" which are divided by an electrolyte thin coat. This may be in a liquid state or in a gel state and recently also in a solid state. The electrolyte is isolated towards the outside through a membrane permeable to gas. Gas enters in the sensor by diffusion, through the membrane, and there is an oxidization reaction (reduction that causes an electrical current directly proportional to gas concentration) if a polarization tension is applied to electrodes.





In summary ...

- This method is based on the measurement of the current established between a sensing electrode and a counter electrode.
- A reference electrode is often used to stabilize the measurement.
- Gases react electrochemically to the sensing electrode: gases are reduced or oxidised.



Oxygen electrochemical sensors

- There are two fundamental variations in fuel-cell oxygen sensor designs:
- Partial atmospheric pressure, is that fraction of the total atmospheric pressure due to oxygen
- Capillary-pore, these sensors are much less influenced by changes in presure than partial pressure oxygen sensor designs.

Mechanisms of oxygen sensor failure

- Oxygen sensors may be affected by prolonged exposure to acid gases
- Such as carbon dioxide (CO2)
- Most oxygen sensors should not be used continuously in atmospheres containing more than 25%CO2
- Limitation of operations in extrem cold or excessivily hot temperatures…

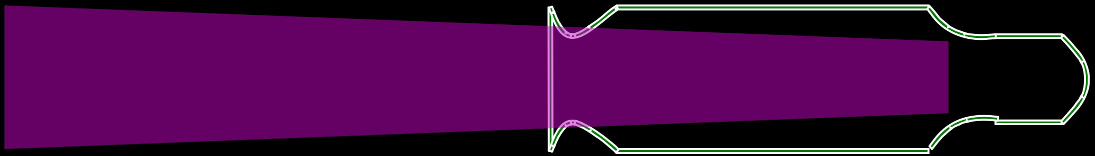
PID Sensor Technology

A PID sensor works differently than other sensors and often used in situations where high sensitivity (sub-ppm levels) and limited selectivity (broad-range coverage) is desired.

INDUSTRIAL SCIENTIFIC

OLDHAM

Detector Operation



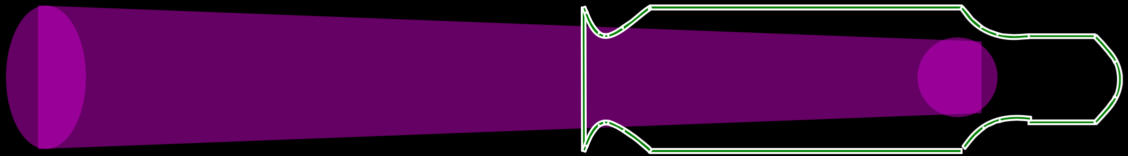
UV Lamp

A photoIonization device contains of a vacuum lamp that emits UV light at a specific energy .Some common lamps avaible are 9.8eV, **10.6eV** and 11.7eV.

Detector Operation

- The UV light is generated by the excitation of the gas contained

- within the bulb (**Krypton** and argon are two gases commonly used).

