Larbi Ben M’Hidi University Oum El Bouaghi
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Sector : Chemistry

Online courses :

Spectroscopic methods -I-(SAE 3)

Courses and exercises

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Chapter I

GENERAL PRINCIPLES OF THE SPECTROSCOPY

Summary

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LIST OF SYMBOLS AND ABBREVIATIONS

HAS	Absorbance
E	Extinction coefficient
C	Concentration
L	Thickness of the tank expressed in centimeters
UV	Ultraviolet

I. GENERAL PRINCIPLES OF SPECTROSCOPY.

I.1. Definition

Spectroscopy is the study of electromagnetic radiation emitted, absorbed or scattered by atoms or molecules. It provides information about the identity, structure and energy levels of atoms and molecules through the analysis of the interaction of electromagnetic radiation with matter.

The analysis of radiation at its different frequencies is carried out using devices called spectrographs or spectrometers: it allows their electromagnetic spectra to be obtained.

I.2 Fields of application of Spectroscopy

Spectroscopy can explain a large number of phenomena that constantly surround us: the color of our clothes, the color of the sky, etc.

In laboratories, it allows:

- Identification of molecules
- Determination of structures
- The study of reaction kinetics
- Determination of reaction mechanisms
- Dosages
- The analyses medical (MRI, scintigraphy, mammography...) It also has important applications in astrochemistry.

I.3. RADIATION-MATTER INTERACTION

I.3.1. Radiation

I.3.1.1. Wave nature

Electromagnetic radiation (or electromagnetic radiation) is a wave consisting of two oscillating fields: an electric field E and a magnetic field H both perpendicular to each other and perpendicular to the direction of propagation (Figure I.1).

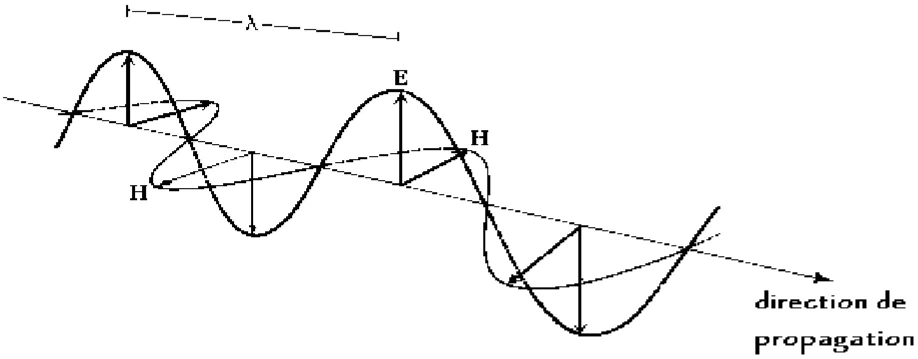


Figure I.1. Propagation of electromagnetic radiation

Electromagnetic radiation is characterized by its frequency, wavelength or wavenumber (Figure I.2).

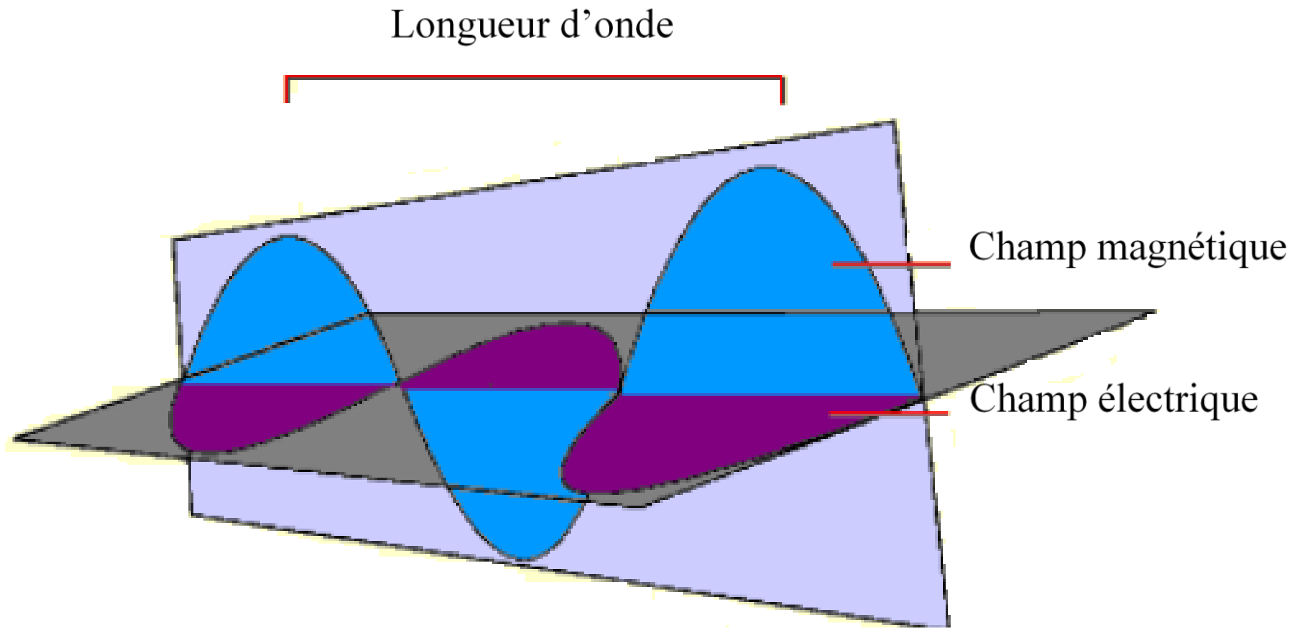


Figure I.2. Characterization of electromagnetic radiation

fréquence (Hertz)

$$\nu = \frac{1}{T}$$

période (seconde)

longueur d'onde (mètre)

$$\lambda = cT = \frac{c}{\nu}$$

vitesse de la lumière (3.10^8 m.s^{-1})

nombre d'onde (cm^{-1} ou m^{-1})

$$\bar{\nu} = \frac{1}{\lambda}$$

The energy of the radiation is related to the previous quantities by the fundamental Planck relation: E = hν; h is Planck's constant. It is equal to $6.624.10^{-34}$ Js

All radiation constitutes the electromagnetic spectrum (Figure I.3).

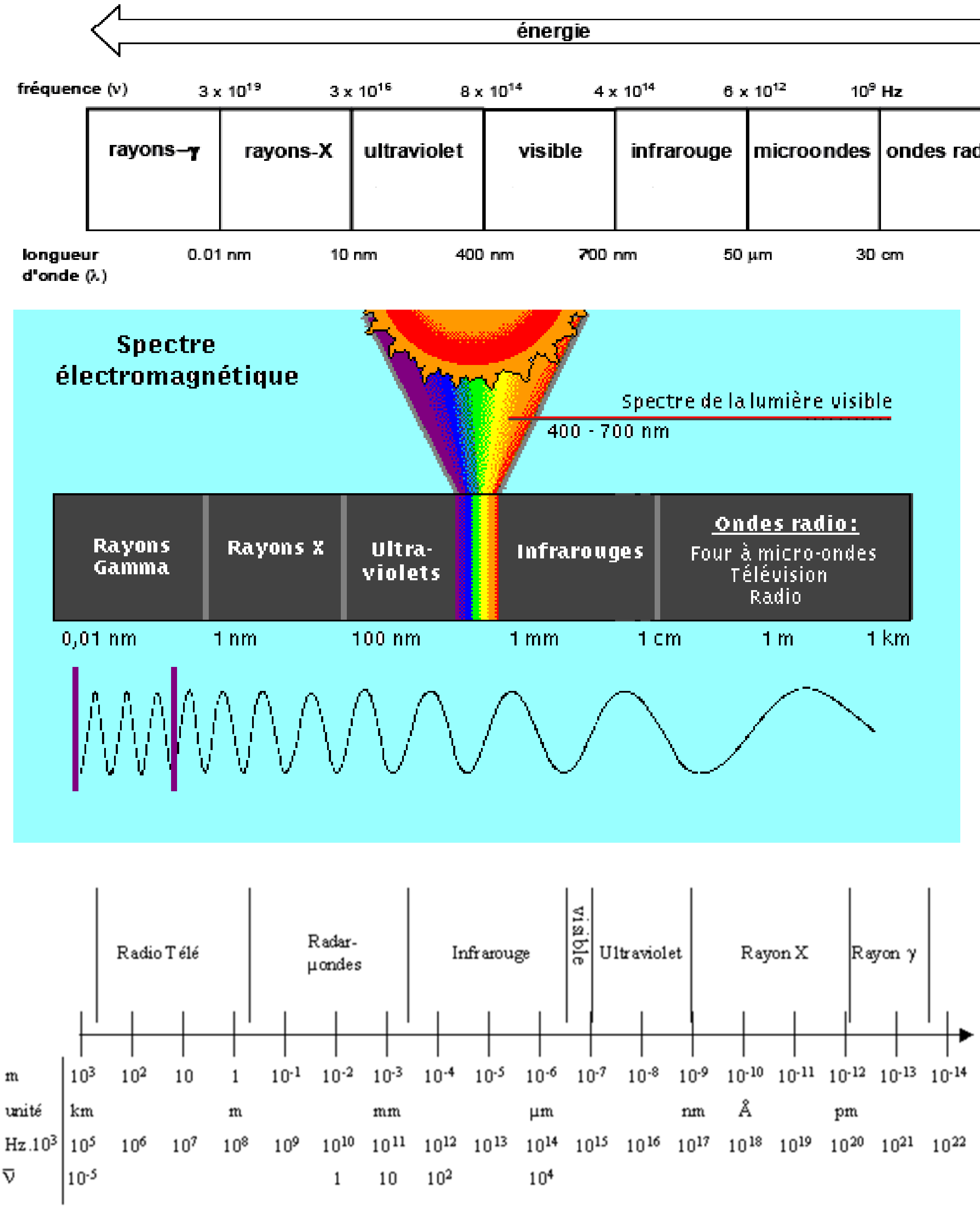


Figure I.3. Set of radiations constituting the electromagnetic spectrum.

I.3.1.2.Corpuscular nature

The wave nature of light alone does not allow us to interpret the phenomena of interaction between light and matter.

PlanckThen**Einstein**proposed quantum theory:

Light is made up of grains of energy: photons.

The photon is a particle that propagates at the speed of light and has a quantum of energy:

$$E = h\nu$$; h is Planck's constant.

I.3.2. MOLECULAR ENERGY LEVELS

An elementary particle (atom, ion or molecule) can only exist in certain quantized energy states. In the case of a molecule, we consider that the energy total is the sum of the terms:

$$\mathbf{E = E_{electronic} + E_{vibration} + E_{rotation} + E_{spin}}$$

The orders of magnitude are very different:$\mathbf{E_e -- E_v -- E_r -- E_s}$.

The electronic, vibrational and rotational energy levels are represented by a diagram in which each level is schematized by a horizontal line and characterized by a set of quantum numbers n, v and J linked respectively to the electronic, vibrational and rotational movements of the molecule (Figure I.4).

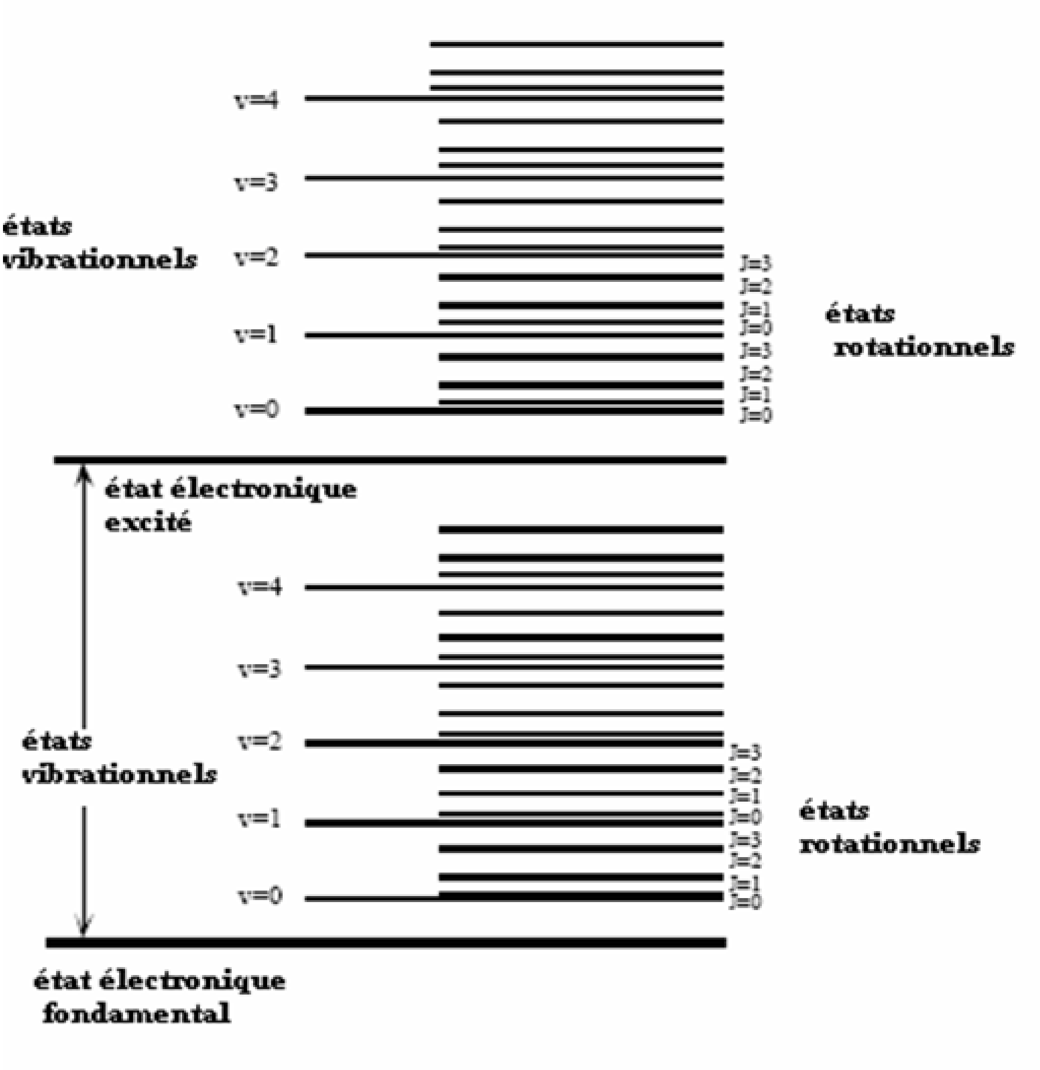


Figure I.4. Molecular energy levels

Each elementary particle (atom, ion or molecule) has a unique set of energy states. The particle can be in any of these states.

The number of particles on a given energy level is called the**population**. The population at a level i relative to the population at the fundamental level obeys**the Maxwell-Boltzmann distribution law**:

$$N_i / N_0 = (g_i / g_0)\, e^{-((E_i - E_0) / kT)}$$

N_i:number of particles in excited state i **N_0:**number of particles in the ground state 0 **$g_i$and g_0**:degeneracy of states i and 0 respectively **$E_i$summer$_0$**:energy of states i and 0 respectively **k:**Boltzmann constant ($1.38.10^{-23}JK^{-1}$) **T:**temperature in Kelvin.

Using this relationship, we show that at ordinary temperature (Figure I.5):

- Several rotation levels are populated;
- The fundamental vibrational level is populated by more than 90% of the molecules, with a few % being placed on the first excited level;
- All molecules are in the ground electronic state.

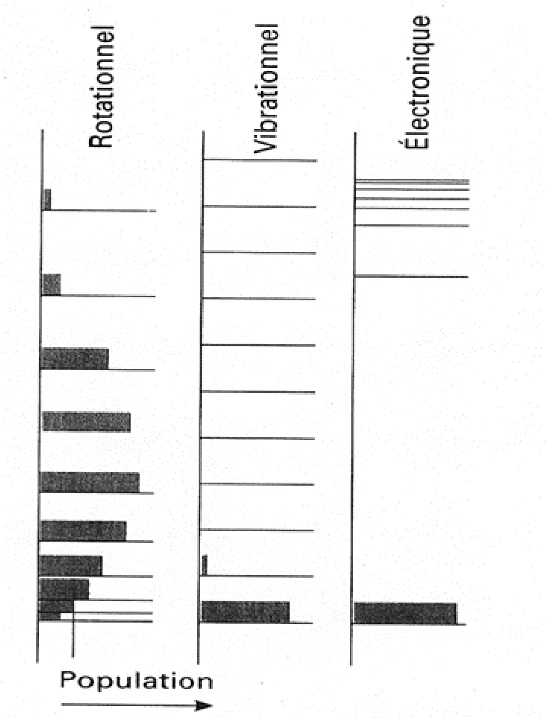
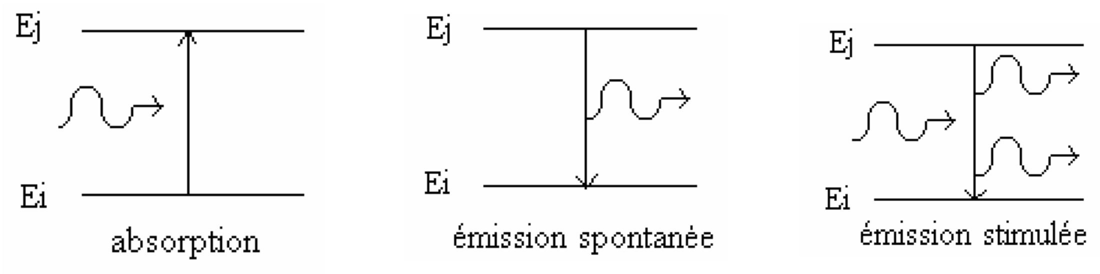


Figure I.5. Population of energy levels, according to the Maxwell-Boltzmann distribution law, at ordinary temperature

I.3.3. INTERACTION BETWEEN WAVE AND MATTER

Energy exchanges between matter and radiation can only take place by quanta:ΔE **= h**-.

Four processes are at the basis of spectroscopic phenomena: absorption, spontaneous emission, stimulated emission (case of lasers) and diffusion (Figure I.6).



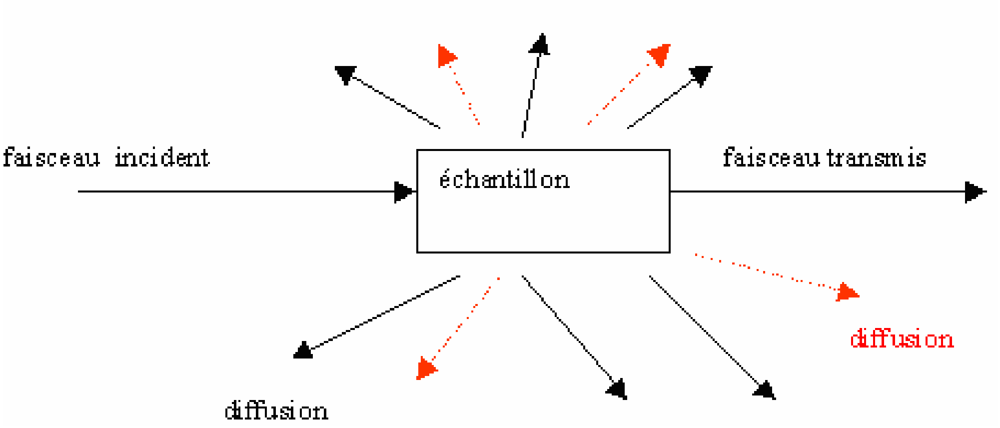


Figure I.6. Processes underlying spectroscopic phenomena.

As a result of the energy exchange, electromagnetic radiation causes a disturbance of the internal molecular motion. A transition from one energy level to another energy level occurs depending on the motion induced (Table I.1).

Absorbed radiation	**Effect on matter**
Radio waves	Nuclear spin transitions (nuclear magnetic resonance NMR)
Microwave	Molecular rotation. Electronic spin transitions (electron paramagnetic resonance EPR)
Infrared	Molecular rotation and vibration
Visible and ultraviolet	Jumping of valence electrons
X-rays	Extraction of electrons from the inner shells of the atom

Table I.1. Effects of absorbed electromagnetic radiation on matter.

I.4. SELECTION RULES

The interactiono nd e -matterbeing a quantum phenomenon, itis accompaniedof selection rules.
Selection rules determine whether a transition is allowed or prohibited.

The wave-molecule interaction can only occur if:

- The frequency of light corresponds to the energy gap**(-E)**between the levels concerned
- The movement causes, at the same frequency, the variation of the dipole moment**μ**of the system.

If μ is the electric dipole moment, then the**transitions are of electric dipole type**(responsible for the phenomena observed in UV, visible and IR).

If μ is the magnetic dipole moment, the**transitions are of the magnetic dipole type**(responsible for the phenomena of nuclear magnetic resonance and electronic paramagnetic resonance).

I.5. LAW OF LIGHT ABSORPTION - BEER-LAMBERT'S LAW

When light hits a homogeneous medium of lengthL (optical path), a part of this incident light noted$I_0$is absorbed by the medium and the remainder, noted**I**, is transmitted (Figure I.7). The fraction of incident light absorbed by a substance of concentration C contained in a tank of lengthLis given by

Beer-Lambert's law:$A = \log(I_0/I) = \varepsilon LC$.

