VII.1.6 - Detector:

VII.1.6.1 Definition: Chromatographic detector:

A **chromatographic detector** is an instrument placed at the outlet of the column that measures **the** concentration of solutes present in the column effluent. It converts this measurement into an **electrical signal** proportional to the concentration of the solute, thus producing a **chromatogram.**

✓ Principle of detection:

The principle of detection is based on measuring a physical or **chemical property** of the solute as it passes through the detector. These properties may include:

- Light absorption **(UV-visible)**
- Conductivity
- Refractometry
- Ionization **or** mass variation **.**

Variations in these properties are converted into **signals** by the detector, which are then recorded as a **chromatogram** .

VII.1.6.2.Tthe different types of detectors in chromatography:

There are several types of detectors used depending on the type of chromatography and the properties of the solutes. Detectors can be classified into two main categories: **universal detectors** and **specific detectors** .

a) Detectors for Liquid Chromatography (HPLC):

- **UV-Visible (UV-Vis) Detector**: Measures the absorption of UV or visible light by solutes. Light-absorbing compounds generate a signal proportional to their concentration.
- **Differential Refractometry Detector (RID):** Measures the variations in the refractive index between the pure mobile phase and the mobile phase containing the solute.
- **Fluorescence Detector:** Measures the emission of light by solutes after excitation by a light source.
- **Electrochemical Conductivity Detector:** Measures the electrical conductivity of the solution in the presence of ionic compounds.

b) Detectors for Gas Chromatography (GC):

- **Flame Ionization Detector (FID):** Burns organic solutes in a hydrogen flame, generating ions that are detected as an electric current.
- **Electron Capture Detector (ECD):** Measures the capture of electrons by electronegative compounds (often halogens).
- **Mass Detector (MS):** Ionizes solutes and separates them according to their mass/charge ratio (m/z).

Conclusion:

***Detection results: The chromatogram** A **chromatogram** is the graph produced by the detector. It represents the **signal** as a function of **time** .*

VII.1.6.3 Chromatogram:

A chromatogram is the graphical result of a chromatographic analysis, allowing to visualize the separation of the components of a mixture according to their retention time in the column. Here is a detailed explanation of its elements and how to interpret it.

(a) Definition of a Chromatogram :

A chromatogram is a graphical representation where the intensity of the detected signal (usually by a UV, fluorescence, or mass detector) is plotted against time. It allows one to observe the separation of compounds in a mixture, with each compound appearing as a distinct peak.

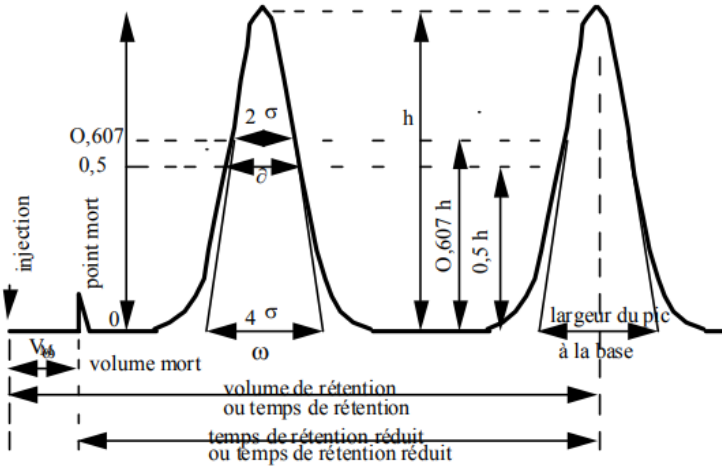

Fig. VII. 4: Chromatogram[1]

✓ Chromatogram: Variations and Coordinate Axis:

In a chromatogram, the y-axis **represents** the intensity of the detected signal, which is often related to the concentration or amount of a compound in the sample. The x-axis **represents** time, and each peak on the chromatogram corresponds to a specific time of detection, that is, the retention time of the compound.

- **Signal variation over time** : The chromatogram shows how the detected signal varies over time, where each peak appears at the time a specific component is detected.
- **Interpretation of results** : By comparing the retention times obtained with the known retention times for standard compounds, each peak can be identified.