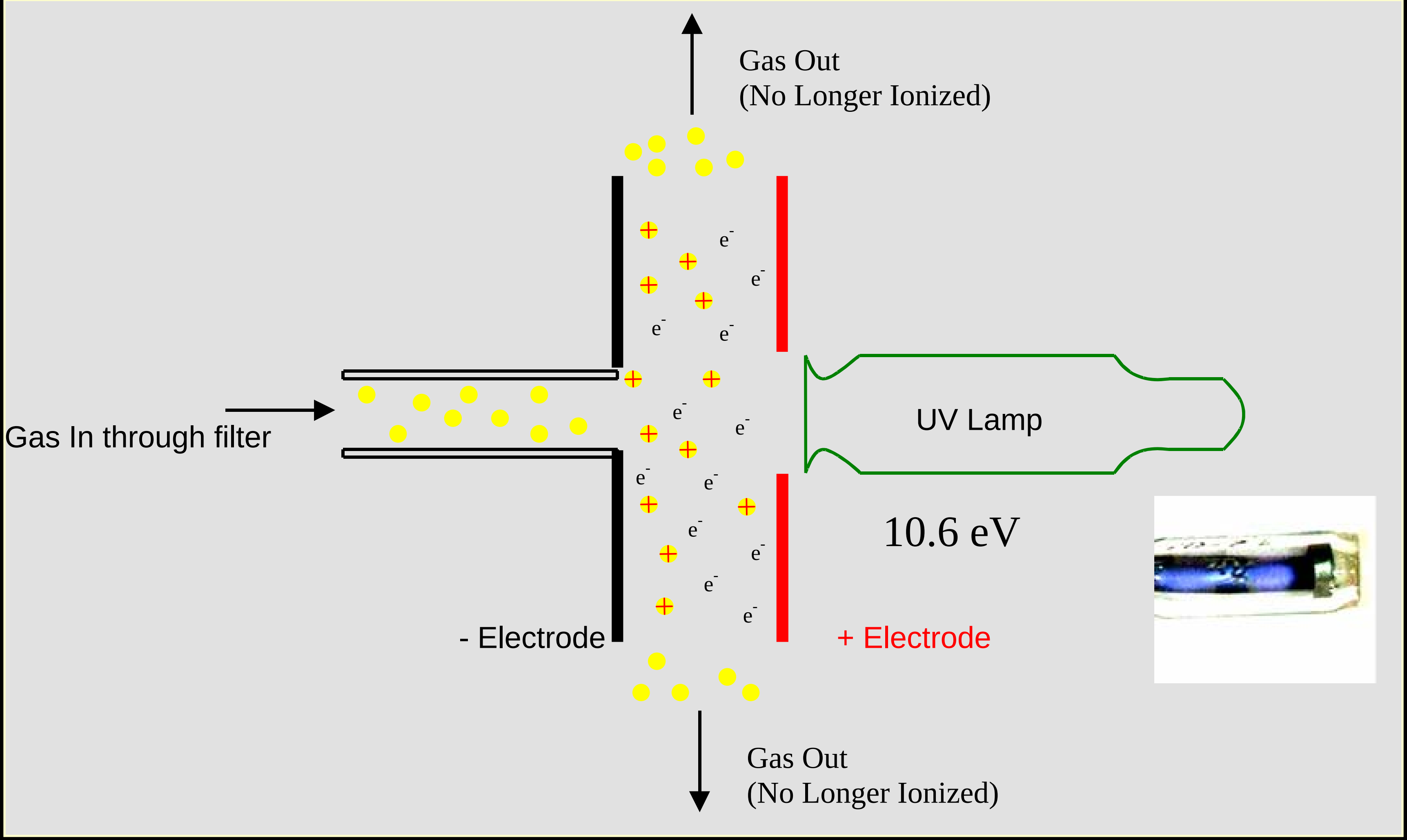


- The gas in the lamp is excited with an electrical field or **a radio frequency field**.

PID Lamps

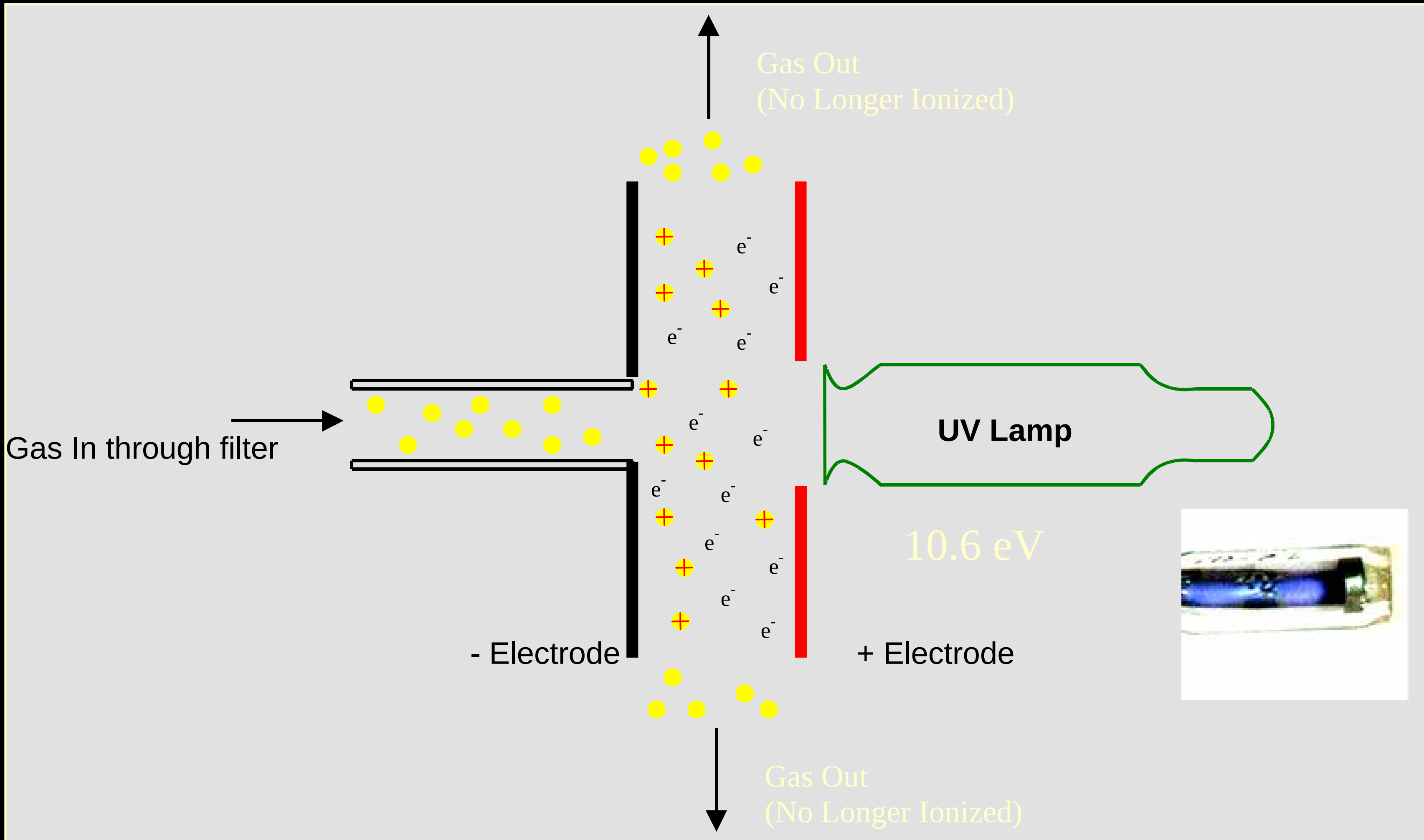
- *The VX500 has a **10.6 eV** lamp*
- *A 11.7 lamp has a short life and needs special treatment as dehydrating and frequent calibration, it is basically only suited for leak detection*

