

## General

- ECOPROBE 5 has two autonomous analyzers in one case.
- The combination of analyzers provides a set of data designed for Soil Contamination Survey and various environmental tasks.
- Each analyzer uses a different principle for gas analyses. The interpretation of resulting values from each analyzer thus require a different “interpretation view”.
- Following is an explanation of both analyzer principles in general and also their utilization in ECOPROBE 5 instrumentation and methodology.

# Photo Ionization

## Detection

A square logo with a purple-to-blue gradient background and a dark border. The letters "PID" are written in a bold, white, serif font in the center.

Photo Ionization Detectors (PID's) measure low levels (0,1 ppb -2 000 ppm) of VOCs (Volatile Organic Compounds) and other toxic gases. Many Hazardous Material incidents are VOCs and the sensitivity of PID's to VOCs make them an invaluable tool for initial incident assessment, leak detection and spill delineation.

What are some common VOCs ?

VOCs are chemical compounds widely used in industry and include:

- Fuels (produce the majority of Hazardous Materials incidents)
- Greases, Oils, Degreasers
- Solvents, Paints, Plastics and Resins

(not all can be measured by PID)

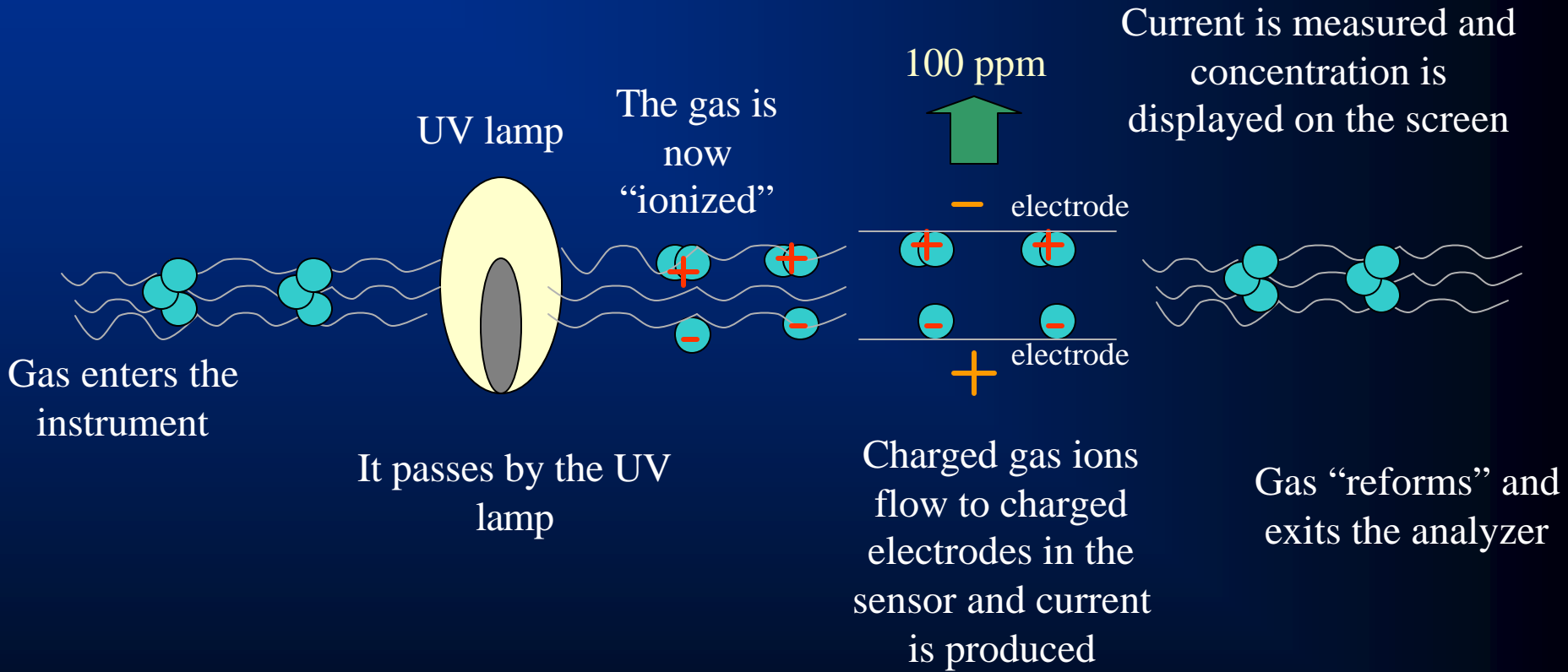
# Photo Ionization Detection

How does a PID work?