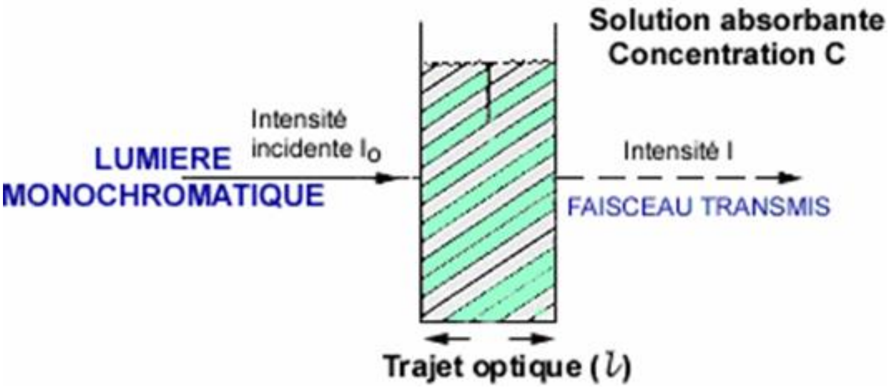


Figure I.7. Passage of monochromatic light through a medium.

HAS :absorbance formerly called optical density (OD)
L :thickness of the tank expressed in centimeters
ε:extinction coefficient. This is a characteristic quantity of the compound. If the concentration is in grams per liter,εis called the specific extinction coefficient. If the concentration is in moles per liter,εis called the molar extinction coefficient.

Transmission is also defined**T**as the ratio of transmitted intensity to incident intensity:

$$T = I / I_0 \qquad \log(1/T) = A$$

The percentage of transmission (%T) is the**transmittance.**

<u>ValidityofBeer-Lambert's law</u>

- Monochromatic light
- Low concentrations

- The solution must be neither fluorescent nor heterogeneous (bubbles, precipitate, etc.)

- The solution must not be the site of a photochemical reaction.

I.6. ABSORPTION SPECTRUM

The graphical recording - made by a device called a spectrophotometer - of the quantity of light absorbed or transmitted by a substance as a function of the wavelength, frequency or wave number gives the absorption spectrum of the substance. According to an absorbance or transmittance representation, we have the following forms (Figure I.8):

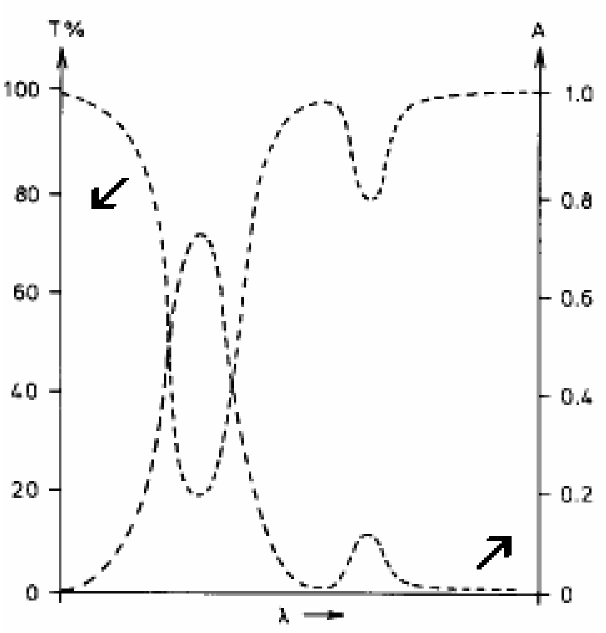


Figure I.8. Absorption spectrum of a substance.

The position of the absorption maximum of a band corresponds to the wavelength of the radiation that caused the transition. As for the intensity, it is related to the dipole moment.

I.7. UNITS, CONVERSIONS AND COMMON CONSTANTS

Tables I.2, I.3 and I.4 present commonly used units, conversions and constants.

For convenience, we use to characterize the wave:

IR:the wave number (cm_{-1}).

UV-visible:the wavelength (nanometer nm).

Table I.2. Conversion factors for energy units used in spectroscopy

Unit	kJ.mole^{-1}	eV	Hz	cm^{-1}
1 cm^{-1}	1.19.10^{-2}	1.24.10^{-4}	3.10^{10}	1
1 Hz	3.98.10^{-13}	4.13.10^{-15}	1	3.33.10^{-11}
1 kJ.mole^{-1}	1	0.18	4.39.10^{13}	1,68.10^{3}
1 eV	96.56	1	2.42.10^{14}	8.07.10^{3}

Table I.3. Usual constants

Electron charge	e = 1.6021773.10^{-19}C
Electron rest mass	m_e= 9.1093898.10^{-31}kg
Proton mass	m_p= 1.6726231.10^{-27}kg
Avogadro's Number	*N*=6,0221367.10^{23}molecules.mole^{-1}
Planck's constant	h = 6.6260755.10^{-34}Js^{-1}
Speed of light in vacuum	c = 2.9979246.10^{8}ms^{-1}
Boltzmann constant	k = 1.3806581.10^{-23}JK^{-1}

Table I.4.Multiples and submultiples.

Multiples and submultiples			
Prefix	Symbol	Multiple	Example
Mega	M	10^{6}	Mm
Kilo	K	10^{3}	km
Decided	D	10^{-1}	dm
Cent	C	10^{-2}	cm
Milli	M	10^{-3}	mm
Microphone	--	10^{-6}	-m
Nano	N	10^{-9}	nm
Pico	P	10^{-12}	pm

NB: For further information, some bibliographical references are provided at the end of each chapter.

BIBLIOGRAPHICAL REFERENCES

Primer;***Fundamental of modern UV-visible spectroscopy***;**1996**; Hewlett-Packard® Company12-5965-5123E

Mr. Hesse; H. Meier and B. Zeeh;***Spectoscopic methods for organic chemistry***; **1997**, Masson 2-225-83050-9.

F. Rouessac; A. Rouessac;***Instrumental techniques for chemical analysis***;**2011**; Dunod.

Mr. Hesse; H. Meier; B. Zeeh;***Spectroscopic methods for organic chemistry***; **1997**;Mason.

JM Hollas;***Modern Spectroscopy;*****2010**; Wiley.

Z. Nait Abdellah;***UV-visible and chromatography: theory and practical work***; **2024**;European University Editions.

JR Released;***UV-visible reflection spectroscopy of liquids***;**2004**;Springer Libri

Mr. Patin; K.Nys; H. Wouters; H. Thienpont; W. Meulebroeck; Using UV-Vis-NIR absorption spectroscopy as a tool for the detection of iron and cobalt in glass: A case study on HLLA material from the Low Countries;***Journal of Archaeological Science: Reports;***(44)**2022**; 103517.

AB Nnach; Advances in UV Spectroscopy for Monitoring the Environment; ***Research Invention Journal of Biological and Applied Sciences***; 3(1):,**2024**; 82-89

DK Mehta;***UV-VIS.Spectroscopy (Theory Principle Application)***,**2024**; scrib company.

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Series of tutorials No. 1

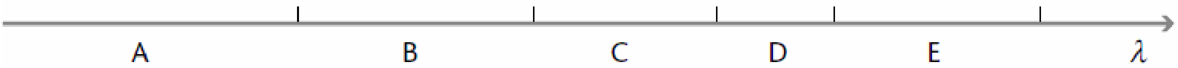
Chapter I: GENERAL PRINCIPLES OF SPECTROSCOPY

Data : h = $6{,}624.10^{-34}$Js c = 3.10^{8}ms^{-1} 1 eV = $1{,}602.10^{-19}$I

N = $6.02.10^{23}$ k = 1.38.10-23 JK^{-1}

Exercise 1

1- The electromagnetic spectrum is made up of several domains:
Ultraviolet / X-rays / Visible / Gamma rays / Infrared.
Classify these different radiations in order of increasing wavelength on the following axis:



2-Give the relationship between the energy of a photon and its wavelength. Specify the units of each term.

3-Among the areas indicated in question 1, which one has the most energetic radiation? Justify.

4-We have a laser with a wavelength of 633 nm. To which domain of the electromagnetic spectrum can we associate this light? What is the energy in joules and eV of the photon associated with this wave?

Exercise 2

The energy gap between a first excited vibrational level (v = 1) and the fundamental vibrational level (v = 0) of the molecule $^{129}I^{35}Cl$ is 4.597 kJ.mole^{-1}.

1- Determine the wave number in cm^{-1}of the transition between these two levels in absorption and in emission.
2-Diagrammatically represent these two transitions.

Exercise 3

The infrared spectrum of the CO molecule exhibits an absorption that is observed at 2140 cm^{-1}attributable to a transition v = 0 -> v = 1.

1- Calculate the relative population at 25°C.

2- Repeat the calculation at 1000°C.

Conclude

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Chapter II:

ABSORPTION SPECTROSCOPY IN UV-VISIBLE

Summary

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

HAS	Absorbance
ε	Extinction coefficient
c	Concentration
L	Thickness of the tank expressed in centimeters
UV	Ultraviolet

II. UV-VISIBLE ABSORPTION SPECTROSCOPY

II.1. UV-VISIBLE DOMAIN

The UV-visible range extends from approximately 800 nm to 10 nm:

- visible: 800 nm (red) - 400 nm (indigo)
- near-UV: 400 nm - 200 nm
- Far UV: 200 nm - 10 nm.

II.2. PRINCIPLE AND RULES OF SELECTION

A UV-visible transition (often 180 to 750 nm) corresponds to a jump of an electron from an occupied fundamental molecular orbital to a vacant excited molecular orbital. Matter then absorbs a photon whose energy corresponds to the energy difference between these fundamental and excited levels.

Not all energetically possible transitions are allowed. Allowed transitions are those that cause a change in the dipole moment.

II.3. ABSORPTION SPECTRUM

A UV-Visible spectrum is the plot of absorbance as a function of wavelength (in nm). The absorption band is characterized by its wavelength position (λmax) and by its intensity related to the molar extinction coefficient εmax ($A = \varepsilon\ l\ C$); the value of ε can indicate whether the transition is allowed or forbidden.

II.4. THE DIFFERENT TYPES OF ELECTRONIC TRANSITIONS

Electronic transitions correspond to the passage of electrons from filled bonding or nonbonding molecular orbitals to unfilled antibonding molecular orbitals:

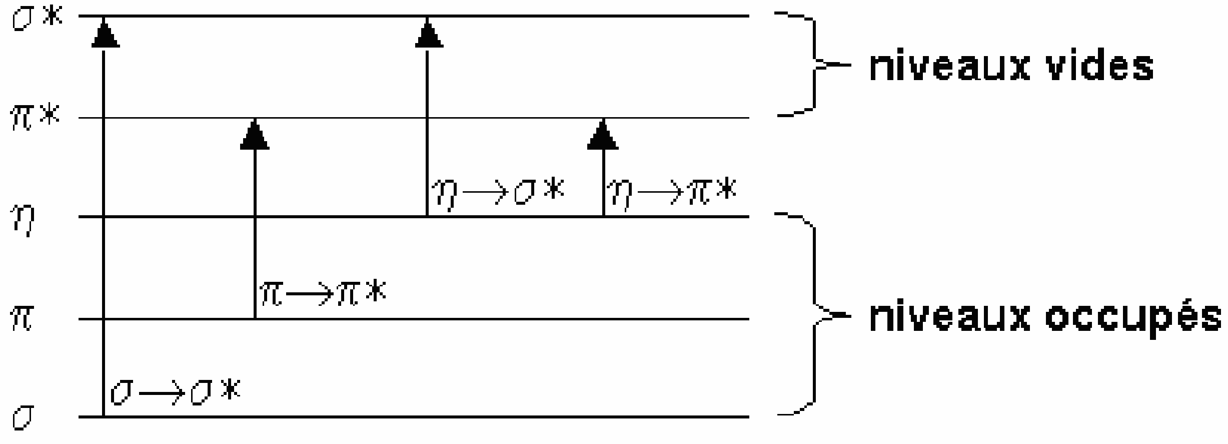


Figure II.1. Electronic transitions.

The absorption of a photon in the UV-visible range can often be attributed to electrons belonging to small groups of atoms called chromophores (C=C, C=O, C=N, C≡C, C≡N...). The absorption wavelength depends on the nature of the orbitals involved.

II.4.1. Transition σ -> σ*

The high stability of σ bonds in organic compounds means that the transition of an electron from a σ-bonding OM to an σ*-antibonding OM requires a lot of energy. The corresponding band is intense and located in the far-UV, often around 150-200 nm for many compounds.

II.4.2. Transition n ->π*

This transition results from the passage of an electron from a non-bonding OM n to an anti-bonding OM π*. This type of transition occurs in the case of molecules containing a heteroatom carrying free electron pairs belonging to an unsaturated system. The corresponding band is generally weak because the transition is often forbidden.

II.4.3. Transition n -> σ*

The transfer of an electron from the n-doublet of a heteroatom (O, N, S, Cl...) to a σ* level is observed for alcohols, ethers, amines as well as for halogenated derivatives. This transition gives a band of medium intensity which is located at the limit of the near-UV.

II.4.4. Transition π -> π*

The electronic transition in compounds with an isolated double bond leads to a strong absorption band around 170-190 nm (Table II.1).

Table II.1. Examples Transition π -> π*

Example	**Transition**	**λ_{max}, nm**	**ε**
Ethylene (C=C)	π→ π*	165	15000
1-hexyne (C≡C)	π→ π*	180	10000
Ethanal (C=O)	n→ π* π→ π*	293 180	12 10000
Nitromethane (NO_2)	n→ π* π→ π*	275 200	17 5000
Methyl bromide (H_3C-Br)	n→ σ*	205	200

II.5. EFFECT OF THE ENVIRONMENT ON TRANSITIONS

II.5.1. Terminology

- **Auxochrome group**:saturated group linked to a chromophore and which modifies the wavelength and the intensity of the absorption. Ex.: OH, NH_2, Cl...
- **Bathochrome effect**:shifting the bands towards long wavelengths.
- **Hypsochrome**:shift of the bands towards short wavelengths (towards blue).

- **Hyperchrome effect**:increase in absorption intensity.
- **Hypochromic effect**:decrease in absorption intensity. These effects are illustrated in the following figure:

II.5.2. Effect of substitution

The position of the absorption band depends on the presence or absence of substituents (Figure II.2).

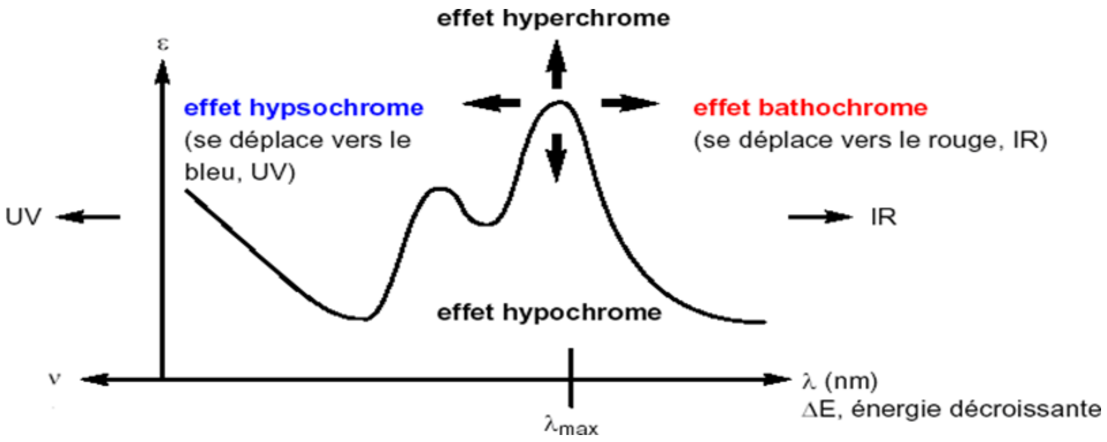


Figure II.2. Effects of substitution on the absorption band.

On the chromophore group. For example, the more the ethylenic group is substituted, the wider the absorption band due to the π transition→ $\pi^*$is shifted towards the visible: bathochromic effect (Figure II.3).

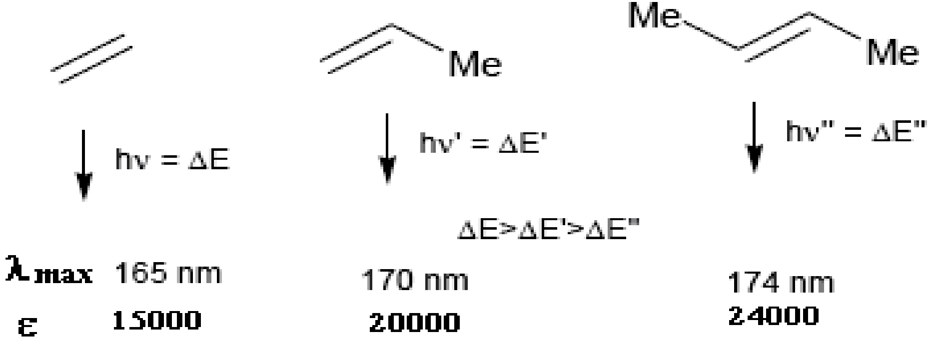


Figure II.3. Effect of substitution on the ethylenic group.

Mesomeric effect substituents (auxochromes -OH, -OR, -X, -NH2, ...) carried by a chromophore C=C or C=O give bathochromic and hyperchromic effects.

II.5.3. Effect of conjugation

II.5.3.1. Ethylene compounds

The chain of unsaturations leads to the delocalization of the π electrons. This delocalization, which reflects the ease with which the electrons move along the molecule, is accompanied by a rapprochement of the energy levels (Figure II.4).

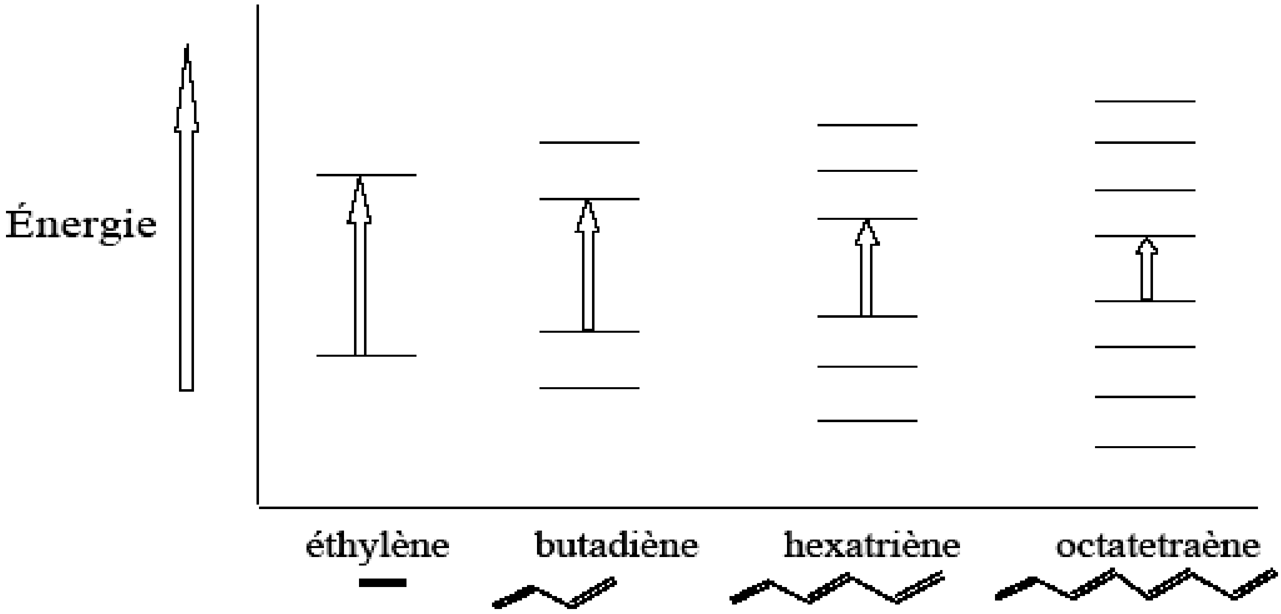


Figure II.4. Influence of the sequence of establishments on the energy levels of compounds ethylenic.

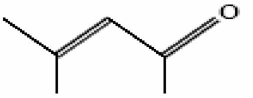
This results in a bathochromic effect and a hyperchromic effect on the absorption band corresponding to the π π* transition (Table II.2).

Table II.2. Bathochromic and hyperchromic effect during the sequence of establishments of the compounds ethylenic (π transition→ π*).

Compound	λ_{max}	-$_{max}$
Ethylene $CH_2=CH_2$	165	15000
Buta-1,3-diene $CH_2=CH-CH=CH_2$	217	20900

The same effect is observed on the n transition→π* (Table II.3).

Table II.3. Bathochromic and hyperchromic effect during the sequence of establishments of the compounds ethylenic (transition n→ π).*

Compounds	Transition π→ π*	Transition n→ π*
Propanone CH_3-CO-CH_3	188 nm	279 nm
Methyl isobutyl ketone or mesityl oxide 	236 nm	315 nm

Noticed : Bathochromic shift is the origin of the color of many natural compounds that exhibit extended conjugated chromophores.

β-carotene The orange color of β-carotene comes from the union of eleven conjugated double bonds (Figure II.5): λ_{max}= 497 and 466 nm (in chloroform).

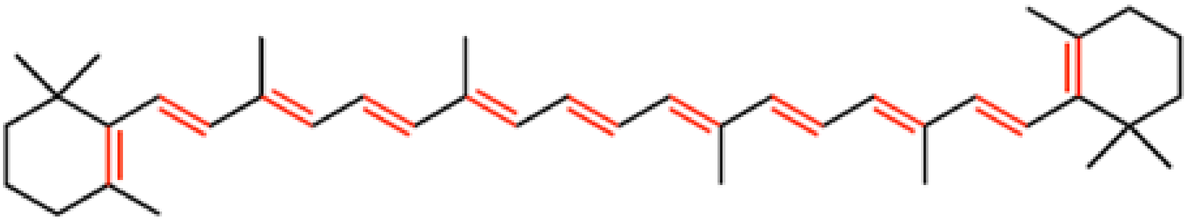


Figure II.5. Structure of β-carotene.