INDUSTRIAL SCIENTIFIC
OLDHAM

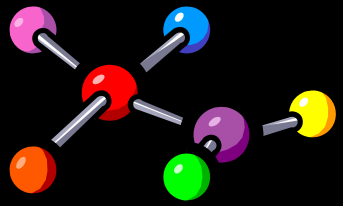


-In addition to the lamp the PID contains two electrodes a positive and a negative electrode :

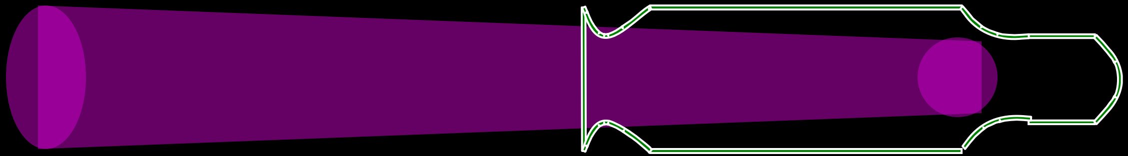
- The negative electrode is often referred to as the collecting electrode
- The positive electrode is referred to as the biased electrode
- The distance between the two electrodes is 20 000 of an inch.



- Gas molecules that pass through the light emitted from the ignited lamp are ionized if their ionization potential is less than the ionization potential of the lamp.

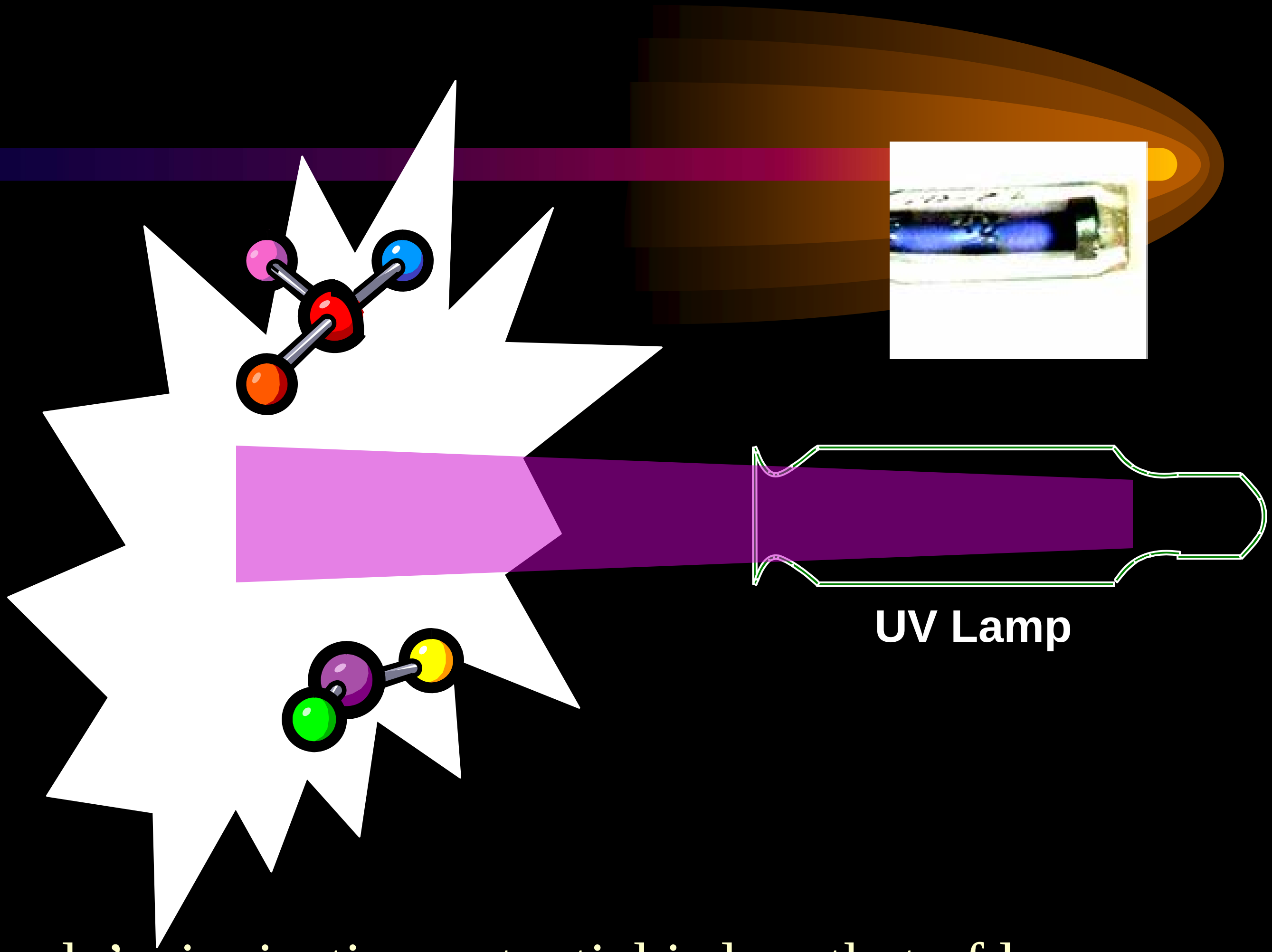


Detector Operation



If the molecule’s ionization potential is above that of lamp, then nothing happens !