A PID uses an ultraviolet light source (Photo = light) to break down chemicals to positive and negative ions (Ionization) that can easily be measured with a detector. The detector measures the charge of the ionized gas and converts the signal into current. The current is then amplified and displayed as “ppm”.

After measurement the ions reform the original gas. PIDs are non-destructive, they do not permanently alter the gas, and allow the gas to be used for further analysis.

# Photo Ionization Detection



# Photo Ionization Detection

## Ionization Potential

All elements and chemicals can be ionized, but they differ in the amount of energy they require. The energy required to displace an electron and ionize a compound is called Ionization Potential (IP), measured in electron volts (eV). The light energy emitted by an UV lamp is also measured in eV. If the IP of the sample gas is less than the eV output of the lamp, then the sample gas will be ionized.

## Example:

Benzene has an IP of 9.24 eV and can be detected by a “standard” 10.6 eV lamp. Methylene Chloride has an IP of 11.32 eV and can only be seen by an 11.7 eV lamp. Carbon Monoxide has an IP of 14.01 eV and cannot be ionized by a PID lamp.

# Photo Ionization Detection

## What does a PID measure?

The largest group of compounds measured by a PID are the Organics -- compounds containing Carbon molecules. These include:

- **Aromatics** - compounds including a benzene ring such as benzene, ethyl benzene, toluene and xylene.
- **Ketones & Aldehydes** - compounds with C=O bond including: acetone, methyl ethyl ketone and acetaldehyde.
- **Amines & Amides** - Carbon compounds containing Nitrogen, like diethyl amine.
- **Chlorinated hydrocarbons** - trichloroethylene, perchloroethylene.
- **Sulfur compounds** - mercaptans
- **Unsaturated hydrocarbons** - like butane and octane
- **Ammonia (Inorganic)**
- **Semiconductor gases** - Arsine (Inorganic), Phosphine
- **Nitric Oxide**
- **Bromine and Iodine**

# Photo Ionization Detection

What PIDs do not measure?

- Radiation
- Air ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ )
- Common Toxics ( $\text{CO}$ ,  $\text{HCN}$ ,  $\text{SO}_2$ )
- Natural Gas (Methane, Propane, Ethane)
- Acid Gases ( $\text{HCl}$ ,  $\text{HF}$ ,  $\text{HNO}_3$ )
- Others - Freons, Ozone ( $\text{O}_3$ )

# Photo Ionization Detection

What's a Correction Factor (CF) ?

Correction Factors (CF) are used to adjust the sensitivity of the PID to directly measure a particular gas compared to the calibration gas.

Example:

PID is nearly twice as sensitive to benzene ( $CF = 0.53$ ) as it is to its calibration gas of Isobutylene ( $CF=1.0$ ). So if we are measuring 1 ppm of benzene, after calibration on Isobutylene, we will see approximately 2 ppm on the display of the PID. If we multiply 2 ppm by CF 0.53 we will get the true reading of benzene (about 1 ppm).

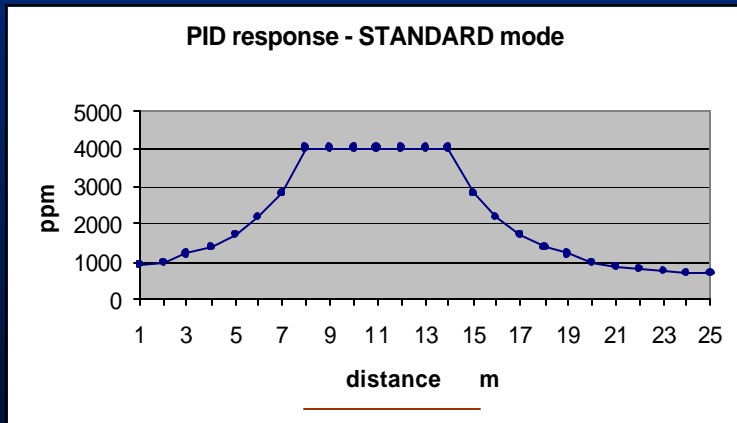
Correction Factors are applied automatically in the ECOPROBE 5: ECOPROBE 5 contains the list of gases. You can select any gas from the list directly in the instrument and the appropriate Correction Factor is automatically applied. The resulting values are directly and automatically related to the selected gas.