II.5.3.2. - Benzene compounds

The absorption of aromatic compounds is more complex than that of ethylenic compounds. Several π transitions→ π*are observed.

The UV spectrum of benzene shows three bands due to π transitions→ π*.

- λ_{max}= 184 nm, ε = 60000
- λ_{max}= 203 nm, ε = 7900
- λ_{max}= 256 nm, ε = 200

For polynuclear aromatics, as the number of condensed rings increases, the absorption shifts to longer wavelengths until it reaches the visible region.

II.5.4. Solvent effect

The position, intensity and shape of the bands of compounds in solution depend on the solvent. These changes reflect physical solute-solvent interactions that modify the energy difference between the ground state and the excited state.
By increasing the polarity of the solvent:

Transition n→ π* :bathochromic effect
Transition π→ π* :bathochrome effect
In water, the spectra are very often sensitive to pH which modifies the ionization of certain chemical functions (Figure II.6).

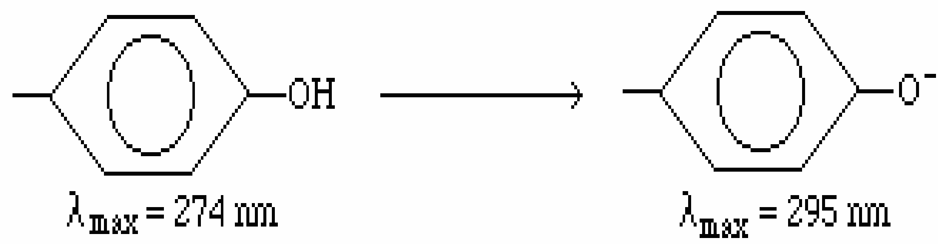


Figure II.6. Effect of the pH of the medium.

II.6. EXPERIMENTAL TECHNIQUES

II.6.1. Equipment

The study of absorptions requires the use of a device called a spectrometer. The following figure shows the basic diagram of a double-beam UV-visible absorption spectrometer. It consists of the following elements (Figure II.7):

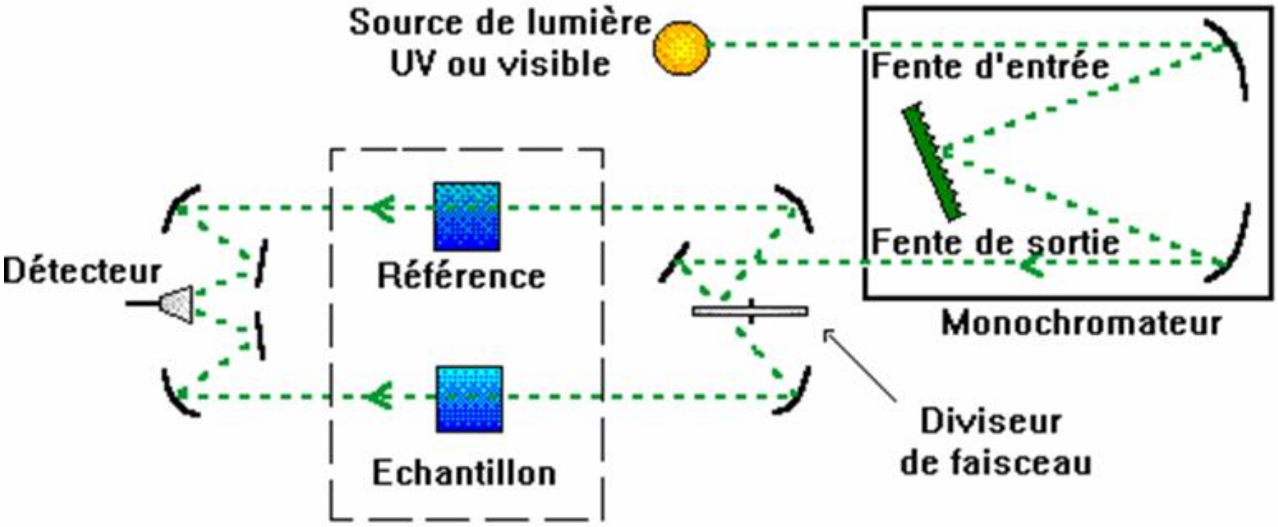


Figure II.7. Schematic of a dual-beam UV-visible absorption spectrometer.

It consists of the following elements:

II.6.1.1. Source

The role of the source is to provide light radiation.

II.6.1.2. Monochromator

The monochromator's role is to disperse the polychromatic radiation coming from the source and to obtain monochromatic radiation. In order to avoid damaging the sample with the UV radiation coming from the source, it is placed at the exit of the monochromator and will therefore only be crossed by a narrow range of wavelengths.

II.6.1.3. Beam splitter or photometer

The monochromatic light emerging from the monochromator is split into two beams that pass through the sample and reference compartments.

II.6.1.4. Detector

The detector converts the received light into an electrical signal. It is connected to a recorder which allows an absorption spectrum of the sample analyzed to be plotted.

II.6.2. Sampling

Compounds can be studied in various physical states (gas, liquid, solid, etc.). Typically, spectra are recorded from dilute solutions.

II.6.2.1. Solvents

For the solution study, the solvent must be properly chosen: it must dissolve the product and be transparent (does not absorb) in the region examined. Figure II.8 gives the absorption zone of some solvents and materials.

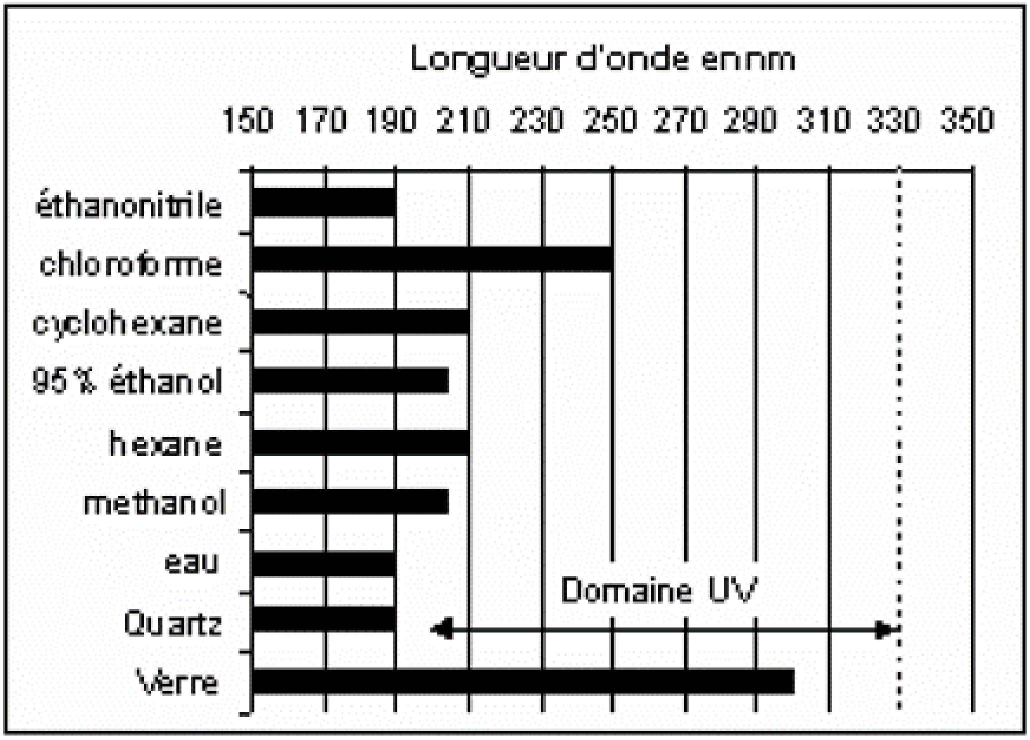


Figure II.8. Absorption zone of some solvents and materials.

Example : Hexane can be used as a solvent for samples that absorb at wavelengths greater than 210 nm.

II.6.2.2. Cells

The solution to be studied must be placed in a cell or tank. The tanks have different thicknesses and are made of quartz for the UV-visible range. Glass is reserved for measurements in the visible range only (Figure II.9).

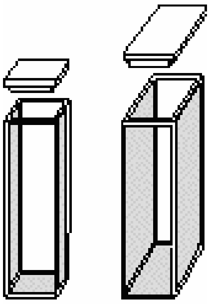


Figure II.9. Example of tanks.

II.7. APPLICATIONS OF UV-VISIBLE SPECTROSCOPY

II.7.1. Qualitative analysis

The UV or visible spectrum does not allow the identification of a product but that of the chromophore group that it contains.

II.7.2. Quantitative analysis

Quantitative analysis by UV-visible spectrometry is widely used thanks to the use of the Beer-Lambert law. These measurements have applications in various fields:

- In the laboratory:
  - ➢Monitoring the kinetics of a reaction
  - ➢Measurement of acid and base dissociation constants or complexation constants…

  - ➢Determination of the composition of a mixture (benzene in cyclohexane)
  - ➢Study of cis-trans isomerism or tautomerism
- Scientific police
- Legal expertise
- Environment :
  - ➢Ozone in city air
  - ➢Heavy metals in water

➢Measurement of phenol in water (at the 200-300 nm band)
➢Organic matter, suspended matter, nitrates contained in water

- Anti-doping fight

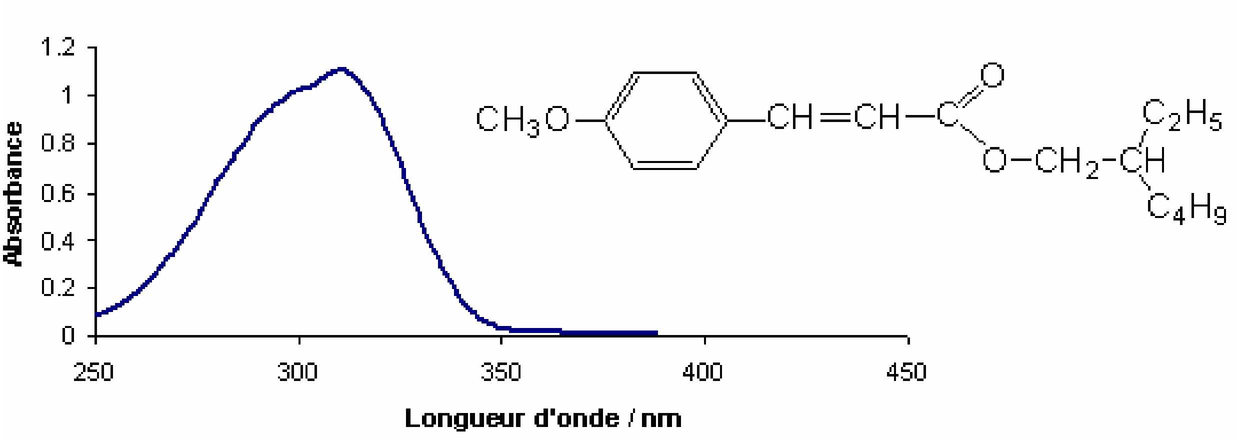
- Agri-food

- Color measurement

- Pharmacy :
  ➢Iron dosage in a drug
  ➢Dosage of active molecules in a pharmaceutical preparation

- Perfumes and cosmetics: sun creams contain UV filters or “sunscreens”.

UV spectrum of [2-ethyl-1-hexyl]-4-methoxycinnamate, typical UV B filter (Figure II.10):



ε = 30,000 $L.mol^{-1}.cm^{-1}$to λ_{max}=310 nm

Figure II.10. UV spectrum of [2-ethyl-1-hexyl]-4-methoxycinnamate, typical UV B filter.

BIBLIOGRAPHICAL REFERENCES

AB Nnach; Advances in UV Spectroscopy for Monitoring the Environment; ***Research Invention Journal of Biological and Applied Sciences***; 3(1)**2024**; 82-89

DK Mehta;***UV-VIS.Spectroscopy (Theory Principle Application)***,**2024**; scrib company.

JR Released;***UV-visible reflection spectroscopy of liquids***;**2004**;Springer Libri.

Z. Nait Abdellah;***UV-visible and chromatography: theory and practical work***; **2024**;European University Editions.

DK Mehta;***UV-vis instrumentation***;**2022**;scrib company.

Mr. Patin; K.Nys; H. Wouters; H. Thienpont; W. Meulebroeck; Using UV-Vis-NIR absorption spectroscopy as a tool for the detection of iron and cobalt in glass: A case study on HLLA material from the Low Countries;***Journal of Archaeological Science: Reports;***(44) **2022**; 103517.

F. Rouessac; A. Rouessac;***Instrumental techniques for chemical analysis***;**2011**; Dunod.

JM Hollas;***Modern Spectroscopy;*****2010**; Wiley.

Mr. Hesse; H. Meier and B. Zeeh;***Spectoscopic methods for chemistry organic***;**1997**, Masson 2-225-83050-9.

Primer;***Fundamental of modern UV-visible spectroscopy***,**1996**; Hewlett-Packard® Company12-5965-5123E

Series of tutorials No. 2

Chapter I: UV-VISIBLE ABSORPTION SPECTROSCOPY

Exercise 1

What are all the possible electronic transitions for the following molecules: CH_4, CH_3Cl, $H_2C=O$

Exercise 2

The UV spectrum of acetone shows two absorption bands at: λ_{max}= 280 nm with ε_{max}= 15 and λ_{max}= 190 nm with ε_{max}= 100.

Identify the electronic transition of each of the two bands.

Which is the most intense?

Exercise 3

1) From the values of λ_{max}(in nm) of these molecules, what are the conclusions that we can draw concerning the relationship between $\lambda_{max}$and the structure of the molecule that absorbs? Ethylene (170); Buta-1,3-diene (217); 2,3-Dimethylbuta-1,3-diene (226); Cyclohexa-1,3-diene (256) and Hexa-1,3,5-triene (274).

2) Explain the following variations in λ_{max}(in nm) of the following compounds: CH_3-X, when X=Cl (λ_{max}= 173), X=Br (λ_{max}= 204) and X=I (λ_{max}= 258).

Exercise 4

1) Calculate the $\varepsilon_{max}$of a compound whose maximum absorption (A) is 1.2. The length of the cell l is 1 cm, the concentration is 1.9 mg per 25 ml of solution and the molecular mass of the compound is 100 g/mol.

2) Calculate the molar absorption coefficient of a solution of concentration 10^{-4}M, placed in a 2 cm tank, with I_0= 85.4 and I = 20.3.

Exercise 5

An aqueous solution of potassium permanganate (C = $1.28.10^{-4}$M) has a transmittance of 0.5 at 525 nm, if a 10 mm optical path cuvette is used.

1) Calculate the molar absorption coefficient of permanganate for this wavelength.

2) If the concentration is doubled, calculate the absorbance and transmittance of the new solution.

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Exercise 6

We want to determine the concentration of two salts A and B in an unknown sample in aqueous solution.

A visible spectrum of each of these two compounds taken separately in aqueous solution is recorded, as well as the sample solution to be analyzed. The optical path of the cells used is 1 cm.

The absorbance values measured at 510 and 575 nm on the three spectra are as follows:

	510 nm	575 nm
Compound A (C = 0.15M)	A = 0.714	A = 0.0097
Compound B (C = 0.06M)	A = 0.298	A = 0.757
Sample solution	A = 0.4	A = 0.577

1) Calculate the 4 molar absorption coefficients $\varepsilon_{A(510)}$, $\varepsilon_{A(575)}$,$\varepsilon_{B(510)}$,$\varepsilon_{B(575)}$.
2) Calculate the molar concentrations of A and B in the sample solution.

Exercise 7

We have a stock solution of copper sulfate at 1 mol.L^{-1}. Various dilutions are made, the absorbance of which is measured for the wavelength 655 nm. which correspond to the maximum of the curve A = f (-) for a copper sulfate solution.

The width of the tank is 1cm. We obtain the following table:

C (mol.L^{-1})	0.20	0.10	0.050	0.020	0.010	0.0050
HAS	0.601	0.302	0.151	0.060	0.031	0.016

1) Make a schematic diagram of a UV-visible spectrophotometer.
2) Why did we choose to work at this wavelength?
3) Is Beer-Lambert's law verified?
4) Determine the molar absorbance coefficient under these conditions.
5) What is the concentration of a copper sulfate solution whose absorbance is A = 0.200.

Chapter III

VIBRATION SPECTROSCOPY IN THE INFRARED

Summary

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

HAS	Absorbance
E	Energy
F	High vibration frequency
f	Low vibration frequency
FT	Fourier transform
FTIR	Fourier transform spectroscopy Planck
H	constant
IR	Infrared
k	Bond force constant Frequency
ν	of vibration Symmetrical valence
	vibration Asymmetrical valence
	vibration Average vibration
m	frequency Mass
m	
-	Shear
T	Transmittance
-	Twist
μ	Reduced mass
-	Swinging

III. INFRARED VIBRATION SPECTROSCOPY

III.1. INTRODUCTION

The movements of atoms in a molecule can be classified into three categories:
- translations
- rotations
- vibrations

Infrared (IR) spectroscopy studies the vibrations of molecules when they are irradiated by an electromagnetic wave in the infrared range: approximately 0.8 to 1000 μm. This spectral region is divided into:
- Near-IR 0.8-2.5 μm 12500-4000 cm^{-1}
- Mid IR 2.5-25 μm 4000-400 cm^{-1}
- Far IR 25-1000 μm 400-10 cm^{-1}

The wavenumber range generally used is 4000 cm^{-1} to 400 cm^{-1} (i.e. wavelengths from 2.5 μm to 25 μm). Infrared spectroscopy is one of the most widely used spectroscopic tools for the characterization of molecules.

III.2. PRINCIPLE

The principles underlying IR spectroscopy are very similar to those governing UV-visible spectroscopy. The difference comes from the energy levels used by this technique: these are molecular vibration energies. When the vibrational level changes, an electromagnetic wave can only be absorbed (or emitted) if there is a simultaneous variation in the electric dipole moment.

III.3. MOLECULAR VIBRATIONS

III.3.1. Diatomic molecule

The vibration of two atoms linked by a chemical bond can be compared to that of two balls of masses $m_{HAS}$and mass m_B, connected by a stiffness spring

Figure III.1. Comparison of the vibration of two atoms linked by a chemical bond to that of two balls of masses $m_{HAS}$and mass $m_B$connected by a spring.

In the harmonic oscillator approximation, the fundamental vibration frequency ν is given by the relation (Hooke's law):

$$\upsilon = \frac{1}{2} \sqrt{-} \qquad = \; . \; \frac{}{+}$$

ν: frequency of vibration μ: reduced mass k:
force constant of the bond
$m_{HAS}$and m_B: masses of atoms A and B respectively
This frequency depends on k and μ. The vibration frequency is proportional to the square root of the force constant k and inversely proportional to the square root of the reduced mass μ.

Effect of k : The vibration frequency is proportional to the square root of the force constant k (Figure III.2).

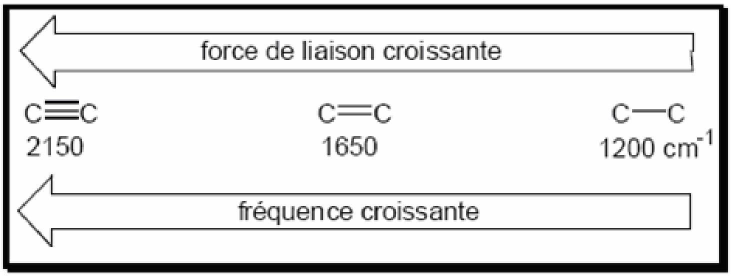


Figure III.2. Proportionality of the vibration frequency to the square root of the force constant k.

Effect of μ : The vibration frequency is proportional to the square root of the inverse of the reduced mass μ (Figure III.3).

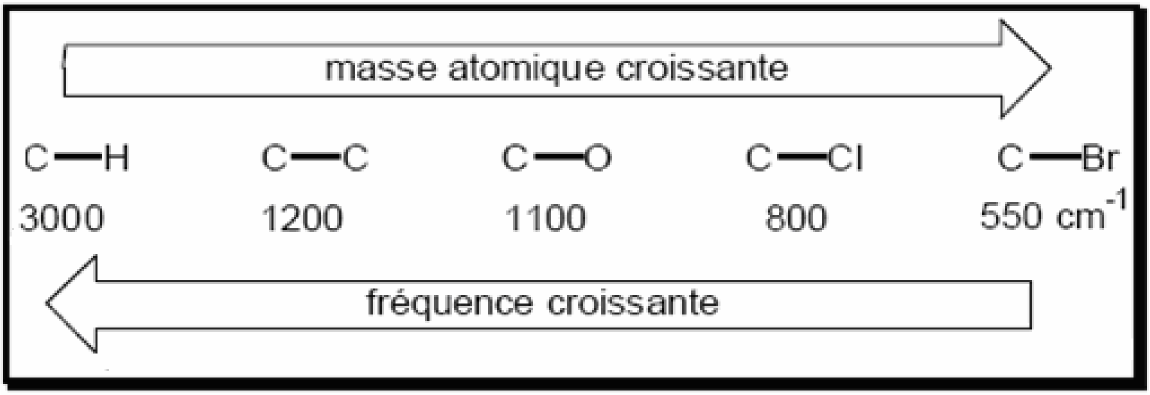


Figure III.3. Proportionality of the vibration frequency to the square root of the inverse of the reduced mass μ.