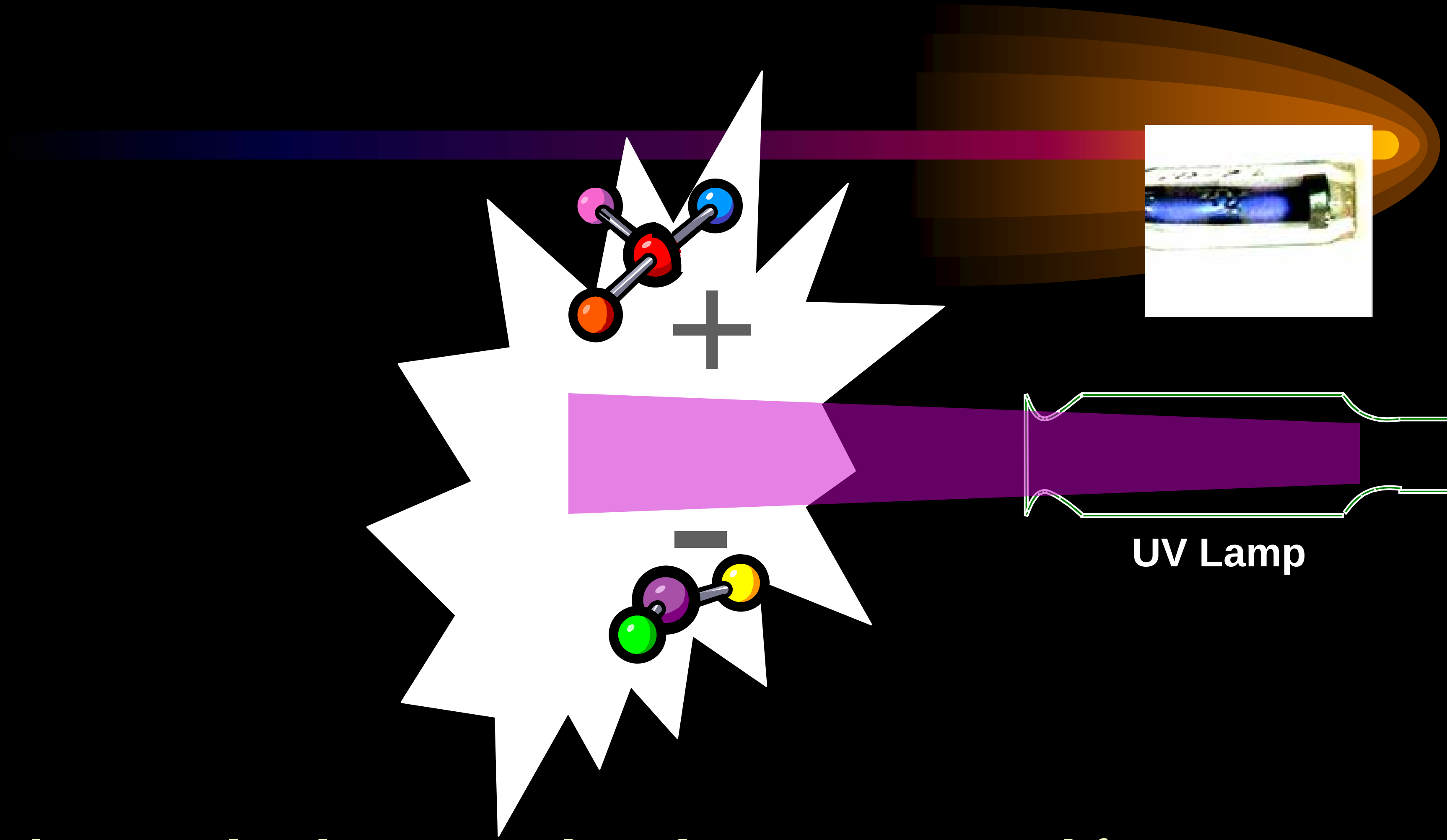
Detector Operation



If the molecule's ionization potential is less that of lamp,

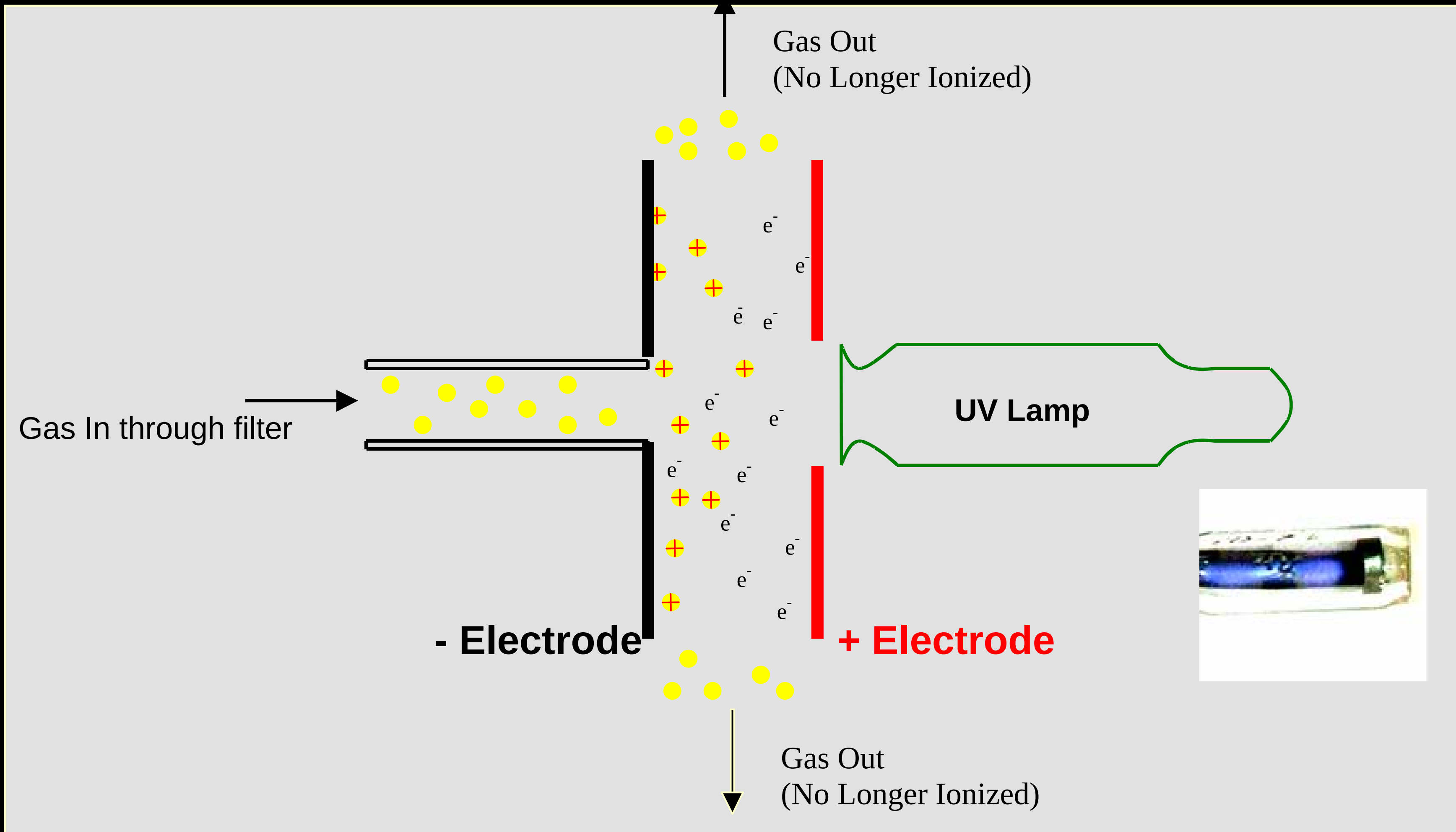
then the molecule is ionized !

Detector Operation

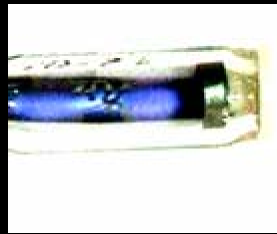