# Photo Ionization Detection

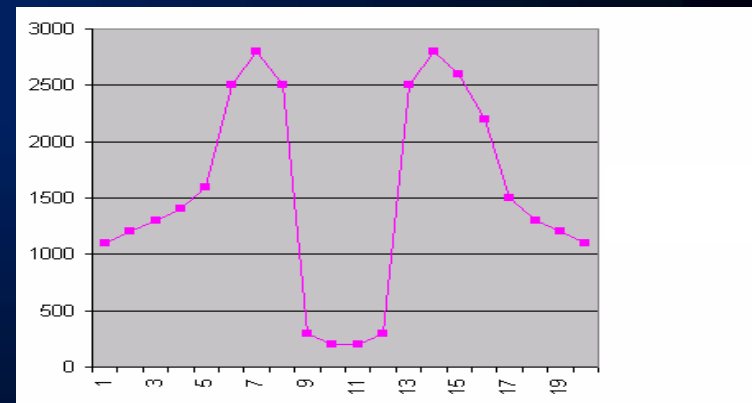
What is a photoionization breakdown phenomenon ?

Photo Ionization Detectors (PID's) measure low levels (0,1ppb -3 000 ppm) of VOCs. For a concentration higher than a given limit the ionization process will breakdown. Further increase of concentration may even lead to the decay of output (the resulting values may vary around 300 ppm for the concentrations higher than photoionisation breakdown limit). The average value of photoionisation breakdown limit is around 3000 ppm and this value varies for different spectral compounds. To indicate this phenomenon by means of operating software is not usually possible and is not available for PID instruments.



Localization of the highest contaminant concentration

*Response of ECOPROBE 5 PID unit to rising concentration of contaminant for STANDARD mode*



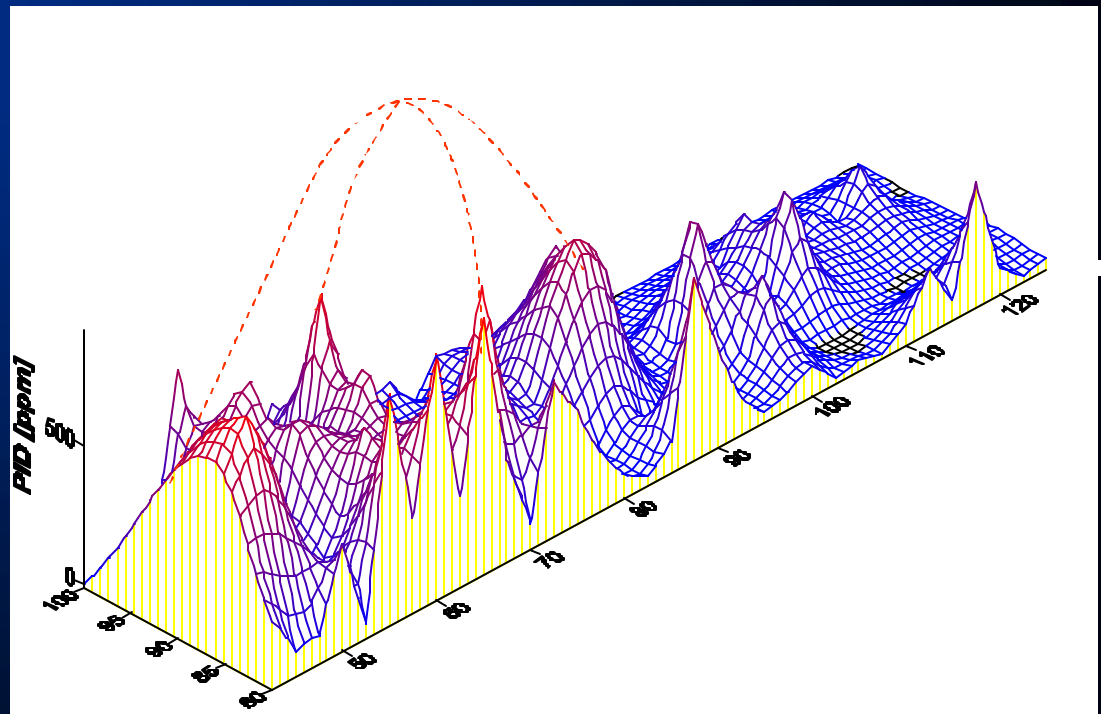
Localization of the highest contaminant concentration

The operator should always keep this fact in mind to avoid interpretation errors.