III.3.2. Vibration movements

For a nonlinear (respectively linear) polyatomic molecule having n atoms, there are 3n−6 (respectively 3n−5) so-called fundamental vibrations. As a first approximation, these movements or vibration modes are classified according to their vibrational characteristics and symmetry:

- vibration mode that modifies bond lengths: valence vibration noted - (Figure III.4)

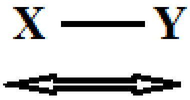


Figure III.4. Elongation (variation of interatomic distance).

Vibration mode that changes lengthsof thebonds: valence vibration noted ν. For groups formed of identical bonds (NH_2, CH_3, CH_2, etc.), these bonds vibrate simultaneously. A vibration mode that preserves molecular symmetry is said to be symmetric (index s). It is asymmetric or antisymmetric if it leads to the loss of one or more elements of symmetry of the molecule (index a) (Figure III.5).

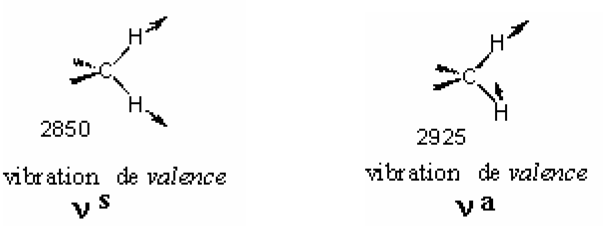


Figure III.5. Symmetric valence vibration (ν_s) and asymmetric (-has).

- angular deformation modes that modify the angles between bonds (Figure III.6):

Figure III.6. Angular deformation (variation of the angle between two adjacent bonds).

For a group formed by a single bond (OH, C=O, etc.), the notations δ and γ are used for in-plane and out-of-plane deformations respectively.
For groups like NH_2, CH_3, CH_2, etc., several notations are used. This can be illustrated with the example of methylene (**Figure III.7**).
Angular deformation modes that modify the angles between bonds:

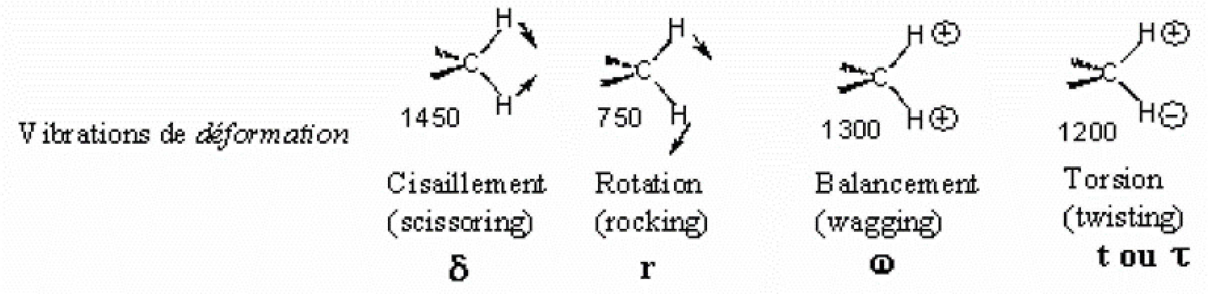


Figure III.7. Deformation vibrations (methylene)

Noticed : In addition to the fundamental vibrations 3n-6 (for non-linear molecules) or 3n-5 (for linear molecules), other types of bands are added to the spectrum:

- Multiple harmonics of fundamental bands (2ν essentially).
- Combination bands (ν1 + ν2 for example).

III.3.3. Selection rules

For a vibrational transition to be possible, Bohr's law ΔE = hν must be verified. This condition is necessary but not sufficient. The vibration must also cause a variation in the dipole moment of the molecule (Figure III.8).

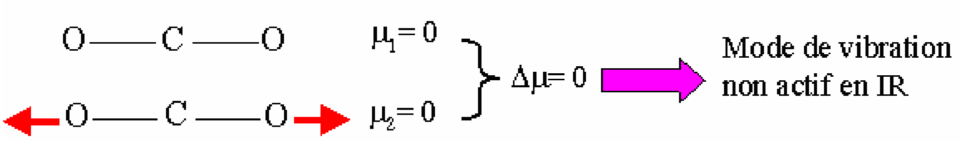


***Figure III.8.**Example of a molecule not active in IR (--=0).*

For a harmonic oscillator, the selection rule between vibrational levels of quantum numbers v is: Δv = ± 1, the + sign corresponds to an absorption, the - sign to an emission.

III.4. SHAPE OF THE IR SPECTRUM

In practice, an infrared spectrum is often represented as the transmittance (%T) as a function of the wave number (cm^{-1}). Each band is characterized by its ν\ value at the absorption maximum; its relative intensity is also specified (F: strong, m: medium, f: weak, etc.) (Figure III.9).

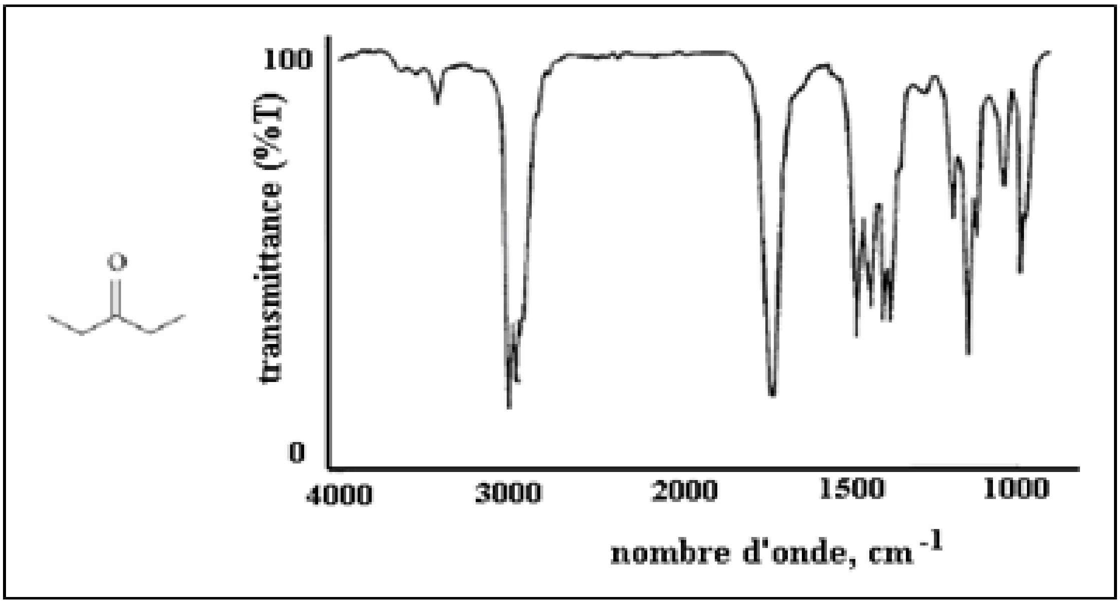


Figure III.9. IR spectrum of pentanone-3-one.

III.5. CHARACTERISTIC VIBRATION FREQUENCIES

Despite the apparent complexity of IR spectra, due to the large number of absorption bands, there are absorptions at characteristic wavenumbers which allow the identification of the different groups of a molecule (Figure III.10).

We can distinguish four main regions:

- 4000-2500 cm^{-1}: XH (OH, NH, CH) elongations
- 2500-1900 cm^{-1}: Elongations of triple bonds ………. NC≡N as well as cumulative double bonds …… (allenes, isocyanates, carbodiimides…)
- 1900-1500 cm^{-1}: Elongations of double bonds (……….
- 1500-200 cm^{-1}: Single bond elongations (….: strong at ≈ 1350 cm^{-1}); ..OC−O: strong between 1000 and 1300 cm^{-1}…). This area, called the fingerprint region, is used to identify a compound with certainty and attest to its purity.

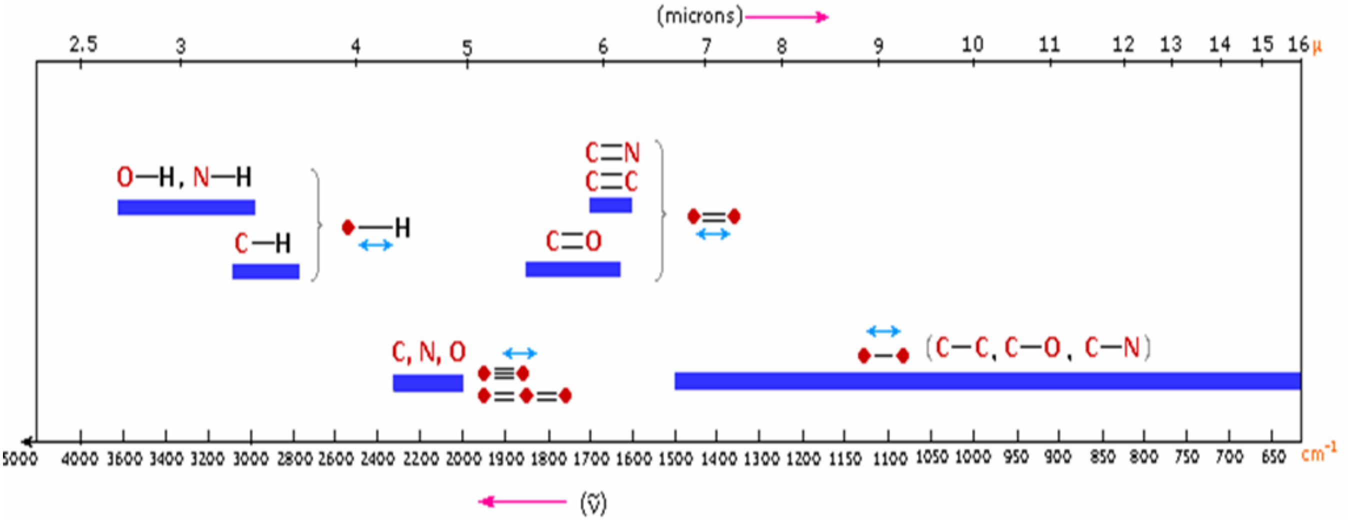


Figure III.10. Tables of characteristic frequencies in IR, allowing the identification of the different molecular groups.

III.6. SPECTRAL ANALYSIS METHOD

The procedure is generally as follows:

1. Examine the spectrum starting with the highest wavenumbers.
2. Identify the most characteristic bands using the tables.
3. Determine the absence of bands in characteristic regions.
4. Do not attempt to elucidate all bands, especially in the fingerprint region (< 1500 cm^{-1}).

III.7. APPLICATIONS OF VIBRATION SPECTROSCOPY IN INFRARED

III.7.1. Functional analysis

Infrared spectroscopy makes it possible to perform the functional analysis of a molecule, that is to say to describe precisely all the chemical groups that constitute it. It remains to assemble the pieces of the puzzle when this is possible.

Example 1 :CH connections

The vibrations of CH bonds depend on the hybridization of the carbon bearing H: the H bonded to a saturated sp^3 carbon have their vibration bands below 3000 cm^{-1}. In the case of an unsaturated sp^2 carbon, these bands are beyond 3000 cm^{-1} (Figure III.11).

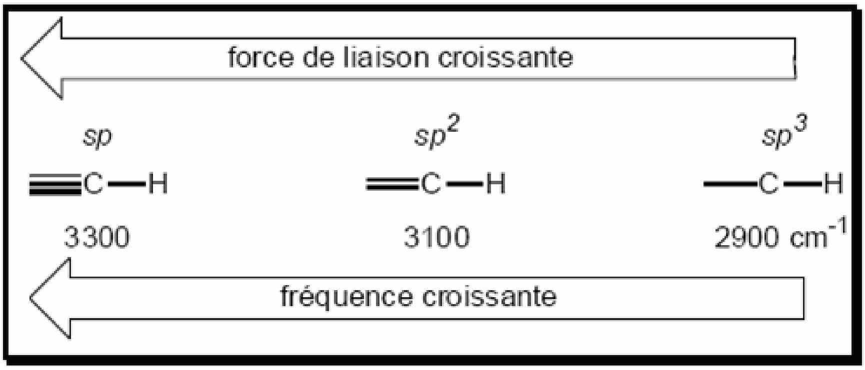


Figure III.11. Variation of the vibration bands of CH bonds according to the hybridization of the bearing carbon H.

Identical bonds of a group (eg CH_3or CH_2) are coupled and vibrate simultaneously.

.

CH Group$_2$ (Figure III.11)

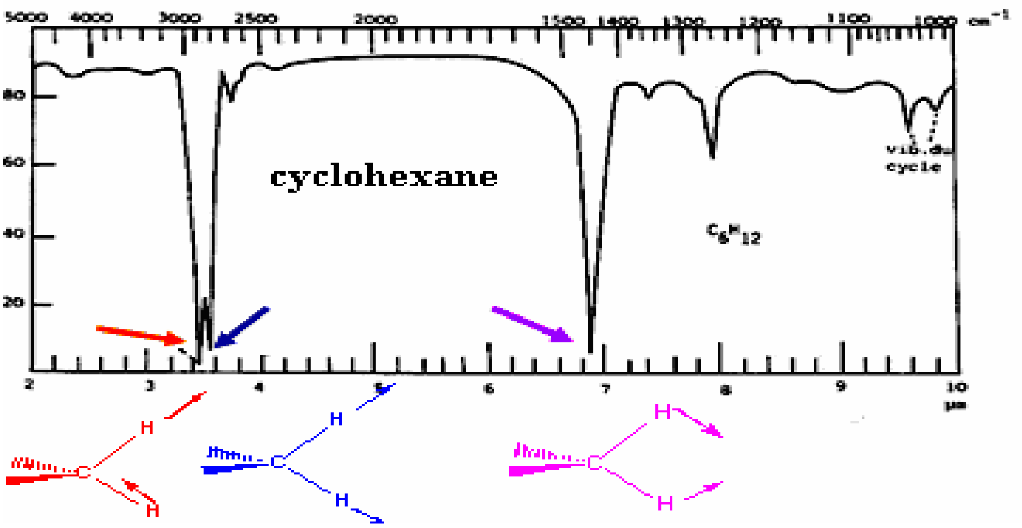


Figure III.12. Characteristic vibration bands of the CH group$_2$.

CH Group$_3$:(Figure III.12)

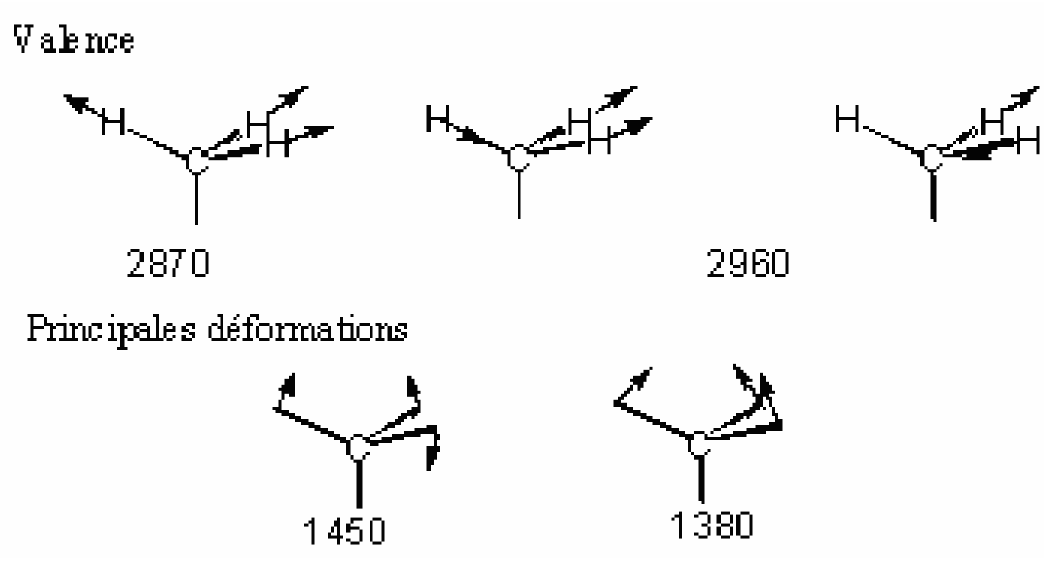


Figure III.13. Characteristic vibration bands of the CH group$_3$.

III.7.2. Hydrogen bonding

The XH bond, where X is a heteroatom (O, N, S), can intervene in molecular associations of the hydrogen bond type (Figure III.14).

The hydrogen bond has the effect of:

- To weaken the XH bond (reduction in the number of vibration waves),
- To cause a broadening of the band due to the vibration ν_{XH}.

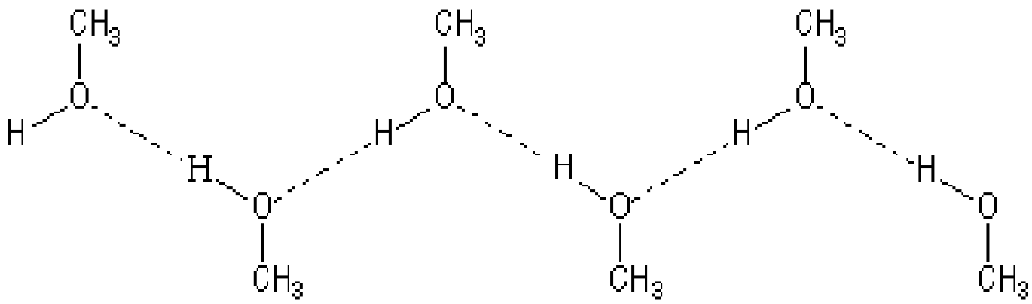


Figure III.14. Hydrogen bonding.

The hydrogen bond has the effect of:

- to weaken the XH bond (**decrease in the number of vibration waves**)
- to provoke**a widening of the band**due to vibration -XH.

Example 2 :Ketone C=O bond (Figure III.15)

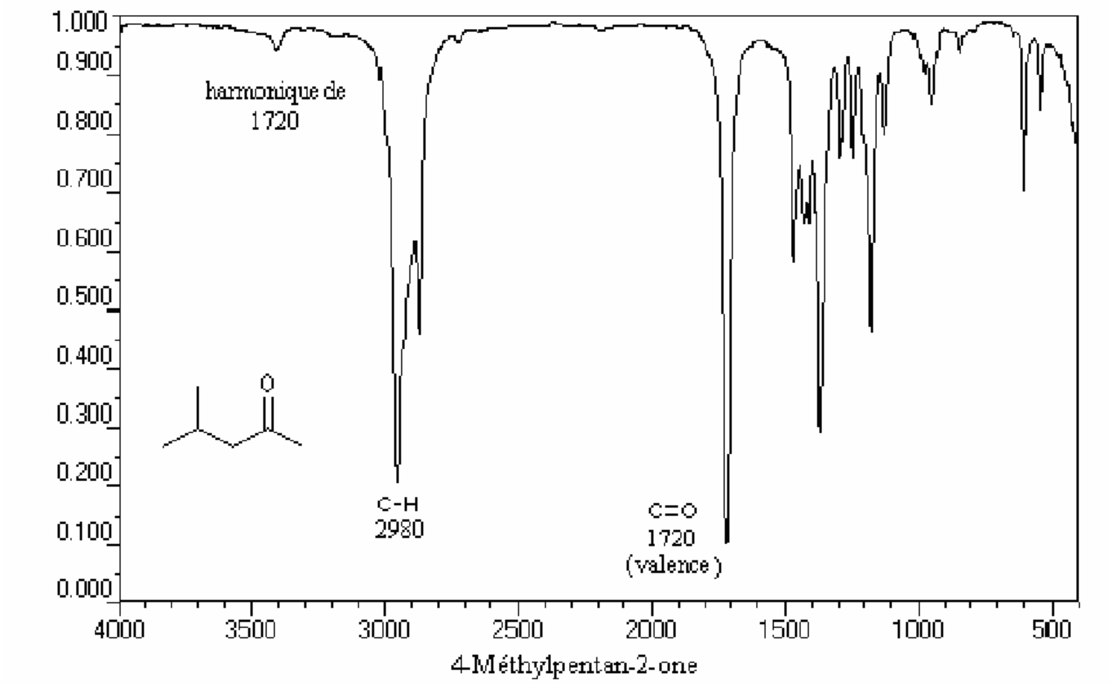


Figure III.15. Characteristic vibration bands of the C=O group.

III.7.2.1. Intermolecular hydrogen bonding in alcohols

Consider the IR spectrum of hexan-1-ol in the pure liquid state (1) and in dilute solution in CCl_4as solvent (2) (Figure III.16).

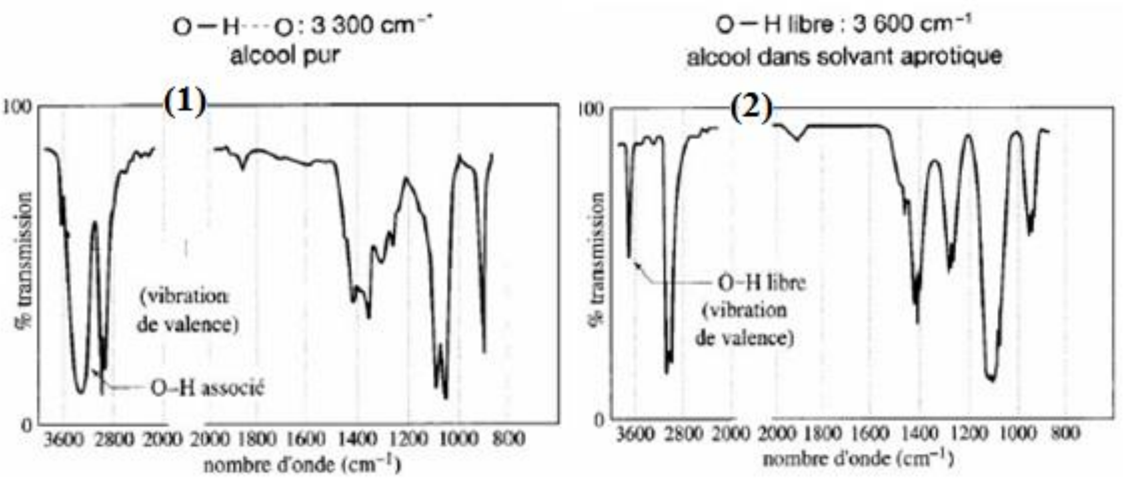


Figure III.16. IR spectrum of hexan-1-ol in the pure liquid state (1) and in diluted solution in CCl4(2).