When a molecule is ionized an electron is removed forming a positively charged ion and an electron.

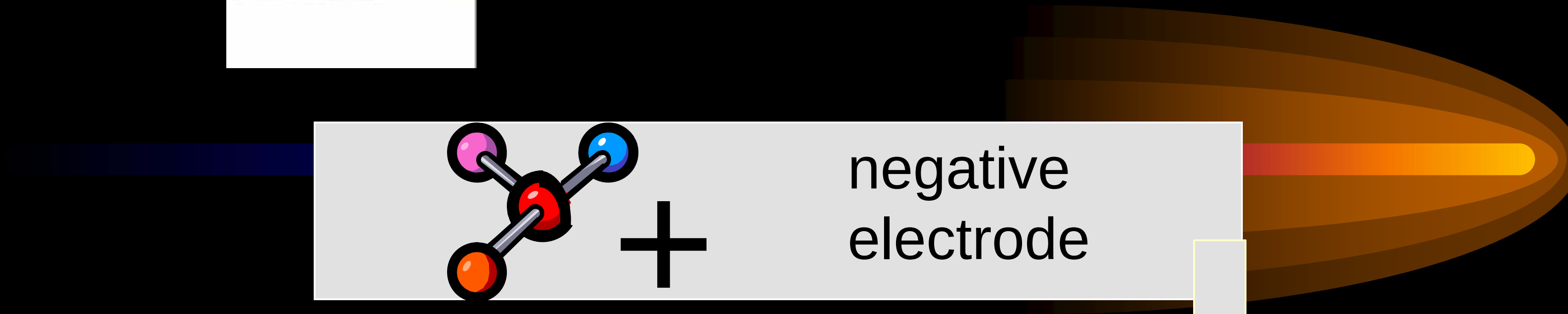
Principle of Operation

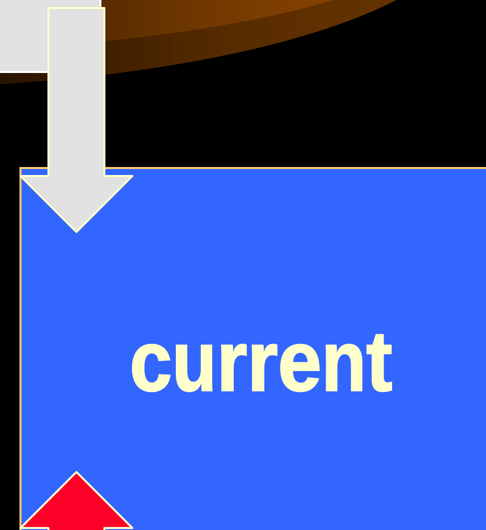


The charged particules then move to the oppositely charge electrode.