# Photo Ionization Detection

## Photoionization breakdown - Interpretation

The wire-frame map (from the PID) on the right was obtained from a polluted site. The part on the left shows high contamination. Its shape may be interpreted as a photoionization breakdown with the largest contamination in the middle part.



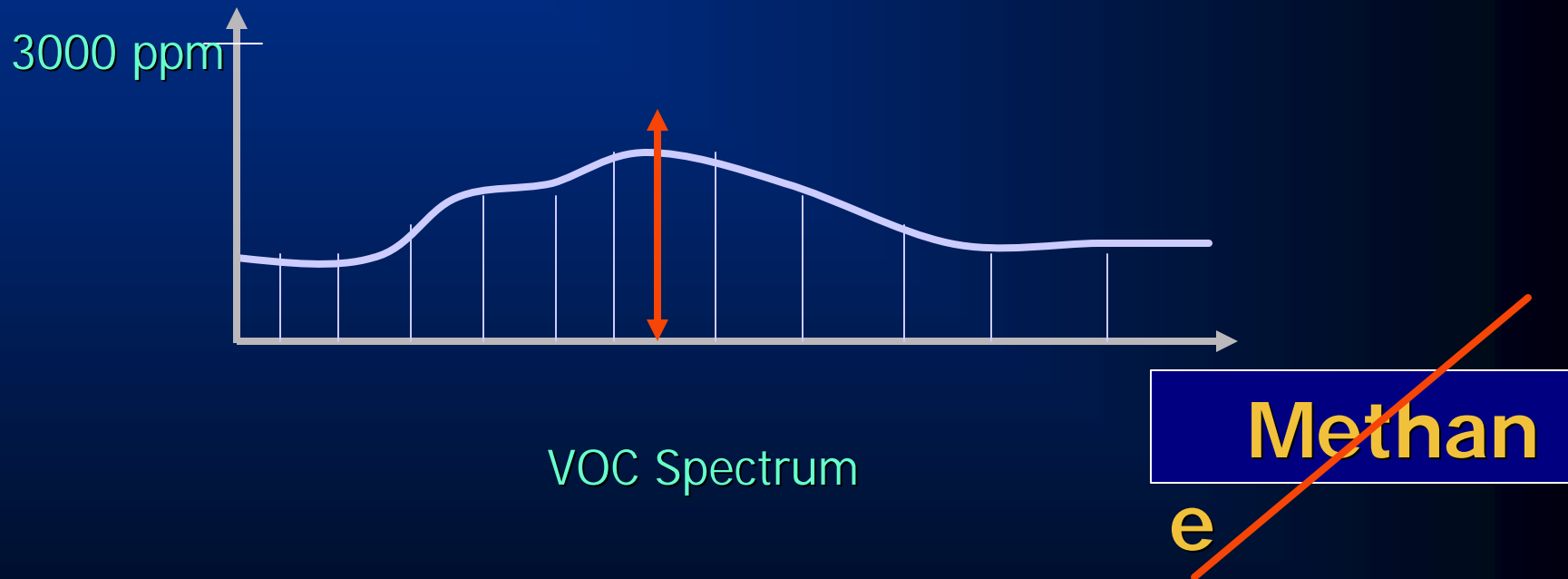
# Photo Ionization Detection

## PID Selectivity

- PID is a very sensitive but not a selective monitor. How may we understand then the fact that the PID analyzer offers more than 200 calibration compounds? -- The user must determine the name of the measured compound to select from the list of calibration compounds. The resulting reading of the selected compound will be then close to quantitative values. To visualize this, let's compare the PID to a ruler.
- A ruler is an accurate means of measuring the width of a sheet of paper. But it cannot tell the difference between grey and white paper. Therefore, if one wants to know the width of the grey sheet of paper, that **person** must first select the proper sheet of paper before measuring with the ruler.
- The PID is similar to a ruler. It can tell us how much of gas is present, but we must determine which gas. When approaching an unknown chemical release, the PID is set to its calibration gas of Isobutylene. Once the chemical is identified, the PID sensitivity can be adjusted to that chemical so that it reads in an accurate scale.
- **Example:** If we calibrate on Isobutylene and happen to measure a benzene leak of 1 ppm the PID will display 2 ppm because it is twice as sensitive to benzene as it is to Isobutylene. Once we have identified the leak as benzene, then the PID scale can be set to benzene calibration gas and the PID will accurately read 1 ppm if exposed to 1 ppm of benzene.

# PID Detection and ECOPROBE 5

In case of contaminant with a complicated mixture of compounds, the resulting value represents the highest measured value of the compounds presented in the contamination spectrum, slightly enlarged by the contribution of other compounds occurring in the spectrum.



PID analyzer selectively excludes Methane from the total sum

# PID Detection and ECOPROBE 5

ECOPROBE 5 PID analyzer is calibrated on Isobutylene. Isobutylene represents the most suitable gas which is also used in laboratory gas chromatographs which brings very close results between ECOPROBE 5 outputs and laboratory analyzed values. As was explained above, ECOPROBE 5 is automatically calibrated for about 200 compounds.

The complete list of measured compounds can be found in “Operator’s Manual” and is also implemented in the instrument to enter the selected compound directly in the field.