(1) The broad band between 3200 cm^{-1} and 3400 cm^{-1} is attributable to the OH valence vibration of an OH group engaged in a hydrogen bond.

(2) By dilution in an aprotic solvent such as CCl_4, this band disappears to leave room for a thin band located in the zone 3590-3650 cm^{-1}. This behavior shows that the nature of the hydrogen bond in the alcohol studied is intermolecular.

III.7.2.2. Intermolecular hydrogen bonding in acids

IR spectra of carboxylic acids exhibit a ν band$_{OH}$much broader than for alcohols and at a lower frequency, giving the spectrum a very characteristic appearance (Figure III.17).

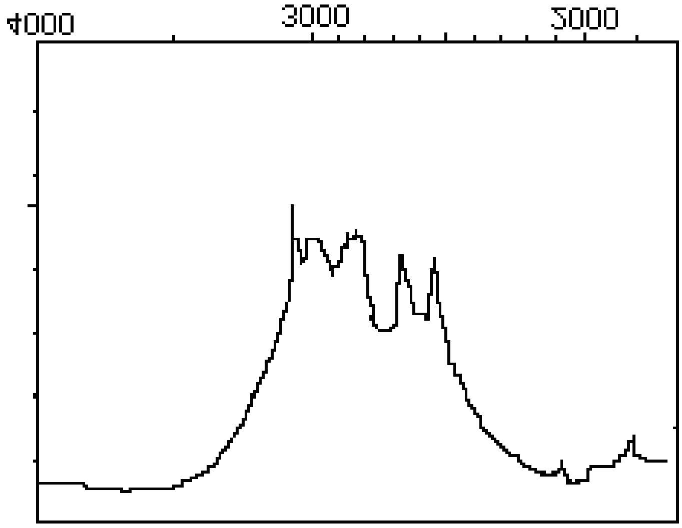


Figure III.17. Characteristic band of carboxylic acids on the IR spectrum.

Carboxylic acids exist as dimers because of the very strong H bonds between O–H and C=O (Figure III.18):

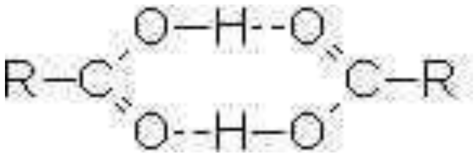


Figure III.18. Hydrogen bonds existing between O–H and C=O of carboxylic acids.

- The νOH band of dimeric carboxylic acids is well located between 3300 and 2500 cm^{-1}, but it should be noted that the band is due to the spreading of strong hydrogen bonds.
- It would be useful to specify that the νC=O band of aliphatic ketones is indeed located around 1715 cm^{-1}, but the precision on the inductive and mesomeric effects could be refined by mentioning more clearly the role of electronegativity and resonances.
- Carboxylic acids exist as dimers because of the very strong hydrogen bonds between O–HO and C=O:
- The νOH absorption band, very broad and very intense, is located between 3300 and 2500 cm^{-1}. The bands due to νCH are superimposed on this band. In very dilute solution in an apolar solvent, νOH moves towards 3520 cm^{-1} (monomer form).
- For the H-bond acceptor carbonyl in the dimer, the C=O bond is weakened by the H-bond. Its νC=O frequency decreases by 40 to 60 cm^{-1} relative to the νC=O band of the monomer, located around 1760 cm^{-1}.

III.7.2.3. Intramolecular hydrogen bonding

In some molecules, such as polyols, intramolecular hydrogen bonds are observed. It is easy to distinguish intermolecular bonds from intramolecular bonds by infrared spectroscopy. By dilution in a solvent such as CCl_4, the absorption band due to the former is shifted, while that due to the latter remains unchanged.

III.7.3. Inductive and mesomeric effects

Consider the case of a carbonyl function. The valence vibration νC=O for an aliphatic ketone is located around 1715 cm^{-1}. The attractive inductive effects, linked to electron-withdrawing atoms or groups, tend to increase this frequency. On the other hand, the mesomeric effects, which promote electronic delocalization by resonance, lead to a decrease in the νC=O frequency.

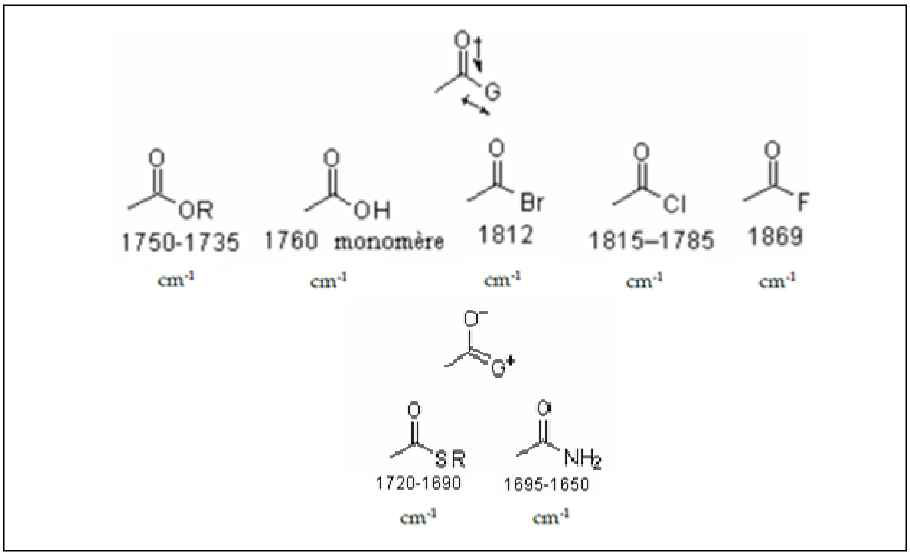


Figure III.19. Attracting inductive effects, linked to electron-withdrawing atoms or groups, on the valence vibration of C=O.

III.7.4. Conjugation

Delocalization of a double bond decreases its force constant and therefore lowers its vibration frequency. For a conjugated carbonyl, $\nu_{C=O}$is lowered by 15 to 40 cm_{-1} (Figure III.20).

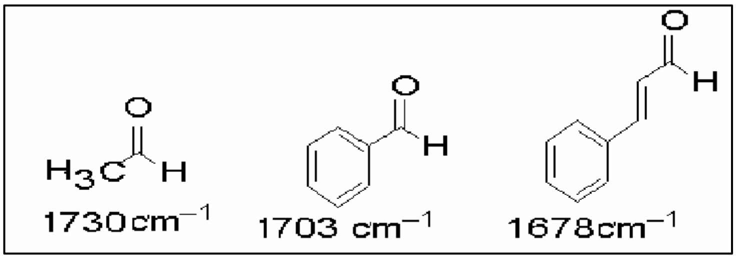


Figure III.20. Effect of conjugation on the characteristic vibration bands of the C=O group.

III.7.5. Cycle voltage

When the oscillator is bound to a sterically strained structure, its vibration frequency is increased (Figure III.21).

Examples:

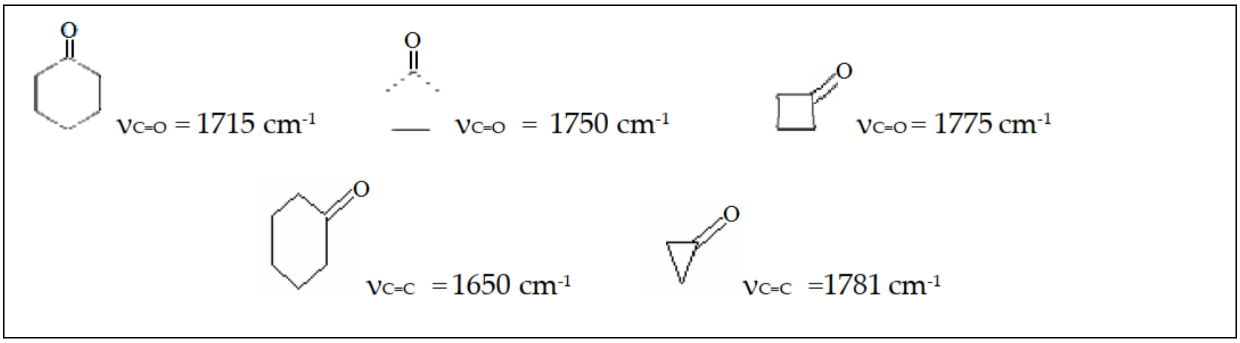


Figure III.21. Influence of steric tension on the characteristic vibration bands of the group C=O.

III.7.6. Isomers

IR spectrometry can differentiate between isomers.
Example :cis and trans isomers of olefins (Figure III.22).

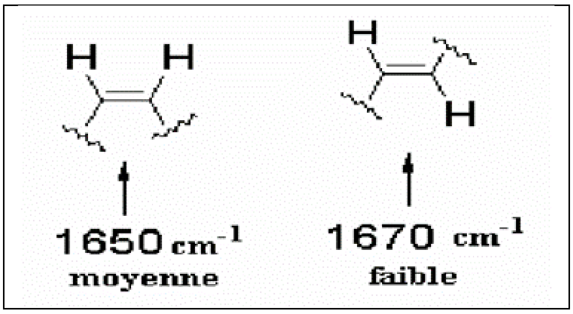


Figure III.22. Vibration bands of cis and trans isomers of olefins.

III.7.7. Quantitative analysis

It is based on the Beer-Lambert law:$A=-\log T = -lC$. Specialized devices for quantitative analysis are capable of precise and rapid dosages.

III.8. Instrumentation and sampling

III.8.1. Apparatus

Two main techniques are used to obtain IR spectra:
- The first, and oldest, is called scanning,
- The second is called Fourier transform (Fourier transform or FT). The main elements of an IR spectrometer are an infrared radiation source, a radiation separation system or dispersive system (monochromator), a signal detector and a recorder (Figure III.23).

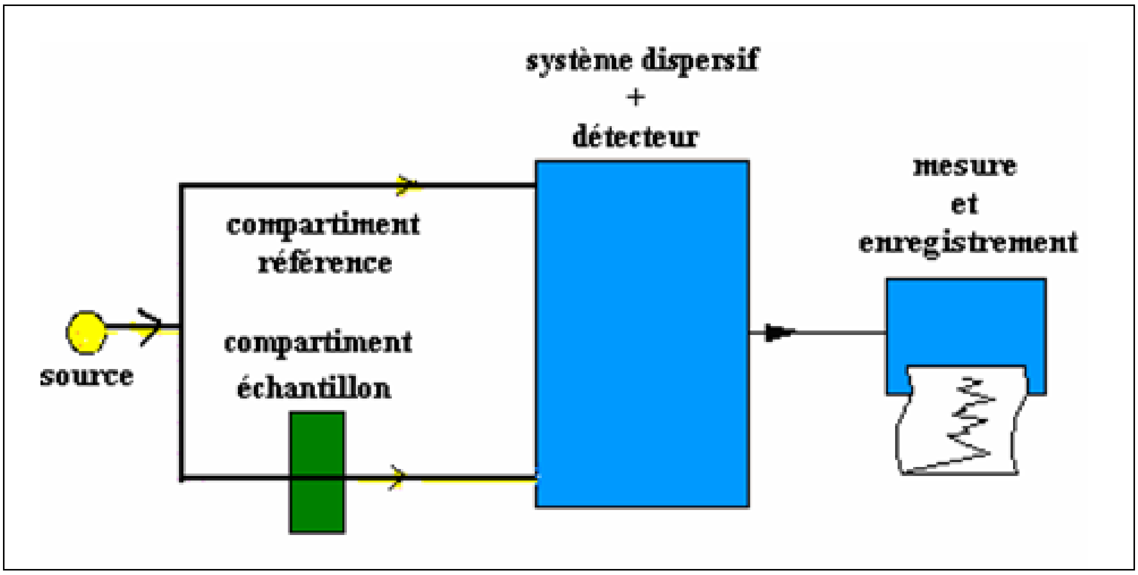


Figure III.23. Schematic diagram of the principle of a dual-beam IR spectrometer.

III.8.1.1. The source

In most cases, we work in the mid-infrared region (4000 and 400 cm^{-1}). We then use a Globar source, made of heated silicon carbide.

III.8.1.2. The radiation separation system (monochromator*)*

The sample is illuminated with polychromatic IR radiation.
For scanning spectrometers, prisms or diffraction gratings are used as the dispersive system.
For Fourier transform spectrometers, an interferometer (Michelson interferometer) is used. The interferometer has three main components: a beam splitter, a fixed mirror, and a movable mirror.

III.8.1.3. The detector

Signal detection is carried out by a component that converts the incident radiation into an electrical signal. The detector used is of the thermal type, such as a bolometer or a thermocouple. It detects temperature variations and transforms them into intensity variations.
Noticed : Scanning IR spectroscopy is relatively old and requires a lot of time. The advantages of FTIR are a significant time saving and high frequency accuracy.

III.8.2. Sampling

It is possible to perform IR spectra of solid, liquid or gaseous compounds. Depending on the physical state of the sample, the techniques differ. For cells, it is necessary to choose a material that does not absorb IR: often NaCl or KBr.
If the compound is liquid, a drop is placed between the windows of the cell to

form a film of liquid.
If it is solid, it can be dissolved in a solvent or mixed with anhydrous KBr; the powder obtained is then subjected to high pressure using a press to obtain a pellet. Finally, it can be suspended in a liquid paraffin (such as nujol).

Gaseous compounds are studied in gas cells, often of large volumes, although smaller volume cells with long optical path lengths can also be used.

If it is solid, it can either be dissolved in a solvent or mixed with anhydrous KBr, the powder obtained then being subjected to high pressure using a press to obtain a pellet. Finally, it can be suspended in a liquid paraffin (e.g. nujol).

Gaseous compounds are studied in large volume gas cells.

BIBLIOGRAPHICAL REFERENCES

BH Stuart;***Infrared Spectroscopy: Fundamentals and Applications***;**2004**; John Wiley & Sons, Ltd.

S. Adriana; S. Leandro;***English FTIR Spectroscopy: Advances in Research and Applications***;**2022**; Nova.

N. Abidi;***FTIR Microspectroscopy***;**2021**; Springer.

Oliveira, PhD (Editor) – Universidade Federal de Minas Gerais, Brazil
K. Sharma and A. Aathew;***Spectroscopy, theory, modes of vibration and sample handling***;**2019**; scrib company.

PR Dahoo; A. Lakhlifi;***Infrared spectroscopy of triatomic molecules for space observation***;**2019**; ISTE Group**.**

PR Dahoo; A. Lakhlifi;***Infrared spectroscopy of symmetrical spinning tops and spherical for space observation 2***;**2019**; ISTE Group**.**

PR Dahoo; A. Lakhlifi;***Infrared spectroscopy of diatomic molecules for space observation***;**2018**; ISTE Group**.**

J. Buzon; JC. Roussel;***Infrared absorption spectrometry Methods***; ***Engineering techniques***;**1981**; Ref.: P2855 V1.

B. Malingrey;***Infrared absorption spectrometry Devices; Techniques of the engineer***;**1984**; Ref.: P2845 V2.

Mr. Dalibart; L. Servant;***Infrared spectroscopy; Engineering techniques***; **2000**; Ref.: P2845 V3.

P. Richard; Dahoo; A. Lakhlifi;***Infrared spectroscopy of diatomic molecules for space observation; Publications; Collections Encyclopedia Sciences Open Science Reviews Collection: Wave; Series: Infrared spectroscopy;*****2018.**

Series of tutorials No. 3

Chapter III: VIBRATION SPECTROSCOPY IN INFRARED

Exercise 1

Hydrogen chloride gas has a peak at 2890 cm^{-1} due to the stretching vibration of the H-Cl bond.

1) Calculate the spring constant of the H-Cl bond.

2) Calculate the wave number of the absorption peak of the D-Cl bond assuming that the spring constant is equal to that of the H-Cl bond. Conclude.

$_{2}D$: deuterium (isotope of hydrogen).

Exercise 2

Let the series of IR bands (in cm^{-1}) next:

a) 3372 (l,F), 3045 (f), 1595 (m), 1224 (F)

b) 2962 (F), nothing between 2800-1600 cm^{-1}, 1450 (m), 721 (f).

(c) 3371(f), 2924(f), 1617(f), 1467(m), 1378(f).

d) 3070(f), 1765(F), 1594(m), 1370(m), 692(f). F: strong, f: weak, m: medium, l: large

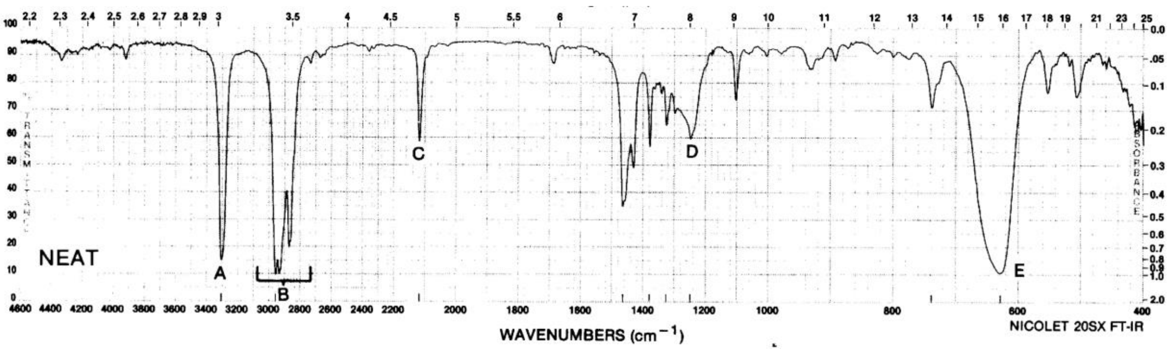
Each series corresponds to one of the following compounds: phenyl acetate, octylamine, phenol, dodecane.

Assign each compound its IR spectrum by indexing all bands.

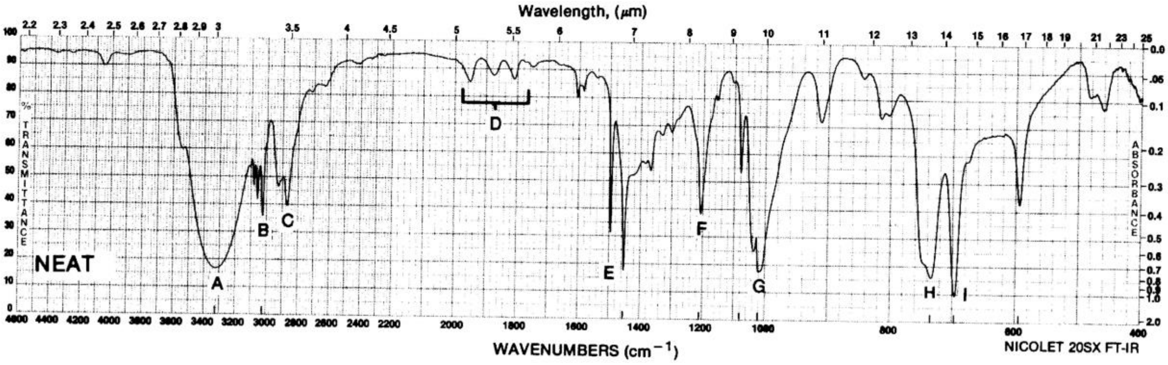
Exercise 3

Consider infrared spectra 1-3 shown below. They each correspond to a compound from the following list: aminobenzene, pentan-2-one, phenylmethanol, methylbenzene, hex-1-yne, phenol.

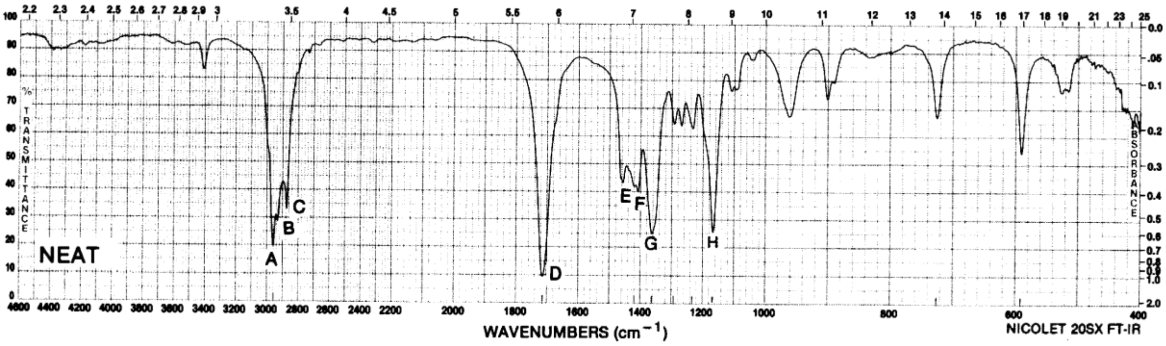
Assign each spectrum to the corresponding compound, indexing the most important bands.



Spectrum 1



Spectrum 2



Spectrum 3

Exercise 4:

Some important IR bands (in cm) are given-1) characteristics for four isomers of a compound whose empirical formula is C_4H_8O. Isomer A: 3000, 1718, 1370 and 1176.

Isomer B: 3300 (b), 2940, 1666 (w), 1075, 1000 and 962 (s).

Isomer C: 2970, 2718 and 1724.