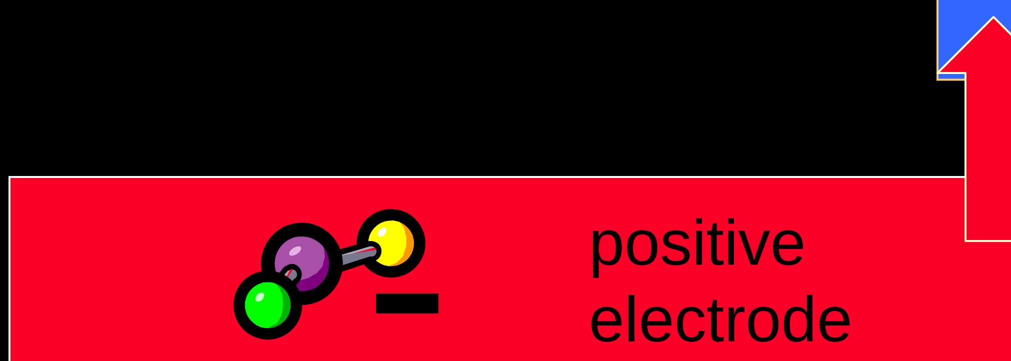


Detector Operation

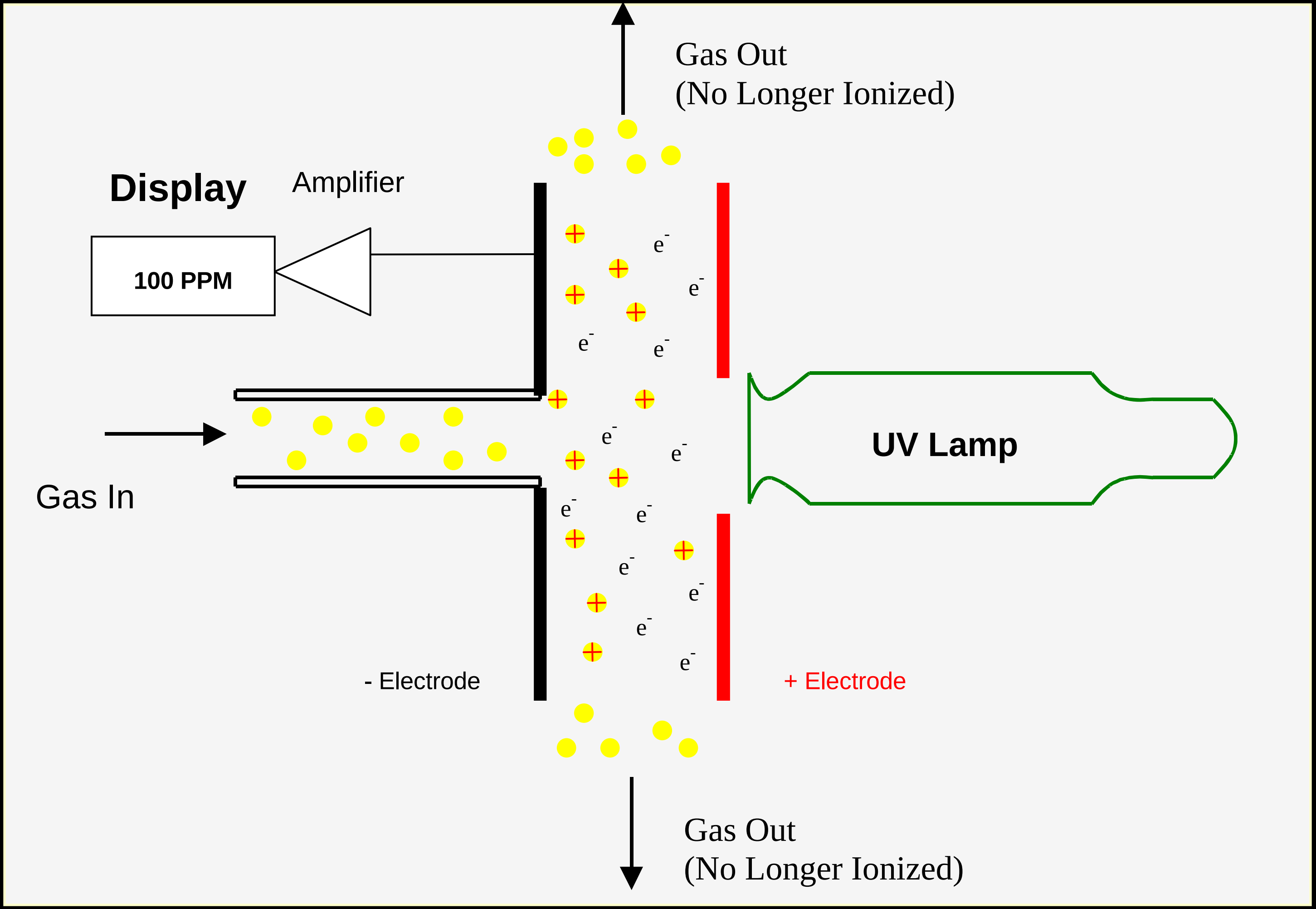




The positive and negative ions are collected on Electrodes which produce a signal.
This signal is directly proportional to the amont of ions present at the electrodes!