## Simple Gas Detection

- Imagine the simplest situation when composition of contamination is known and created by one compound. Select the compound from the list of measured compounds included in the instrument and you will always get precise quantitative results.

# PID Detection and ECOPROBE 5

## Gas Mixture Detection

- Commonly the contaminant is a *complex mixture of compounds*. In case of common hydrocarbon contaminant, the operator can select one of the hydrocarbon mixtures (diesel fuel, jet fuel..) from the list of measured compounds. The resulting values are then closer to quantitative results.
- If you are not sure about the contaminant composition, select the calibration gas Isobutylene.
- In case the operator wants to be sure about the contaminant composition, it is recommended to have some samples analyzed in the lab. Then the prevailing compound (or the most toxic compound) in the spectrum is selected from the list of compounds implemented in the instrument and the results are much closer to the quantitative results

## PID Detection and ECOPROBE 5

Above mentioned selection of the calibration gas and obtained values are sufficient for the common Soil Contamination Survey tasks, providing fast and cost effective identification of relative concentration cloud, contaminant sources, direction and size of the contaminated area.

In case the given Soil Contamination Survey task requires more precise evaluating (not standard), keep to the following procedure:

- Supposing contaminant and soil characteristics are approximately equal over the given environment
- Select the compound characterizing the contaminant in the list of measured compounds.
- Compare for example four or five ECOPROBE 5 values and laboratory-analyzed samples from the same sampling hole.
- 
- Set the correlation coefficient for these samples. If the coefficient is approximately the same for all matching samples, use it to multiply the whole set of values of the locality measured with ECOPROBE 5 to get approximate quantitative results.



# PID Detection and ECOPROBE 5

ECOPROBE 5 PID analyzer has two ranges:

**HISENS** - detection limit: low ppb values; upper limit is 100 ppm (output also in  $\mu\text{g}/\text{m}^3$ ).

HISENS mode is extremely sensitive, suitable for measuring air contamination – near petrol pumps etc.. (it is not suitable for measuring a contamination of the ambient air). For the Soil Contamination Survey tasks it is necessary to keep thoroughly the methodology of the field measurement (cleaning procedures etc.) since factors like moisture, presence of Methane or under-pressure may influence the results. Using HISENS mode even cutting or transformer oils can be measured in the sub-surface environment.