Isomer D: 2950, 1612 (s), 1100, 1030 and 962.

s = strong, w = weak, b = broad.

1)- Indicate the allocation of vibration bands in the form of a table, indicating the corresponding chemical function.

2)- Give the developed formulas of these isomers?

Chapter IV

ATOMIC SPECTROSCOPY

Summary

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

HAS	Absorbance
°C	Degree Celsius
HPLC	High performance liquid chromatography
CPG	Gas chromatography
Ddp	Potential difference
EDTA	Ethylene Diamine Tetraacetic Acid
ICP	Inductively Coupled Argon Plasma Atomic
ICP-AES or ICP-OES	Emission by Kelvin Inductively Coupled Plasma
K	
my	Milliampere
mmHg	Millimeter mercury
ppb	Parts per trillion
ppm	Part per thousand
ITS	Atomic spectroscopy
SAAE	Electrothermal atomic absorption
SAAF	Flame atomic absorption
SEAF	Flame atomic emission Flame
SEF	emission spectroscopy Ultraviolet
UV	
Screw	Visible
V	Volt

IV. ATOMIC SPECTROSCOPY

IV.1. GENERAL INTRODUCTION

Atomic spectroscopy (AS) is a spectral analysis technique that studies the absorption or emission of light by the free atom. The inorganic elements (metals and non-metals) contained in a sample are identified and quantified using their atomic spectrum. This is only possible if a significant portion of the sample, whether molecular, solid or liquid, is transformed into atomic gas (vaporization and atomization).

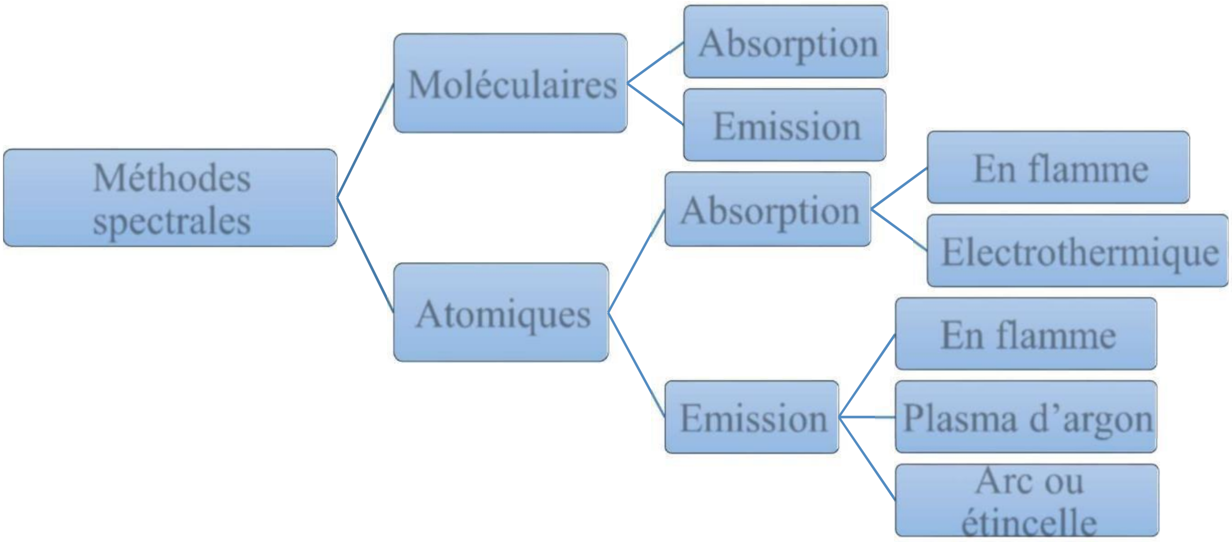


Figure IV.1. Classification of spectral methods.

The main techniques involving atomic spectroscopy (AS) are (Figure IV.1):

- Flame atomic absorption (SAAF) and flame atomic emission (SEAF)

- Electrothermal atomic absorption (EAA)
- Inductively coupled plasma atomic emission (ICP-AES or ICP-OES) Arc
- or spark emission spectroscopy

The choice of method will be made according to the type of information that one wishes to obtain, but also according to the type of sample to be analyzed. Due to the atomization process, all these methods are generally destructive. They allow the analysis of more than 70 elements in liquid, solid or gaseous phase, and the detection limit can vary between ppm and ppb. Although it is theoretically possible to treat all the elements of the periodic table, technological limitations do not always allow satisfactory results to be obtained for elements such as hydrogen, nitrogen, oxygen, as well as certain halogens and rare gases.

IV.2. ATOMIC ABSORPTION SPECTROSCOPY (AAS)

SAA is a technique first described by Walsh in 1955. It provides a powerful quantitative analytical tool.

*IV.2.1.*Principle

It is the analysis by the absorption of radiation of a certain wavelength (UVvis), by free atoms in the fundamental state leading to the passage of one of their external electrons from one electronic orbit to another and to a change in energy. This absorption is specific to each element.
A radiation source emits specific radiation corresponding to the energy difference between the ground state and an excited state of the sample to be analyzed.

The analyte must be transformed into free atoms in the ground state capable of absorbing part of this radiation. The unabsorbed radiation passes through a monochromator to a detector. The absorption is then measured; it depends directly on the number of particles in the ground state, this number being a linear function of the concentration of the analyte (= ,where k is a coefficient specific to each element). However, in practice, this relationship is difficult to verify. The dosage range generally given by the manufacturer depends on the line used. The calibration curve can be determined by the direct method for a simple matrix (a single element to be dosed) or by the method of dosed additions if the matrix is complex or unknown.

The ratio of the number of atoms in the ground state, N_0, and the number of atoms in the excited state, N_I, is weak. It is described by Boltzmann's law:

$$\frac{N_j}{N_0} = \frac{g_j}{g_0} e^{-\frac{\Delta E}{kT}}$$

Where g is the ratio of statistical weights (g = 2J + 1), J is the quantum number of the electronic angular momentum, T is the temperature in kelvin, k is the Boltzmann constant (1.38×10^{-23} J/K), ΔE is the energy difference in joules.

*IV.2.2.*Equipment

The instrumentation is almost identical for all atomic methods although the configuration of the components must be modified. An atomic absorption spectrophotometer generally consists of a source, an atomizer, a monochromator, a detector and an acquisition device. Its cost is relatively low compared to that of emission spectroscopy. There are single-beam and double-beam spectrometers.

Sensitivity is determined by the radiation source and the atomizer. The lamps used usually have the same linewidth; thus, the main difference in sensitivity comes from the type of atomizer.

IV.2.3. The source

It is a light source that emits the characteristic spectrum of the element to be analyzed. It is important that the source emits lines that are narrower than the absorption line. Thus, two types of lamps meet this requirement well:

IV.2.3.1. Hollow cathode lamp

This is the most widely used source, it emits a discontinuous spectrum. It consists of a sealed glass envelope containing a hollow cylindrical metal cathode and a tungsten or nickel anode. The envelope is also provided with a glass or quartz window (Figure IV.2). The bulb is filled with a rare gas (argon or neon) under a pressure of a few mmHg.

The emission spectrum has intense lines that depend on the element constituting the cathode. 40 metal species are commonly used. The high selectivity of SAA is due to the fact that a specific lamp is used for each element.

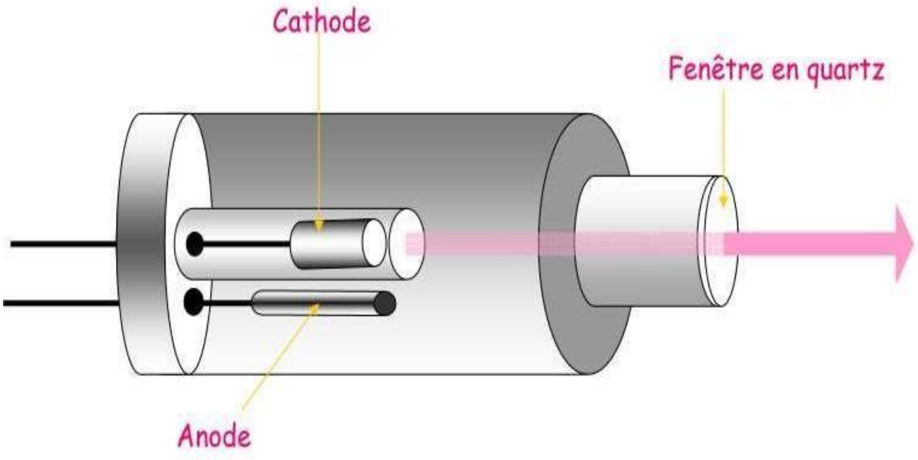


Figure IV.2. Schematic of a hollow cathode lamp.

By applying a ddp (about 300 V) between the two electrodes, the rare gas ionizes and bombards the cathode. Free and shock-excited atoms are thus torn off. There is subsequently a characteristic radiative de-excitation of these atoms as they return to their ground state.

IV.2.3.2. Electrodeless discharge lamp

It consists of a sealed quartz tube containing an inert gas and a small amount of a metallic species, or one of its salts, all under a pressure of a few mmHg. The energy is provided by an intense electrostatic field. The inert gas ionizes and the ions are accelerated to an energy necessary to tear off and excite the metallic atoms. There is then, just as for the hollow cathode lamp, a characteristic radiative de-excitation.

IV.2.4. The atomizer

AAS requires atoms to be in the ground state in order to observe the characteristic lines of the element. The atomizer must therefore provide free atoms without exciting them. Heat is required to convert the sample, usually in solution, to the atomic gas state. This heat can be generated by a flame or a graphite furnace. Flame AAS analyzes only solutions, while graphite furnace AAS analyzes solutions, liquid slurries, and solids.

IV.2.4.1. Flame atomizer

It consists of a nebulizer and a burner. At the nebulizer orifice, due to the ejection of a gas at high speed and under the effect of the pressure difference, the analyte solution, generally aqueous, is then sucked into a capillary and, at the outlet, it is sprayed into an aerosol made up of fine droplets (Figure III.3.). This aerosol, containing the oxidizer (generally the high-pressure gas), is mixed with the fuel. This mixture reaches the burner which releases a large flame composed of four zones. The solvent is eliminated in the primary zone. The salts or solid particles remain which are then melted, vaporized and then atomized. Vaporization takes place in the secondary region. Atomization takes place in the tertiary zone. The flame is characterized by its chemical reactivity, its temperature and its spectrum.

The duration of the sample passage in the flame is very short, so a significant portion does not have time to be atomized, which limits the sensitivity of the method. The latter can be improved by playing on the temperature (2000-4000 K), which depends on the fuel-oxidant mixture used. This mixture is chosen appropriately according to the sample to be analyzed. In addition, the number of atoms in the ground state is little affected by a small variation in temperature (Boltzmann's law). The air/acetylene flame (2500°C) is the most widespread and allows the determination of many elements. The N flame$_2$O/acetylene is used for some elements that form particularly strong refractory oxides and are not atomized by the air/acetylene flame. The detection limit is typically in the ppm range.

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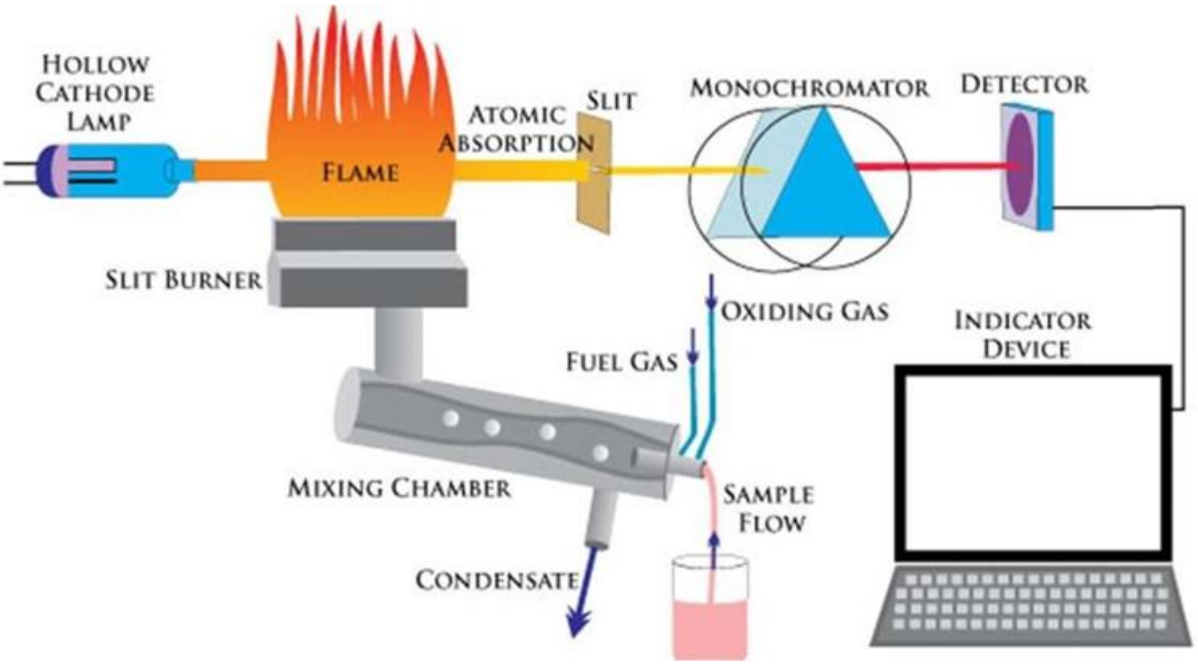

Figure IV.3. Schematic of a flame atomic absorption spectrophotometer

Elements (arsenic, bismuth, tin, selenium) are difficult to reduce to the atomic state when they are in high oxidation states. To measure them, the sample is reacted, upstream of the spectrophotometer, with a reducing agent ($NaBH_4$or $SnCl_2$) in an acidic medium. A volatile hydride of the element is formed, which is carried by a sweep gas to a quartz cell placed in the burner flame.

IV.2.4.2. Electrothermal atomizer

When the detection threshold of the flame atomizer exceeds the required value, the use of an electrothermal atomizer proves useful. Its detection limit is of the order of ppb. Indeed, despite the few restrictions that it presents, it allows an increase in sensitivity. Thus, unlike the flame atomizer where only a fraction of the sample is atomized, here the atomization is total and rapid. In addition, the average residence time of the atoms in the optical path is relatively long (Figure IV.4).
The most suitable commercial electrothermal atomizer in SAA is the graphite furnace, where atomization occurs in a cylindrical graphite furnace, open at both ends and containing a hole in the center for sample presentation. Two streams of inert gas (argon) are used. The external stream prevents air from entering the hearth, and the internal stream ensures that vapors generated in the sample matrix are quickly removed from the furnace.
This atomization is done in three stages: evaporation, decomposition and finally the atomization itself. Heating the sample causes evaporation and decomposition by placing the tube in contact with electrical parts, through which a more or less intense current is passed, which has the effect of raising the temperature (2000 to 3000 °C) and thus allows the sample to be atomized in a few minutes.

milliseconds. The temperature rise is less abrupt and atomization is delayed. In order to improve reproducibility, a platform is often introduced inside the tube so that the sample is no longer in contact with it. Finally, the absorption spectra are collected using a high-speed data acquisition device, the latter being necessary because the atomization products escape rapidly from the tube. Cooling and safety systems (inert gas flows) must be put in place beforehand.

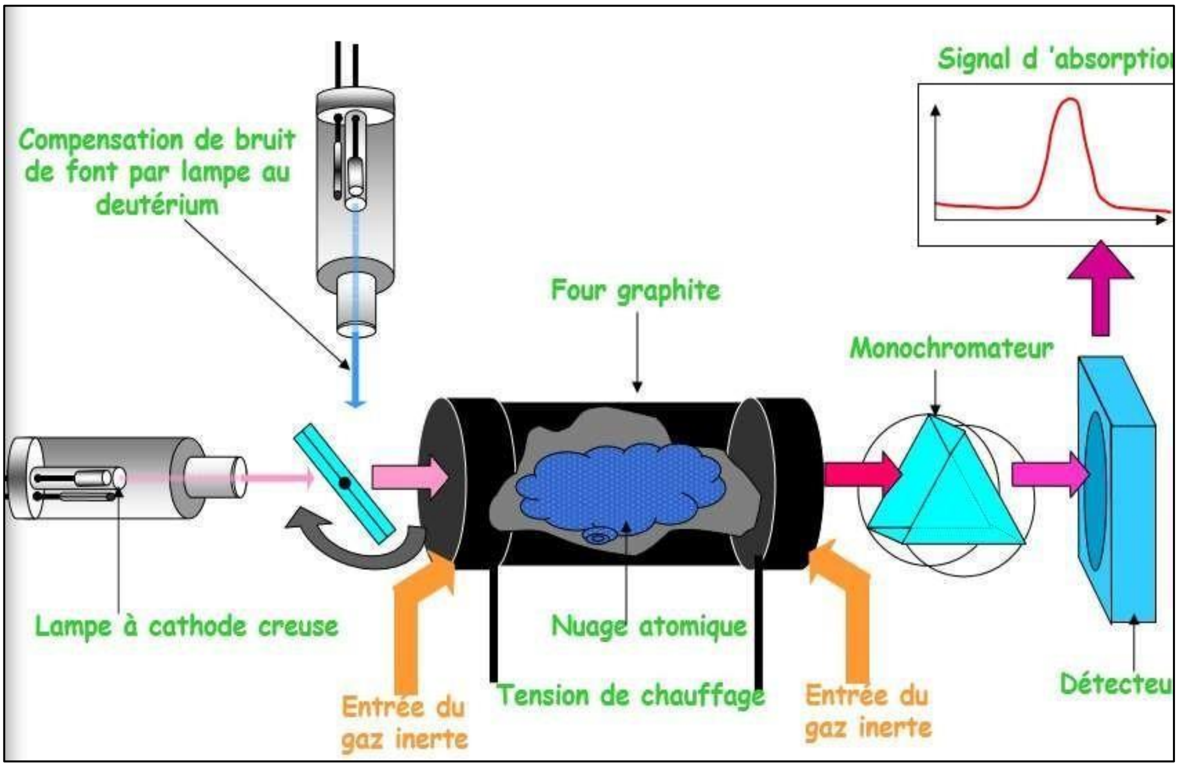

Figure IV.4. Schematic of an atomic absorption spectrophotometer with graphite furnace

Although much more sensitive and less demanding on sample size than the flame atomizer, this type nevertheless retains a greater relative uncertainty. Added to this is the slowness of the experiment due to the manipulations necessary to counter interference problems. This is why the use of the graphite furnace is generally restricted to the detection of ultra-traces.

IV.2.5. The wavelength selector (monochromator)

In general, it is not necessary to use a high-precision monochromator because the linewidth of the source is a first selection. A simple glass filter is often adequate for some alkali metals. However, most AAS instruments are equipped with a monochromator. Its role is to select the most intense line and to eliminate any light, whatever its origin, having a wavelength different from that at which one is working (lines of the filling gas in the source, possible impurities or of the atomizer).

IV.2.6. The detector

It measures the light intensities needed to calculate absorbances. Specific absorption is due to the element to be measured. Non-specific absorption is due to the continuous absorption of the matrix.
We have: Specific absorbance = Total absorbance – Non-specific absorbance Several types of detectors are suitable. The choice of this will be made, for each absorption line selected for the analysis, according to its frequency response. The most commonly used detector is a photomultiplier.

*IV.2.7.*Interferences

An element is determined by its most intense line, which generally corresponds to its resonance line. However, several factors can affect the position of this line, thus leading to inaccurate determinations. Interferences cannot be specified, because their cause may be unknown or of a complex nature. Any behavior of the sample that is different from the reference creates an interference. In general, reference solutions should be used, which should ideally contain all the components of the sample, as well as the solvent and in the same proportions, apart from the element that we want to determine. The influences of the flame, graphite materials, and the quartz cell do not cause interference since the sample and the standard are affected equally. There are two categories of interference:

IV.2.7.1. Spectral or physical interferences (= non-specific absorptions)

They are due to incomplete isolation of the radiation of the element from the sample to be analyzed generally linked to the physical properties of the solutions studied (e.g. change in viscosity between the standards and the samples). These interferences affect the spectral measurement of absorbance of the analyte by causing errors in the determination of its concentration by:

- Superposition of the line of the element to be dosed with the lines belonging to another element.
- Superposition of absorbances from molecules.
- Diffusion of incident light on small solid particles formed in the atomizer during nebulization; other metal salts present at a high concentration in the sample precipitate. To overcome this problem, two measurements are made. The first at the wavelength of the resonance line (absorption and diffusion). The second at a wavelength completely different from the resonance line (the metal no longer absorbs but there is still the diffusion effect). The difference between the two measurements is then taken, hence the absorption of the metal that we want to measure.

IV.2.7.2. Font noise

In order to subtract non-specific absorbance, during the preliminary settings of the device, it is necessary to adjust A = 0 if a correct measurement is to be obtained.

IV.2.7.3.Correction of background noise

- *By deuterium lamp:*

A second continuous source, consisting of a deuterium lamp, is added. The measurements are based on the use of a rotating mirror. The monochromator is first set to the line chosen for the determination of the element to be evaluated. When the deuterium lamp is selected, practically only the absorption background is evaluated because the bandwidth is a hundred times wider than the chosen absorption line. When the hollow cathode lamp is selected, this time the total absorbance is measured (absorption background and absorption of the analyte). Since the absorbances are additive, the difference between the two measurements makes it possible to know the absorption due to the element alone.