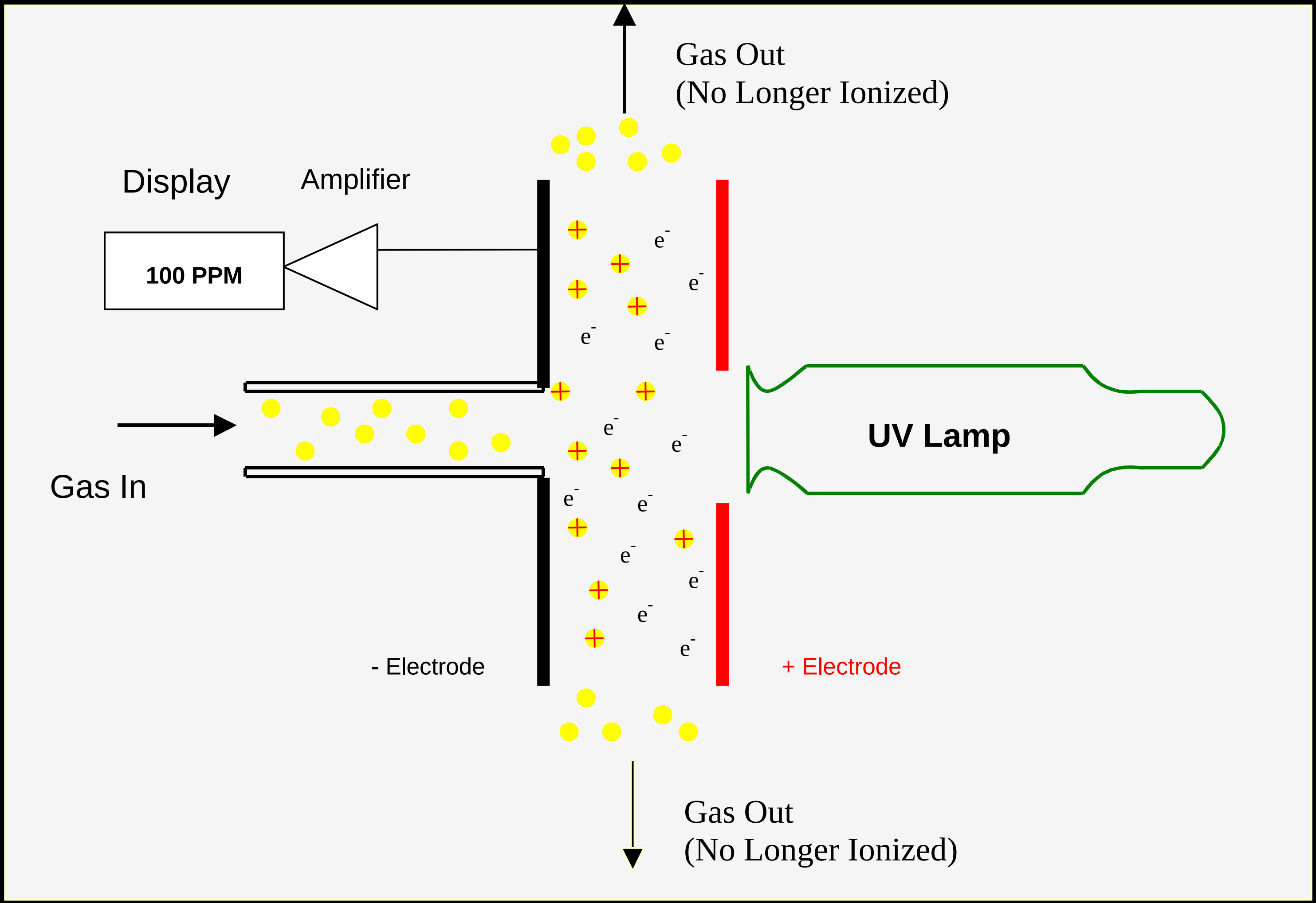


PID Principle of Operation



The signal is then displayed in parts per million (ppm) on the Instrument display.

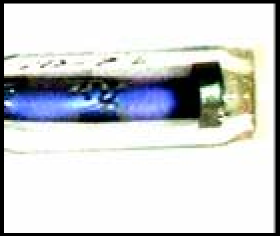
PID Principle of Operation



As the ions leave the chamber they recombine with an electron and The molecules exit in the same state as they entered !

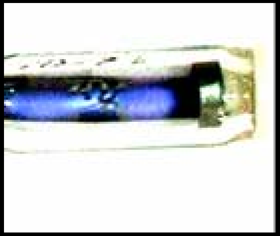
PID sensors

SPECIFICATIONS



PID Lamps

Lamp Energy	Gas Fill	Window Material	Window Characteristics	Expected Life (hours of operation)
10.6 eV	Krypton	Magnesium Fluoride (MgF_2)	Hydrophillic window material, degraded transmittance with continued exposure to moisture.	6,000 hours typical
11.7 eV	Argon	Lithium Fluoride (LiF)	Window material slightly soluble in water, seriously degraded in presence of UV light	40 to 80 hours typical Maximum 150

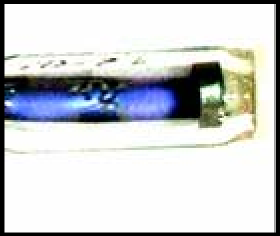


What does a PID detect?

VOC's or Volatile Organic Compounds

- ***Volatile:*** *readily vaporizable at a relatively low temperature.*
- ***Organic:*** *of, relating to, or containing carbon compounds.*
- ***Compound:*** *something formed by a union of elements.*

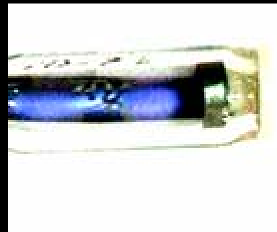
As a rule of thumb organic solvents are VOC's



Volatile Organic Compounds

Alkanes	Alkenes	Aromatics	Alkynes	Terpenes
Examples Butane (a paraffin)	**Examples** Ethylene (Ethene)	**Examples** Toluene	**Examples** Acetylene (welding gas) (Ethyne)	**Examples** 1,8–Cineole (Eucalyptus Oil)
Reactivity Slow	**Reactivity** Fast	**Reactivity** Medium	**Reactivity** Slow	**Reactivity** Fast
Sources Liquid Fuel Exhaust Solvents Natural Gas LPG	**Sources** Exhaust Chemical Feedstock	**Sources** Liquid Fuel Solvents	**Sources** Exhaust Biomass burning	**Sources** Natural Vegetation