**STANDARD** - detection limit 0.1 ppm upper limit 3000 ppm (output also in  $\text{mg}/\text{m}^3$ )

## Application of ECOPROBE 5 PID Analyzer

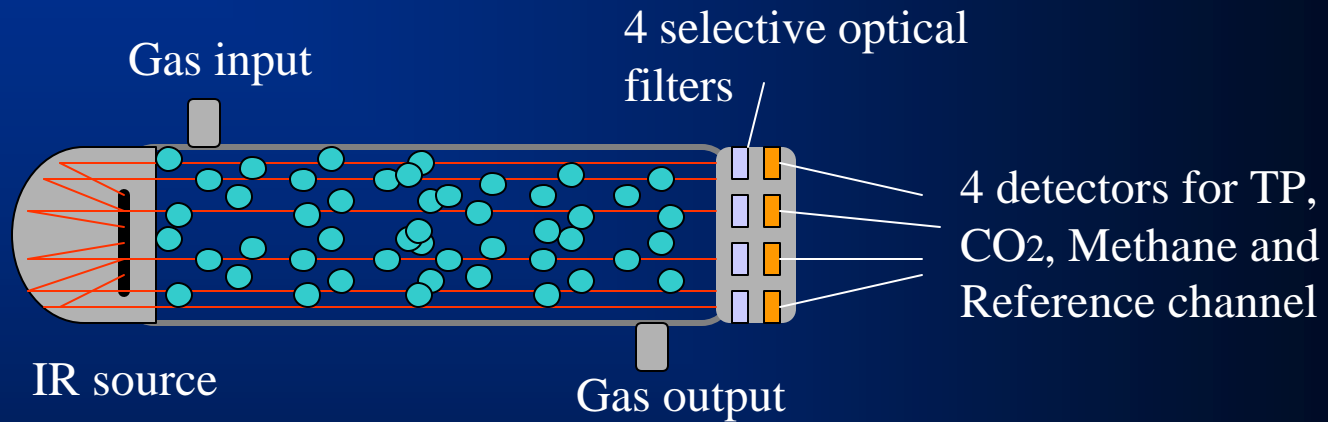
1. For measuring small values of contaminant concentration
2. For measuring a wider spectrum of contaminant
3. For quantitative measurement

# Infra-Red Detection

**IR**

- Infrared radiation is essentially heat radiation. This fact will be familiar to anyone who has ever felt the heat radiated from a hot oven, and had observed the dark red glow arising when the heat becomes stronger.
- Most gases have their characteristic spectra in the infrared. Those spectra derive from the molecule's composition in such a way that no two molecular gases have the same IR spectrum. IR spectra are the fingerprints of gases, and thus allow gases to be uniquely identified.
- By transmitting a beam of IR radiation through the air, or through any particular gas volume, and recording how much is transmitted at selected spectral lines, one may decide which gases are present and how much of each.

# Infra-Red Detection

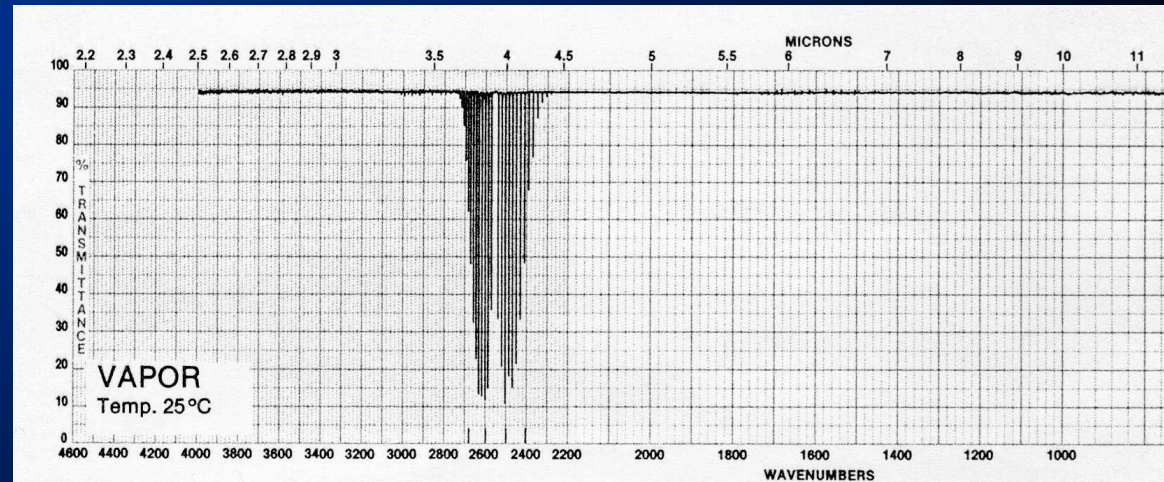


IR wide spectrum radiation is passing through the gas column. At the same time the sampled gas is transported through the tube.