- *By Zeemann effect:*

An electromagnet is placed at the atomizer and a polarizer on the optical path. The magnetic field causes a disturbance of the energy states of the electrons. This phenomenon modifies the appearance of the spectrum of the corresponding element, at least if the value of the field reaches at least 1 tesla. Not all elements behave in the same way. In the simplest case, we observe that the absorption line observed without a field leads to three new polarized lines (see figure IV.5), one of which, called the p component, maintains the initial position while the other two, called the s satellite components, are symmetrically shifted on either side of the p component. The polarization directions of the p and s lines are perpendicular. By interposing a suitably oriented polarizer on the optical path, we can erase or not the p absorption component due to the element while unlike the atoms of the element, the particles and fumes in suspension will not be affected by this effect.

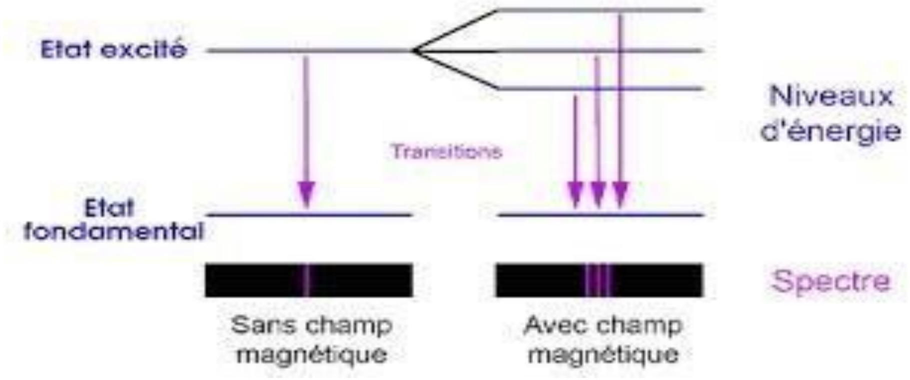

Figure IV.5. Zeemann effect.

- *By the Smith Hieftje method:*

A pulsed lamp is used that alternately switches from normal mode (10 mA) to forced mode (500 mA). In normal mode, the sum of the background absorption and the absorption of the element is measured overall, whereas in forced mode, the lamp emits intense light, but at different wavelengths, so the absorption measured is mainly due to the background, and not to the element to be analyzed. The difference between these two absorbance measurements, made repetitively, therefore make it possible to calculate the absorption of the single element measured.

When the intensity of a hollow cathode lamp is suddenly increased, the appearance of the emission lines changes. Their profile broadens, an expected consequence of the increase in temperature of the cathode, and a less intense part appears in their middle. This phenomenon comes from the cathode, whose high temperature causes a sort of evaporation of the atoms. This cloud of atoms reabsorbs a fraction of the light, precisely of the same wavelength as that which comes from the emissive part of this cathode. This self-absorption can lead to an underestimation of the absorbance of the element of interest.

These three correction methods have advantages and disadvantages. The D2 method uses a more complex optical assembly with a second source, the Zeemann method is expensive, the Smith Hieftje method requires special lamps. The choice of the correction device must be made according to the intended applications.

IV.2.7.4. Non-spectral or chemical interferences

These interferences are due either to the fact that certain metal salts can form refractory compounds that are difficult to atomize, or to the role of the anion that accompanies the cation that is being measured. Example: $CaCl_2$is easier to atomize, therefore easier to dose than Ca in the form of $Ca_3(PO_4)_2$. Therefore, phosphoric acid is never used to redissolve samples after mineralization, because it forms phosphates that complicate the analysis if their concentration is high or if the analysis conditions are not optimal. It will be necessary to do the calibration and the dosages in the same saline form; for example, if we dose Ca in $CaCl_2$, we will take $CaCl_2$to make the calibration range.

Either when the analyte is an easily ionizable element, which can make its quantification difficult. Temperature conditions are therefore chosen that avoid ionization. However, it cannot always be avoided. The addition of another more easily ionizable element modifies the ionization equilibrium of the analyte and can influence the absorbance.

IV.2.8. Advantages and limitations

SAA is a simple, rapid, sensitive, highly selective and relative quantitative method (so a calibration curve must be made). It requires a small amount of sample. Standard solutions are easy to prepare. However, a number of limitations can be noted: • For technological reasons, some elements cannot be analyzed.

• The sometimes existence of severe chemical interferences. • The non-qualitative aspect of the technique requires knowledge of the elements to be measured in order to choose the appropriate source.

• Does not allow simultaneous analysis of elements. • Need to have fairly low concentrations (in order to respect the linearity domain of the Beer-Lambert law).

IV.2.9. Applications

SAA allows the analysis of almost all metals and metalloids (Cu, Zn, Pb, Cr, Fe, Cd, etc.) in biological, metallurgical, archaeological, pharmaceutical and atmospheric samples. It therefore covers a wide range of applications. In the pharmaceutical field, we can cite:

- Dosage of zinc in insulin or zinc oxide preparations.
- Dosage of cobalt in Vit B12.
- Dosage of mercury in organo-mercurial antiseptics.
- Dosage of Al and Mg in gastric dressings.
- Dosage of Mg in nutritional supplements.
- Dosage of Ca in Ca-based preparations.
- The search for Cd, Zn in injectable preparations (plastic adjuvants).
- Search for impurities.
- Beverage analysis.
- Dosage of trace elements and toxic residues in foods.
- Analysis of drinking water.
- Analysis of plant and animal tissues, biological fluids.
- Dosage of Ca, Sr, Zn in bones.

IV.3. ATOMIC EMISSION SPECTROSCOPY (AES)

This elemental analysis technique uses the measurement of optical emission from stimulated atoms to either identify or determine the concentration of the analyte. It is preferred for the determination of alkalis (Na, Li and K) in biological fluids and tissues.

IV.3.1. Principle

An atom excited thermally or electrically to a high energy level can emit characteristic UV-vis radiation. The substance to be analyzed is generally vaporized and atomized before being excited in the stimulation region by a flame, a discharge, or a plasma. These atomization sources provide sufficient energy to excite the atoms. These excited atoms return to lower levels, releasing radiation (emission or luminescence). The intensity of this emitted radiation is then measured. The intensity is proportional to the concentration (Ie = kc, Ie is the luminous intensity emitted, k is a coefficient specific to each element). This formula is again valid only for low concentrations and in the absence of self-absorption or ionization. The concentration is measured using a calibration curve, just as in absorption.

IV.3.2. Apparatus

An emission spectrophotometer is usually identical in composition to an absorption spectrophotometer. In emission, the source of radiation is the sample itself. The atomizer transforms the sample into an atomic gas and excites it.

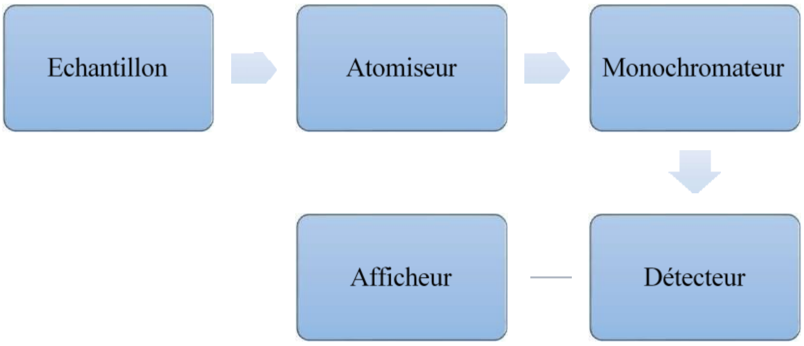

Figure IV.6. Basic design of an atomic emission spectrophotometer.

IV.3.3. Exciters

In emission photometry, we look for the excitation of atoms since these are excited atoms that will emit radiation and it is the emitted intensity that is measured. To transform the sample into the state of excited atoms, we use atomization methods based on flame, gas plasmas, sparks, lasers or glow discharges.

IV.3.3.1. The flame

This atomizer is identical in both emission and atomic absorption. Measurements are made either from burner atomic absorption spectrometers provided that the source is extinguished, or from flame photometers, simpler devices, the purchase price of which is about ten times lower. Some more sophisticated models have two measuring cells, which make it possible to compare the emitted light intensity with that of a reference solution, thereby facilitating the calculation of concentrations (see section VI.2.2.).

Generally, the flame leads to relatively low energies (5 to 6 eV) but sufficient to excite and dose a certain number of elements, in particular alkalis and alkaline earths. Some species require a higher flame temperature than others to emit a usable spectrum. The flame must be stable, i.e. reproducible and repeatable. The flow rate and pressure must be constant. The intensity emitted is proportional to the number of photons emitted which depends on the temperature, the number of excited atoms ($Ie = k' Ne$, with Ie the intensity emitted and Ne the number of excited atoms) and the nature of the atomization. There are several types of atomizers. The suction sprayer, equipped with a capillary tube, sucks up the solution. The ultrasonic sprayer, in which the solution is subjected to ultrasonic vibrations of very high frequency (800 to 3500 kHz). Flame emission spectroscopy (FES) is characterized by its widespread application in quantitative and qualitative elemental analysis. This method is rapid, requires little sample and allows the determination of certain elements that are difficult to analyze.

However, this method presents many interferences and is limited to a few elements (Na, K, Li and Ca).

IV.3.3.2. Inductively coupled argon plasma (ICP)

Despite its high cost, most atomic emission devices include a plasma torch because this device is well suited to samples in aqueous solution. The plasma consists of a weakly ionized argon stream excited by means of a radio frequency (typically 27 MHz) or microwave electric field. The use of microwaves represents an alternative for forming small, torch-shaped plasmas that therefore consume less energy and gas. The variable magnetic field created confines the ions and electrons, creating a plasma ring. The medium, which becomes increasingly conductive, heats up considerably by the Joule effect. Under these conditions, the argon becomes luminous and its temperature can reach up to 10,000°C. At this temperature, the number of excited atoms and therefore the sensitivity of the method increases.

The sample, in the form of an aerosol, is introduced with a constant flow rate of a few µL/min at the base of the torch through another small-diameter tube (1 to 2 mm). The high temperature of the plasma (6000-10,000 °C) has the effect of exciting the atoms. Thus, the spectra are very complex. This results in numerous superpositions of atomic lines. The use of higher-resolution monochromators is then necessary. On the other hand, this high temperature significantly reduces matrix effects.

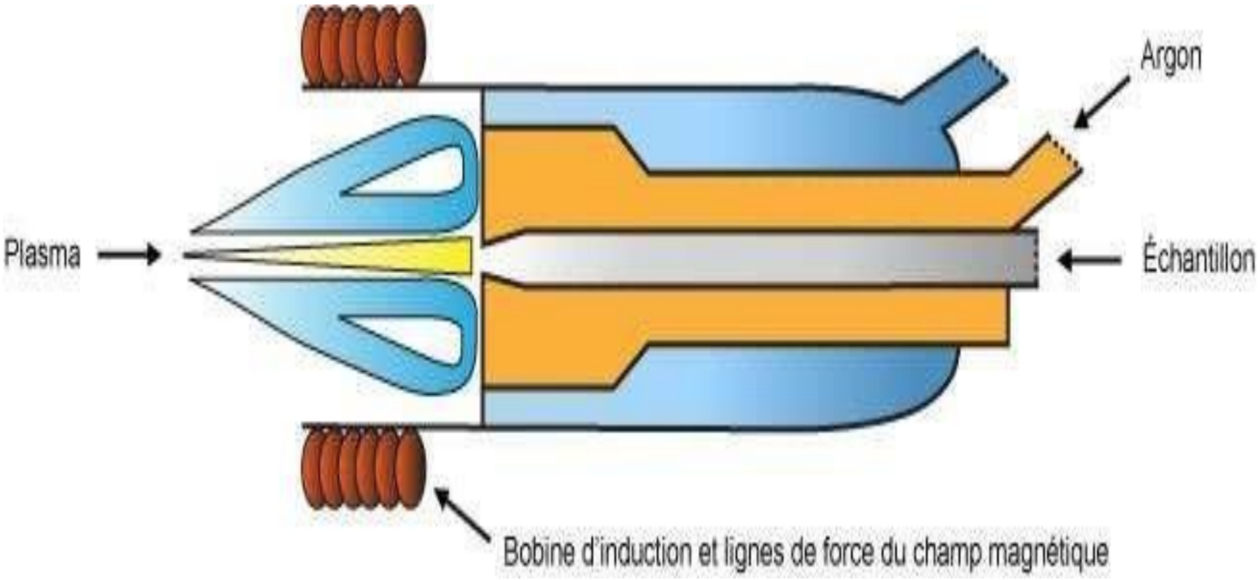

Figure IV.7. Plasma torch.

This technique allows the quantitative analysis of virtually all elements except noble gases such as argon and halogen elements, within a detection limit that typically varies between ppm and ppb. It has the advantage of being able to measure the concentration of several elements in a sample simultaneously. Compared to the flame, it presents few interferences (no formation of refractory salts). The plasma torch can be coupled with other methods such as gas chromatography (GC), high performance liquid chromatography (HPLC) and spectrometry.

mass.

IV.3.3.3. The arc or spark

Other atomization processes are also used. They either use electric arcs or sparks for conductive samples, or a pulsed laser. These are ablation methods that have progressed a lot and are used in industrial analysis. They are found associated with the different optical assemblies of current devices.

Ablation by means of repetitive sparks produces an aerosol from the surface of the sample. The material thus volatilized at the point of impact of the sparks (about 1 mg/min) is then directed by an argon flow into a conventional ICP torch operating under argon with a voltage reaching 20 to 50 kV. Furthermore, the light emission collected directly at the sparks leads to atomic line spectra, whereas with continuous arcs, neutral atomic lines are rather induced.

IV.3.3.4. Excitation using a glow discharge source

If the sample is in solid form and, if possible, conductive to electric current, it is made the cathode of a kind of spectral lamp whose operating principle is identical to that of a hollow cathode lamp. The atoms eroded from the surface of the sample are excited by the plasma. This process is mainly used for surface analyses. It has the advantage of leading to spectra with narrow emission lines, the atomization being carried out at a lower temperature than in other techniques.

The radiation emitted by atoms is not entirely monochromatic. Particularly in plasmas, environments in which collisions are very close together (which greatly reduces the lifetime of excited states), the Heisenberg uncertainty principle comes into play. In addition, the high temperature increases the speed of the atoms; this is the Doppler effect. The natural width of the lines, around 6,000 K, reaches several picometers.

IV.3.4. Interferences

IV.3.4.1. Interference between the emission lines of different atoms

Generally, we work with the resonance line, but in some cases, there may be parasitic emissions due to the presence of another element which gives a line close to the measurement line (example: K emits around 404.4 nm, Mn emits around 403.3 nm). To avoid any interference, we use fairly selective monochromators. We can also change the line; we will have a more selective but less sensitive dosage.

IV.3.4.2. Self-absorption phenomena

This phenomenon results in a weakening of the intensity of the resonance line, due to the fact that the atoms in the ground state (the most numerous) are likely to absorb photons emitted by excited atoms. Indeed, some emitted radiation, instead of reaching the counting devices and being detected, will be absorbed by the atoms in the ground state. We observe a decrease in the emitted intensity and therefore a decrease in the intensity of the resonance line. It is therefore necessary to work in a very dilute medium to have as few atoms as possible.

IV.3.4.3. Interference due to ionization

If the temperature is increased too much, there is a risk of ionization, which is a parasitic phenomenon; therefore, the temperature should not be increased excessively, even if it is a means of increasing the number of excited atoms. To avoid this type of interference, an easily ionizable ion is added.

IV.3.4.4. Interference due to refractory substances

Substances such as $Ca_3(PO_4)_2$ or $CaSO_4$, which are refractory salts that are difficult to dissociate, can be encountered. To remedy this, lanthanum chloride or EDTA is used. The complex obtained is relatively easy to dissociate.

*IV.3.5.*Advantages and limitations

We have seen that most elements can be analyzed by atomic absorption. Why then use methods such as atomic emission? Emission spectroscopy has the advantage that the selection of the line is done after the acquisition of the spectrum. Thus, we will ideally choose a line where there is no spectral interference. We can therefore carry out a qualitative analysis of the composition, even if the sample is initially unknown. This represents an important difference with atomic absorption. With a single analysis, we obtain a multi-element analysis in a few minutes, which represents an appreciable saving of time, and therefore a saving of money, even if a multi-element emission spectrometer costs much more than an atomic absorption spectrometer. However, we can only truly measure elements for which the calibration has been carefully carried out. Some elements can be analyzed with higher sensitivity and less interference. The speed and detection limits, which are below ppb for some elements, make atomic emission one of the great versatile methods of elemental analysis. Some spectrometers more easily accept dominant matrices such as sludge or soil, where the elements Si, Fe and Al are largely in the majority. The device must therefore be chosen according to the analyses being carried out. Unfortunately, not all excited atoms return to the initial state by emitting photons. They can lose their excess energy in other ways. On the other hand, as the temperature increases, the emission spectrum becomes more complex due to the appearance of lines due to ionized atoms.

IV.3.6. Applications

This essential method of analysis has also found various applications in several fields (industrial, environmental, metallurgical, forensic, pharmaceutical, etc.). Alkali metals, which give colored flames, are easily measured by emission. Flame emission can therefore be used in mineral analysis and biology to measure lithium, sodium and potassium (ionogram), as well as certain alkaline earth elements, such as barium (Ba). These analyses can be carried out in the visible or ultraviolet. In bromatology, it can be used for control, for example to measure sodium and calcium in milk. Recently, the laser has been used as an atomizer for the determination of trace elements in organs, tissues, teeth, etc., which has led to the application of atomic emission spectroscopy (AES) in forensic medicine. More generally, it is preferable to use the ICP-AES method for the analysis of several elements, at high concentrations and for solid samples. For example, it can be applied in the pharmaceutical industry, in food analysis, in biological analysis and in toxicology (to measure toxic products such as mercury, cadmium, etc.).

BIBLIOGRAPHICAL REFERENCES

S.Naima; N. Moula; S. Boudjenah and JL Hornick;***Main mineral content camel meat in Algeria***;**Tropical countries livestock and veterinary medicine review 71, n₀4**; 2019): 163.http://dx.doi.org/10.19182/remvt.31672 .

W. Xialong;***High-resolution gravimeters based on interferometry atomic***; Paris 6, 2011.http://www.theses.fr/2011PA066423 .

J. Buzon; JC. Roussel;***Infrared absorption spectrometry Methods***;

Engineering techniques;**1981**;Ref.: P2855 V1.

B. Malingrey;***Infrared absorption spectrometry Devices***; **Engineering techniques**;**1984**;Ref.: P2845 V2.

Mr. Dalibart; L. Servant;***Infrared spectroscopy***;**Techniques of the engineer**;**2000**;Ref.: P2845 V3.

PR Dahoo; A. Lakhlifi;***Infrared spectroscopy of diatomic molecules for space observation***;**Publications; Collections Encyclopedia Sciences Open Science Journals Collection: Waves; Series: Infrared spectroscopy**;**2018**.

Chapter V

ABSORPTION AND EMISSION ATOMIC

Summary

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

HAS	Absorbance (unitless)
c	Concentration of the element
°C	Degree Celsius
ϵ	Specific molar absorption coefficient of the element for the chosen wavelength.
EF	Flame emission also called flame photometry Millimeter
mm	
ppb	Parts per trillion
SAA	Atomic absorption spectrometry

V. ATOMIC ABSORPTION AND EMISSION

Atomic absorption spectrometry (AAS) and flame emission spectrometry (FE), also called flame photometry, allow the determination of one or more predefined elements (metals or non-metals) chosen from a list of approximately 70 in almost any type of sample. All elements colored pink can be determined by atomic absorption.

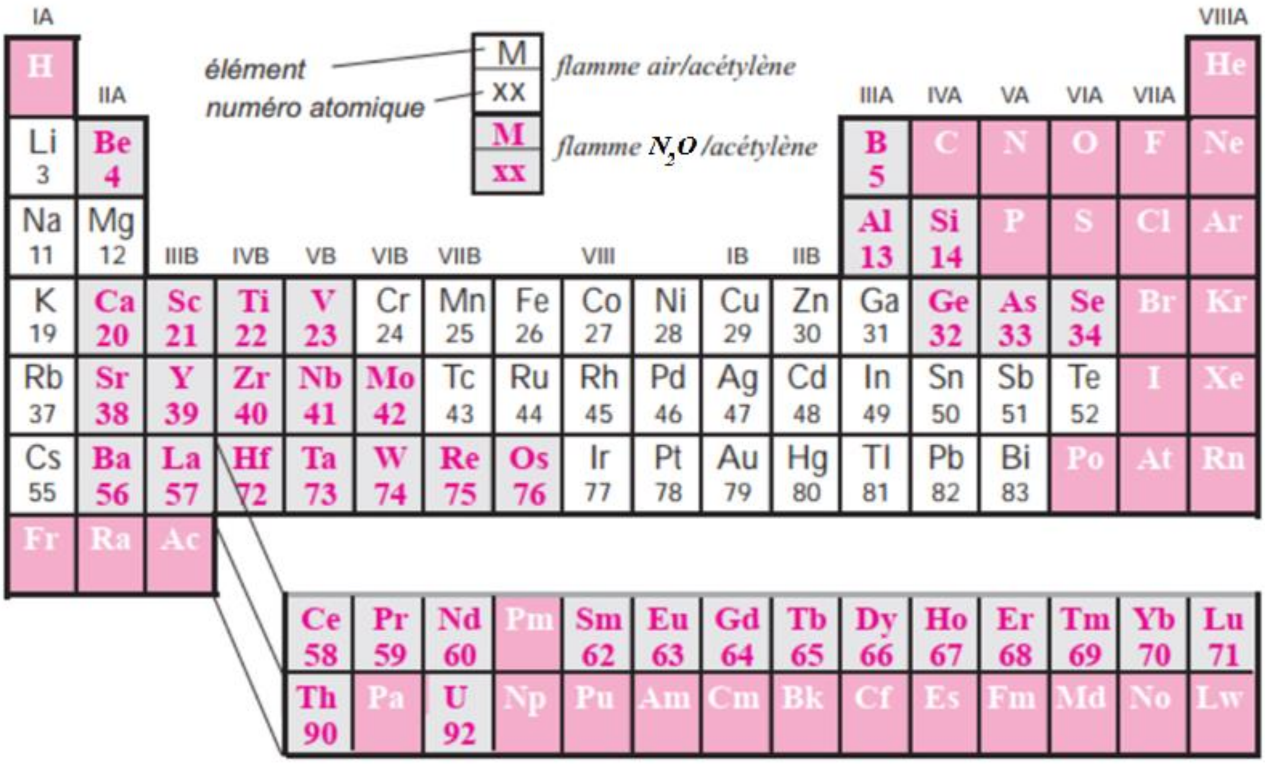

Figure V.1.Elements measured by Atomic Absorption

The corresponding devices allow, for the most part, to carry out dosages by following one or the other of these methods, although the principle of the measurements is different. The sensitivity allows to reach for certain elements concentrations lower than µg/L (ppb). The applications are very numerous.