✓ Meaning of a Straight Line (No Peaks):

- A straight line on a chromatogram (absence of peaks) means that no compounds were detected during that period. This may indicate a phase where there are no components

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[1] https://www.analyticaltoxicology.com/chromatographie-phase-gazeuse-cpg/

retained by the stationary phase or a period where the components are either very low in concentration or undetectable by the detector used.

- A straight line may also appear before sample injection, during the equilibration or signal stabilization period.

✓ Identification of Compounds :

To determine the identity of a compound:

- ✓ **Retention time** : The first indicator is the retention time of the peak. By comparing it to known standards, it is possible to make a first identification.
- ✓ **Analysis of spectrum or other characteristics** : In some techniques (such as chromatography coupled with mass spectrometry), the spectrum of each peak can be analyzed to provide a more precise identification.
- ✓ **Peak intensity** : The intensity and shape of the peak can also give clues to the nature and concentration of the compound.

In conclusion, the chromatogram is a powerful method to analyze and quantify the components of a mixture, each peak corresponding to a distinct compound and its retention time helping to identify the compounds in comparison with standards.

❖ Retention time (t_R):

The **retention time** is the time elapsed between the injection of the sample into the chromatographic column and the appearance of the peak corresponding to the detected solute. It represents the time required for the solute to migrate through the column under the influence of the mobile phase: **Interpretation** : A high retention time indicates that the solute has interacted for a longer time with the stationary phase, while a short retention time indicates a weak interaction.

❖ Retention volume (V_R):

The **retention volume** is the volume of mobile phase required to elute (pull out) a specific solute from the column. It is calculated by multiplying the retention time by the volumetric flow rate of the mobile phase (F):

$$V_R = t_R \times F$$

$$V_R = t_R \times v \times s$$

- (v): linear velocity of the mobile phase
- (s): reduced section of the column
- . $s = s' \times \varepsilon$
- (s'): section of the column
- ε: **porosity**

$$\varepsilon = V_M / V_T \qquad V_M = F \times t_0$$

❖ V_M : volume of the mobile phase in the column:

- The spaces not retained by the stationary phase appear in the effluent after the time (**t_0**) corresponding to the flow of the interstitial volume of the column or volume of mobile phase (**V_M**) contained in the column.

The retention volume (**V_R**) is directly related to the distribution coefficient K by the relation:

$$V_R = V_M + K.\,V_S$$

(V_S): volume of the stationary phase (or mass or specific surface area according to the units of K); this relationship only applies in the case of linear elution, i.e. when K varies linearly with the concentration of the compound in each phase.

❖ Reduced retention time ($t_{R'}$):

The **reduced retention time** is defined as the solute retention time minus the dead time (t_M):

$$t_{R'} = t_R - t_M$$

❖ Reduced retention volume ($V_{R'}$):

The **reduced retention volume** is calculated in the same way as the reduced retention time, taking into account the dead volume (V_M):

$$V_{R'} = V_R - V_M$$

❖ Dead point (Dead time or Dead time (t_M):

The **dead point** or **dead time** is the time required for a molecule not retained (or poorly retained) by the stationary phase to pass through the column. This time is taken as a reference to calculate the reduced retention time:

❖ Dead volume (V_M) :

The dead volume corresponds to the volume of mobile phase required to pass through the column without interaction with the stationary phase.

$$V_M = F \times t_M$$

- **F** : volumetric flow rate of the mobile phase (mL/min).
- **t_M** : time out (in minutes).

If we know the column section and the mobile phase velocity, we can express the dead volume by :

$$V_M = V \times s \times \epsilon$$

- S : cross-section of the column, with r the radius of the column.
- V: linear velocity of the mobile phase
- ϵ : porosity of the column, which represents the fraction of the volume occupied by the mobile phase.

❖ Reduced section of the column :

The reduced column section refers to the column surface area taken into account after reduction by the presence of stationary phase particles.

VII.1.6.4 Partition coefficient (K):

The **partition coefficient** (*Distribution coefficient*) is the ratio between the concentration of the solute (analyte) in the stationary phase (Cs) and in the mobile phase (Cm):

$$K = \frac{C_S}{C_m}$$

- A high partition coefficient means that the solute has a strong affinity for the stationary phase, thus increasing the retention time.