# Infra-Red Detection

Oscillation of the microscopic particles of the compound consumes energy at a group of particular spectral lines.

A general example of a typical IR absorption spectrum



This phenomenon is called infra-red atomic absorption. Consumed energy is directly proportional to the concentration of the measured compound. The higher the concentration, the higher absorption of the energy at the characteristic wavelength. Each selective optical filter lets through only one wavelength of the radiation typical for the measured compound. A detector behind the optical filter measures the attenuation of the energy that is directly proportional to the measured concentration.

# Infra-Red Detection

ECOPROBE 5 IR analyzer provides selective detection of Methane, group of common petroleum hydrocarbons and Carbon Dioxide.

Features:

4 independent channels (ppm or mg/m<sup>3</sup> output) :

- Methane -- ensures separate measurement of Methane with no interference from other compounds.  
Range of measurement: 0 - 500 000 ppm; detection limit: 100 ppm,
- Petroleum Hydrocarbons -- each hydrocarbon pollutant is a mixture of hundreds of different compounds. Total Petroleum channel is defined as a wider spectral window, accepting the range of wavelengths typical for all the petroleum-based Hydrocarbon pollutants. The resulting output represents the concentration of the contaminant as a whole, *including Methane*, with no separation of particular compounds.  
Range of measurement: 0 - 500 000 ppm; detection limit: 30 ppm,

# Infra-Red Detection

- Carbon Dioxide -- ensures separate (one-wavelength) measurement of Carbon Dioxide with no interference from other compounds. Range of measurement: 0 - 500 000 ppm; detection limit: 20 ppm,
- IR analyzer also comprises a reference channel -- reference channel window is located at that wavelength of the IR radiation spectrum where no other compounds interfere. The output value is influenced by temperature, dust, moisture and other possible disturbances. Other IR channels are influenced in the same way. The readings of the other IR channels are related to the reference channel. In this way the undesirable influences from disturbing factors are eliminated. The reference channel considerably prolongs the calibration interval of the IR analyzer.

## Infra-Red Detection

Field experience has proved that an IR analyzer is essential to the general Soil Contamination Survey. The contaminant concentration is often above 3000 ppm, where PID detection cannot be used.

If hydrocarbons are present in the contaminant, consequent continuity between PID and IR outputs can be observed.



# Infra-Red Detection

Both IR Methane and IR Total Petroleum channels are calibrated on Methane.

- ⑦ Reading of IR Methane channel then perfectly corresponds with the real amount of Methane presented.
- ⑦ Reading of IR Total Petroleum channel:
  1. If only Methane is presented and no other hydrocarbons: Reading of Methane channel and IR Total Petroleum channel shows the amount of Methane
  2. If a mixture of Methane and hydrocarbons is presented: IR Total Petroleum channel measures the amount of petroleum hydrocarbons including Methane. This reading is higher than parallel reading of Methane channel.
  3. If only hydrocarbons are presented and no Methane: (there is no reading on Methane channel); IR Total Petroleum channel measures the amount of petroleum hydrocarbons. It is necessary to take into account that this channel is calibrated on Methane and the resulting value does not show precise quantitative value of the hydrocarbon concentration. The resulting value is generally 6 – 10 times higher than the real concentration of hydrocarbons. You can map the area in a relative way or divide the results approximately by 10 (try to compare the IR TP value with the PID value at the station where Methane is not presented – be sure that the PID value is not above the photoionization breakdown limitation).

# Infra-Red Detection

- ⑦ Since the IR TP channel is calibrated on Methane and the PID analyzer on Isobutylene, you will never get the same quantitative data from both analyzers. Reading of IR Total Petroleum channel may be 6 - 10 times higher than reading of the PID analyzer, calibrated on Isobutylene (see previous paragraph). To obtain comparative readings from IR TP channel and PID channel, both analyzers should be calibrated to the same gas!!

## Application of ECOPROBE 5 IR Analyzer

1. Relative and fast in situ monitoring of contaminant
2. Separate reading for Methane, Hydrocarbon group and CO<sub>2</sub>