V.1. PRINCIPLE

This method of elementary analysis requires that the measurement be made from an analyte (element to be measured) transformed into the state of free atoms. The sample is brought to a temperature of 2000 to 3000 degrees so that the chemical combinations in which

the elements are engaged are destroyed.
Atomic absorption spectrometry is based on the theory of the quantization of the energy of the atom (see CHAP I). When an electron passes from one orbit to another, it absorbs or emits a photon. Usually only the outer electrons of the atom are concerned.

Note that light emitted by a polychromatic source, such as sunlight or a polychromatic lamp, will give a continuous spectrum after being dispersed by a prism (Figure V.2).

V.1.1. Atomic absorption

Atomic absorption is the phenomenon observed when an atom in the ground state absorbs electromagnetic radiation at a specific wavelength and changes to an excited state. This results in a spectrum of dark lines on a bright background (Absorption spectrum) (Figure V.2).

Theoretical aspect of atomic absorption: the Beer-Lambert law

In atomic absorption spectrometry, absorbance is measured:

A=ϵ·L·cA = \epsilon \cdot l \cdot cA=ϵ·L·c

With :

- A: Absorbance (unitless) c:
- Concentration of the element
- ϵ\epsilonϵ : Specific molar absorption coefficient of the element for the

selected wavelength.

Since the absorbed photons are characteristic of the absorbing elements, their quantity is proportional to the number of absorbing atoms according to the Boltzmann distribution law. Absorption makes it possible to measure the concentrations of the elements to be measured. If several elements must be measured, this manipulation is carried out for each element of the sample by placing oneself at a specific wavelength.

V.1.2. Atomic emission

Atomic emission East THE phenomenon observed when a radiation electromagnetic is emitted by excited atoms or ions that return to the ground state. This results in a
emission spectrum.

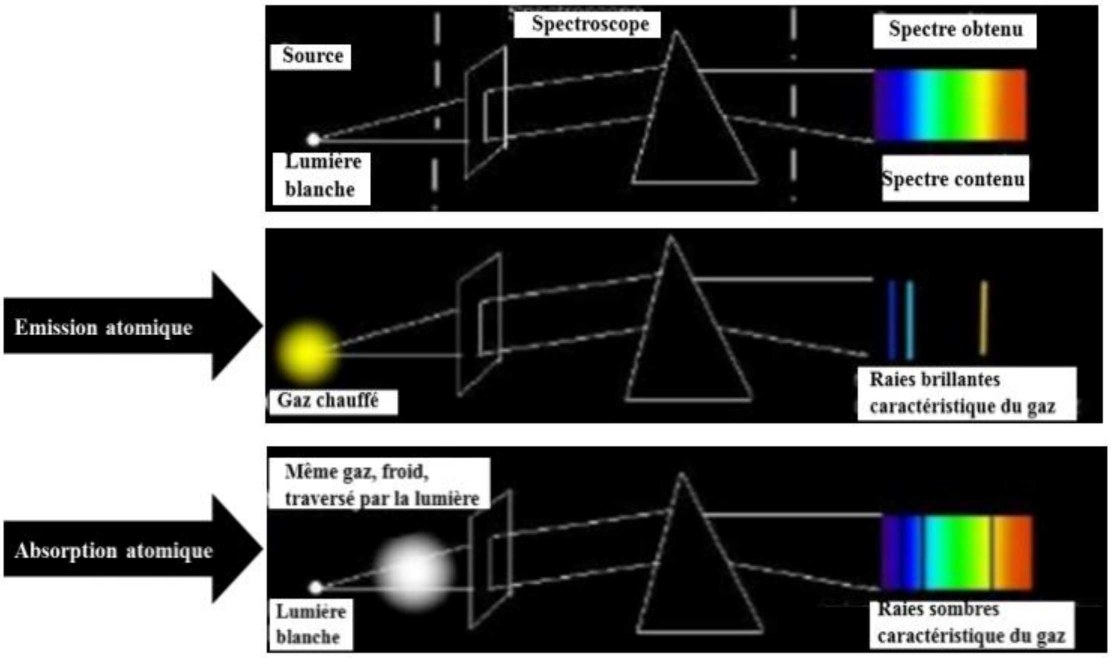

Figure V.2. Kirchhoff line reversal experiment.

Note that in the case of the**atomic emission,**When the lamp is replaced by a Bunsen burner into which NaCl is projected, a spectrum of lines is obtained which corresponds to the few sodium atoms which have passed into an excited state and which emit light on returning to the fundamental state. On the other hand, for the**atomic absorption,**the Bunsen burner is placed in the path of the polychromatic light. We then have a spectrum where we can distinguish dark lines: The atoms remaining in the fundamental state in the flame absorb the light at certain wavelengths.

V.2. INSTRUMENTS

The experimental device used in atomic absorption consists of a source, the hollow cathode lamp, an atomizer (burner and a nebulizer), a monochromator and a detector connected to an amplifier and an acquisition device.

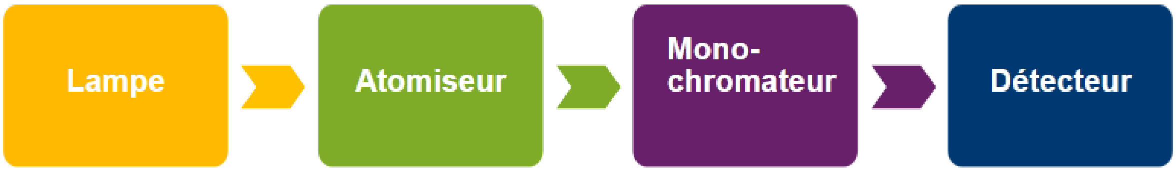

Figure V.3. Schematic diagram of an atomic absorption spectrometer device

The optical scheme of an atomic absorption apparatus, illustrated here by a basic single-beam model (Figure V.4), has four main parts.

The light beam from the source (1) passes through the flame (2) in which the element is brought to the atomic state, before being focused on the entrance slit of a monochromator (3) which selects a very narrow interval of wavelengths. The optical path ends on the entrance window of the detector (4).

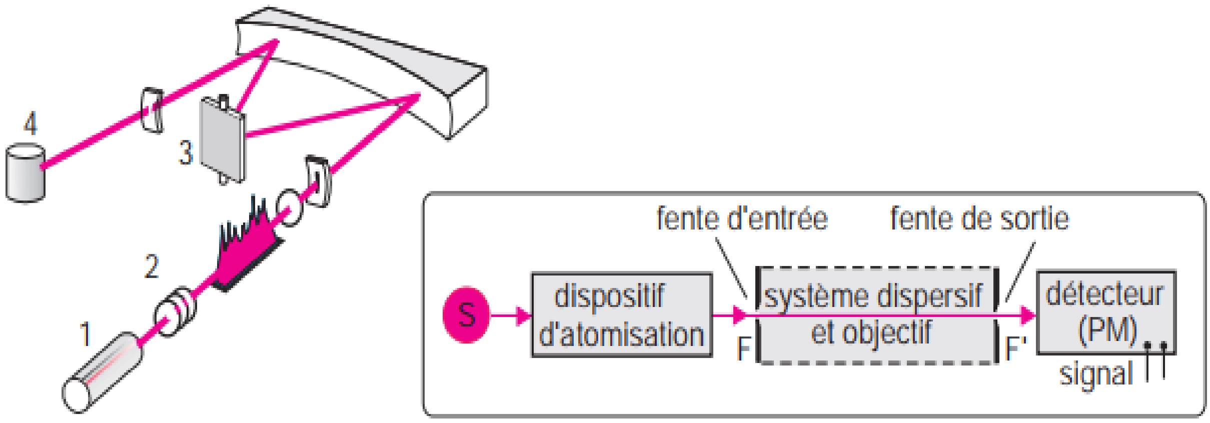

Figure V.4. The various parts of a commercial single-beam atomic absorption apparatus.

Model IL 157: built in the 80s.

1-source (spectral lamp); 2-burner flame; 3-grating monochromator and 4-detector (photomultiplier).

V.2.1. The hollow cathode lamp

The hollow cathode lamp consists of a sealed glass envelope with a glass or quartz window containing a cylindrical hollow cathode and an anode. The cathode consists of the element to be measured. A large vacuum is created inside the bulb, which is then filled with a rare gas (argon or neon) under a pressure of a few mm Hg. When a potential difference of a few hundred volts is applied between the two electrodes, a discharge is established. The rare gas is then ionized and these ions bombard the cathode, tearing atoms from it. These atoms are therefore free and are excited by shocks: there is atomic emission of the element constituting the hollow cathode. The particularity of the radiation thus emitted is that it consists of very intense and very fine lines.

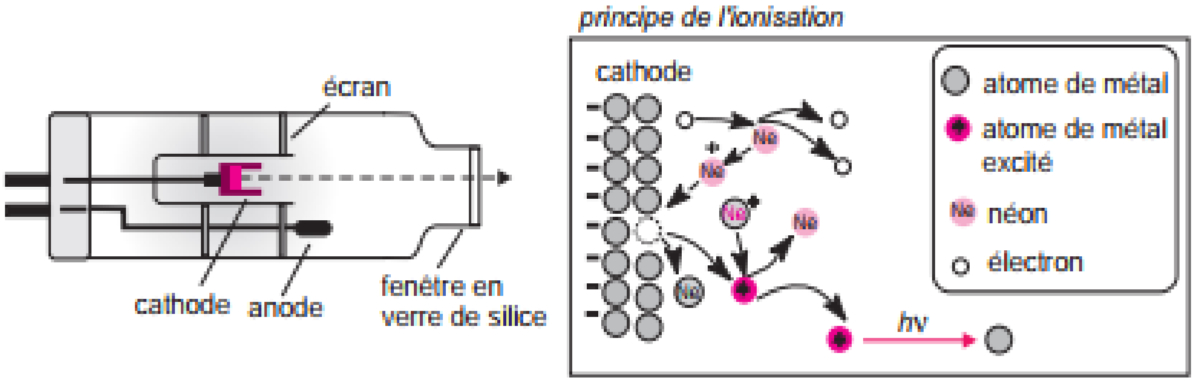

Figure V.5.Chollow atom of an atomic absorption spectrometer.

V.2.2. The nebulizer

The sample to be analyzed is in solution. This is sucked up by means of a capillary by the nebulizer. At the orifice of the nebulizer, due to the ejection of a gas at high speed, a depression is created (Venturi effect). The analysis solution is then sucked into the capillary and at the outlet, it is sprayed into an aerosol made up of fine droplets. This aerosol then enters the nebulization chamber whose role is to burst the droplets and eliminate the larger ones. This homogeneous mist then enters the burner.

V.2.3. The flame - atomization

The aerosol enters the burner and then the flame. After a certain distance at the threshold of the flame, the solvent in the droplet is eliminated, leaving the salts or solid particles which are then melted, vaporized and then atomized.

The air acetylene flame is the most widespread and allows the dosage of many elements. Its temperature is approximately 2500°C.

Instead of a flame, a cylindrical graphite furnace can also be used to atomize the sample. The light leaving the source is not monochromatic. A line spectrum is obtained containing:

- the lines of the element to be measured;
- the lines of the filling gas in the source;
- the lines of possible impurities;
- the atomizer lines (flame).

The role of the monochromator is to eliminate all light, whatever its origin, having a wavelength different from that at which we are working.

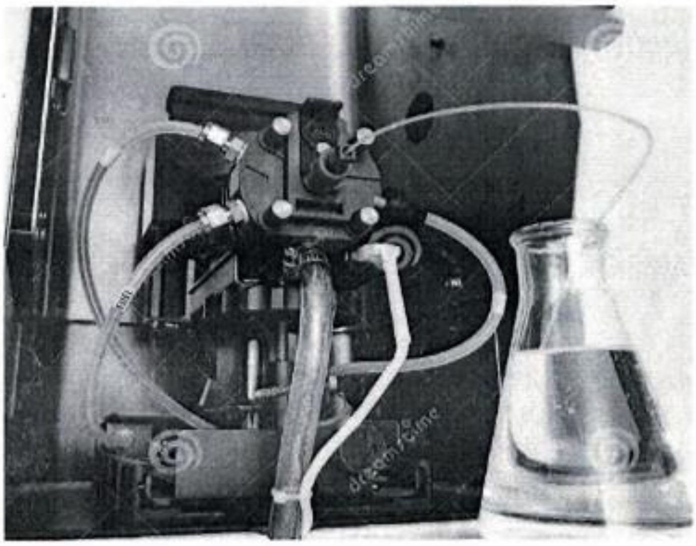

Figure V.6. Photo of a flame atomizer model.

V.2.4. The detector

The beam then reaches the detector. The latter measures the light intensities necessary for calculating the absorbances. It is connected to an amplifier and an acquisition device.

We determine:

Specific absorbance = Total absorbance - Non-specific absorbance

The specific absorbance is due to the element to be measured (on a line).

Nonspecific absorbance is due to the continuous absorbance of the matrix.

Measurements allow correction of nonspecific absorbances.

V.3. ATOMIC ABSORPTION DOSAGE

The calibration curve is determined in two different ways:

- Direct calibration by -› simple matrix (only one element to be measured)
- Standard addition method (standard addition method is used mainly to avoid matrix effects when analyzing complex matrices) by complex or unknown matrix.

Noticed :

- Ensure the similarity of composition (solvent, acid concentration, salt content, etc.) between the calibration solutions and the samples.
- Do not compare samples in organic solution to aqueous standards.

V.4. SOME APPLICATIONS

Atomic absorption spectrometry is essentially a quantitative analysis method that is much better suited to the determination of traces than to that of major components. Atomic absorption spectrometry allows the measurement of many inorganic materials (rocks and ores, metals and alloys, etc.). It is therefore very suitable for the study of archaeological material. It also allows the quantification of metallic elements in solution.

(waste management). Here are some examples:

- Trace element analysis for stone identification;
- Analysis of major and minor constituents of archaeological ceramics;
- Water analysis;
- Analysis of soils, fertilizers and sediments;
- Analysis of industrial products as well as other analyses.

Advantages of the atomic absorption spectrometry method: high sensitivity, high specificity, speed, small amount of substance required (1 ml of the solution may be sufficient) and ease of preparation of standard solutions.

V.5. DISADVANTAGES

Need to use a characteristic source for each element to be measured, destructive analysis technique, field of application limited almost exclusively to metals (Cu, Zn, Pb, Cr, Fe, Cd, etc.), need to have fairly low concentrations.

V.6. ANALYTICAL PROTOCOL

Atomic absorption spectrometry is a comparative analytical method; it involves calibration, and the quality of the results will depend on the representativeness of the standards to the samples. The preparation of standards requires proper care.

BIBLIOGRAPHICAL REFERENCES

- ABBEY, S. (1967-1968): Analysis of rocks and ores by atomic absorption spectroscopy. I. Determination of Mg, Li, Zn and Fe. Geol. Surv. Canada. Paper (1967), 67, V, 35 p. II. Determination of total Fe, Mg, Ca, Na, K. Id. (1968), 68, V, 21 p.
- ADAMS, PB, PASSMORE, WO (1966): Critical factors in the determination of the alkaline earth elements in glass by atomic absorption spectrometry. Anal. Chem., 38, pp. 630-632.
- AGAZZI, JE (1965): Determination of iron in hydrogen peroxide solutions by atomic absorption spectrometry. Anal. Chem., 37, pp. 364-366.
- ALCOCK, NW, McINTYRE, I. and RAnDE, I. (1965): Concentration of magnesium in human plasma or serum. Nature, 206, p. 89.
- ALcOCK, NW and McINTYRE, I. (1966): Methods for estimating magnesium in biological materials. Methods Biochem. Anal., 14, p. 1.
- ALDOUS, KM, DAGNALL, RM, THOMPSON, KC and WEST, TS (1968): Sorne preliminary studies of the analytical potentialities of the atomic hydrogen plasma torch. Anal. Chem. Acta, 41, pp. 380-384.
- ALDOUS, KM, DAGNALL, RM and WEST, TS (1969): Preparation and spectral characteristics of micro-wave-excited electrodeless discharge tubes for palladium, silver, platinium and gold. Analyst, 94, p. 347.
- ALDRICH, DG, VANSELOW, AP and BRADFORD, GR (1951): Lithium toxicity in citrus. Soil Sciences, 71, p. 291.
- ALKEMADE, CTJ (1969): Fundamental aspects of decomposition, atomization, excitation of the sample in the flame, in Flame Emission and Atomic Absorption Spectrometry, by Dean, JA, Rains, TC, vol. 1, Marcel Dekker, New York.
- ALKEMADE, CTJ and HERRMANN, R. (1963): Chemical analysis by Bame photometry. Chemical Analysis, ch. 14, Interscience, New York.
- ALKEMADE, CTJ and MILATZ, JMW (1955): Double beam method of spectral selection with Hames. J. Opt. Soc. Amer., 45, pp. 583-584. Appl. Sei. Res., 4 B, pp. 466-471.
- ALLAIRE, RF, BRACHETT, FP and SHAFER, JT (1967): Analytical benefits of atomicabsorption spectrophotometric methods. J.Soc. Motion Pict. TV. ENGRS, USA, 76, pp. 992-994.

ALLAN, JE (1958): Atomic absorption spectrophotometry. With special reference to the determination of magnesium. Analyst, 83, pp. 466-471.

ALLAN, JE (1959): The determination of iron and manganese by atomic absorption. Spectrochem. Acta, 10, pp. 800-806.

ALLAN, JE (1960): Determination of nickel and cobalt by atomic absorption. Nature, 187, p. 1110.

BIBLIOGRAPHICAL REFERENCES

S.Naima; N. Moula; S. Boudjenah and JL Hornick;***Main mineral content camel meat in Algeria***;**Tropical countries livestock and veterinary medicine review 71, n₀4**; 2019): 163.http://dx.doi.org/10.19182/remvt.31672 .

W. Xialong;***High-resolution gravimeters based on interferometry atomic***; Paris 6, 2011.http://www.theses.fr/2011PA066423 .

J. Buzon; JC. Roussel;***Infrared absorption spectrometry Methods***;

Engineering techniques;**1981**;Ref.: P2855 V1.

B. Malingrey;***Infrared absorption spectrometry Devices***; **Engineering techniques**;**1984**;Ref.: P2845 V2.

Mr. Dalibart; L. Servant;***Infrared spectroscopy***;**Techniques of the engineer**;**2000**;Ref.: P2845 V3.

PR Dahoo; A. Lakhlifi;***Infrared spectroscopy of diatomic molecules for space observation***;**Publications; Collections Encyclopedia Sciences Open Science Journals Collection: Waves; Series: Infrared spectroscopy**;**2018**.

Series of tutorials No. 4

Chapter IV: ATOMIC ABSORPTION AND EMISSION

Exercise 1

In atomic absorption, Zn absorbs at 213.856 nm. Its quantum number is 3.
What is the energy in eV corresponding to this electronic transition?
At 4000 K, what is the number of atoms in the excited state compared to the ground state?

Exercise 2

Na and K are determined by flame emission from an intravenous perfusion solution containing KCl and NaCl. 0.5092 g of NaCl and 0.1691 g of KCl are weighed, transferred and brought to a volume of 1 L with deionized water. Then 20 ml of this solution are transferred into a 100 ml graduated cylinder made up to 100 ml with H_2O.

This solution is used to make a calibration curve as follows: 5; 10; 15; 20; 25 ml are transferred into 100 ml graduated flasks completed with H_2O (solution A, B, C, D, E). On the other hand, 5 ml of the perfusion solution are brought to a volume of 250 ml, then 10 ml of this solution are diluted 10 times before being analyzed by flame emission (solution X). The spectrophotometer is used with a filter to measure Na then with another to measure K of the standards and the sample. Distilled water is used as a blank.

The values read on the spectrophotometer are:

Solutions	**N / A$^+$**	**K+**
White	0	0
Solution A	20.7	22.4
Solution B	41	41.2
Solution C	60.6	61.2
Solution D	80.3	80.3
Solution E	100	100
Solution X	70.2	70.6

What is the molar concentration of $Na^+$and $K^+$of the infusion solution?

Exercise 3

A solution of 100.5g of mannitol is prepared in 250ml of deionized water. A solution of Ni^{2+}(10.6ppm) is used to prepare a calibration line by adding: 0 – 0.5 – 1 – 1.5 ml of this solution to 50ml of the mannitol solution, each volume is brought to 100ml. Analysis of these solutions gives an answer of: 0.378 – 0.543 – 0.718 -0.891. What is the nickel content of mannitol in ppm?