- More accurate description: A VOC is Any hydrocarbon, except methane and ethane, with a vapor pressure equal to or greater than 0.1 mm Hg



Sensitivity and accuracy of a PID

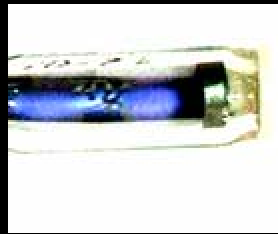
- PID is capable of sub-ppm level detection of most volatile organic compounds (VOCs) (typical resolution 0.1 ppm)
- PID output per unit concentration ie. mV/ppm
- A PID has the sensitivity but not the accuracy

INDUSTRIAL SCIENTIFIC

OLDHAM

I ion Potentials and the Lack of PID Selectivity

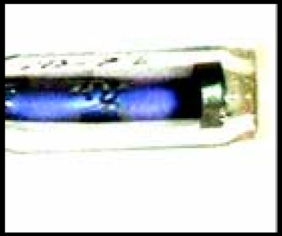
Chemical Name	IP (eV)	Detected with a 10.6 eV lamp	Detected with a 11.7 eV lamp
Benzene	9.25	YES	YES
Toluene	8.82	YES	YES
m-Xylene	8.56	YES	YES
Ethylbenzene	8.77	YES	YES
Ammonia	10.20	YES	YES
Methylene Chloride	**11.32**	**NO**	**YES**
Carbon monoxide	14.01	NO	NO
Oxygen	12.08	NO	NO
Water	12.60	NO	NO



Selectivity

- PID’s are not selective : ***Any molecule with an IP less than the IP of the lamp will be ionized.***
- There is a need to consider:
  - What VOC’s am I likely to see?
  - What of these has the lowest acceptable level?
  - Calculate with response factors

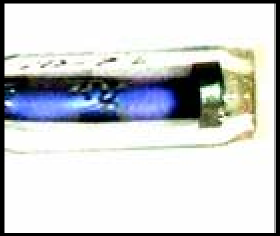
INDUSTRIAL SCIENTIFIC
OLDHAM



Troublesome Conditions

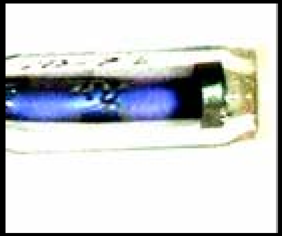
- *Presence of water vapor in sample stream causes quenching of the detector signal due to UV absorption and can short out the two electrodes*

- *Oxygen and methane are also UV absorbers. Significant changes in their concentration can cause both gain and background changes in the PID signal*



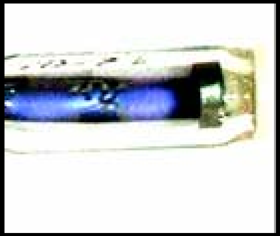
Effect of Environmental Conditions on PID Signal

- Variation in pressure and temperature will have an effect on PID response. These effects will be compensated by the instrument.
- **For maximum accuracy: Calibrate instrument in environmental conditions as close to sample conditions as possible**



PID Lamps Require Periodic Cleaning

- Dust, dirt, or oil residue on lamp window will degrade the the performance of the PID.
- The frequency of cleaning will depend on the application. As a rule of thumb, under normal conditions the lamp should be cleaned after every **40 hours** of service.

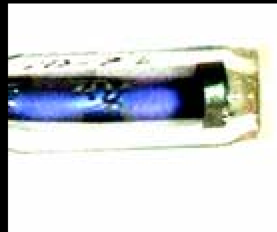


Method of Cleaning

1 - Methanol

- Solvent cleaning with methanol, will save time and may be sufficient depending on the type and amount of residue on the lamp window. Use a q-tip and gently clean lamp window.

INDUSTRIAL SCIENTIFIC
OLDHAM



Method of Cleaning

2 - Abrasive

- Abrasive cleaning or Polishing “cuts” away a very thin layer of lamp widow and will restore the lamp window to like new condition.
- After cleaning, the lamp requires a burn-in period until the output of the lamp stabilizes.
- ***- Lamp burn-in is 24 hrs.-***

Photo, or the "light source"

- *Handle the lamps by grasping their bodies.*
- *Never touch the lens. Touching the lens transfers oil which will decrease the UV output.*

Troublesome Compounds

- Compounds that have a tendency to condense on the inner surfaces of the detector can cause signal drift.
- Ethylene behaves erratically
- Ammonia causes severe degradation of detector performance

INDUSTRIAL SCIENTIFIC

OLDHAM

PID Applications

- Petrochemical
- Oil and Gas
- Hazmat
- Aviation
- Fire Departments
- Environmental
- Drug Enforcement

INDUSTRIAL SCIENTIFIC
OLDHAM

DETECTOR TUBES

- Measure of low concentrations
- specificity to one gas
- easy to use.
- Low cost
- is often the complement of the standard gas detection systems.

Dust particules detection :principles

- **Backscattering:**LASER light backscattered by dust particules (analyser)
- **POSTDIFFUSION:** LASER light postdiffused by dust particules (analyser)
- in-situ measurement of smoke opacity
- Particules detection by triboelectric effect (probes)