Chimie analytique appliquée à l'environnement
Analytical Chemistry applied to the environnement

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Prof Université de Paris, LISA

Organisation of the course

- Unit consists of :
  - 12h of courses
    - Slides available on http://www.lisa.u-pec.fr/~desboeufs/
    - For your own evaluation, 1 multi-choice test for each course
    - If you feel desperate: desboeufs@lisa.ipsl.fr
  - 20h of practical works (4 assignments of 5h)
  - Evaluation: 80% for the final examination and 20 % for practical works

What is analytical chemistry applied to the environment?

- **Definition**

Analytical chemistry is the science that makes it possible to acquire information about a material or a sample and to derive a ***chemical composition (elementary / molecular)*** *using scientific methods.*

- **Application to the environnement:**

Analytical chemistry applied to environmental matrices makes it possible to measure thousands of ***hitherto unknown substances*** *in order to evaluate* ***their environmental risks****.*

What is analytical chemistry applied to the environment?

- Story of environmental regulation:
  - Treaty of water purification from Delhotel (1893):
    - « une eau peut être considérée comme bonne et potable…quand elle est fraîche, limpide, sans odeur, quand sa saveur est très faible, quand elle n'est surtout ni désagréable, ni fade, ni salée, ni douceâtre, quand elle contient peu de matières étrangères, …quand elle dissout le savon sans former de grumeaux et qu'elle cuit bien les légumes…»

  - Today in Europe, 63 parameters control the quality of drinking water (80 in USA) vs 6 at the end of XIXth century.

What is analytical chemistry applied to the environment?

- **Application to the environnement:**

However, to evaluate a risk, it is necessary to be able to compare the values found. It was therefore necessary to integrate the notion of ***measurement uncertainty*** *to compare data from different laboratories, different methodologies, different countries …*

Use of analytical tools adapted to provide ***reliable chemical composition values*** *that will allow the monitoring of the quality of the environment, a real evaluation of the impacts and subsequently to lead to calm and accepted decisions.*

What is analytical chemistry applied to the environment?

- Seawater concentrations:

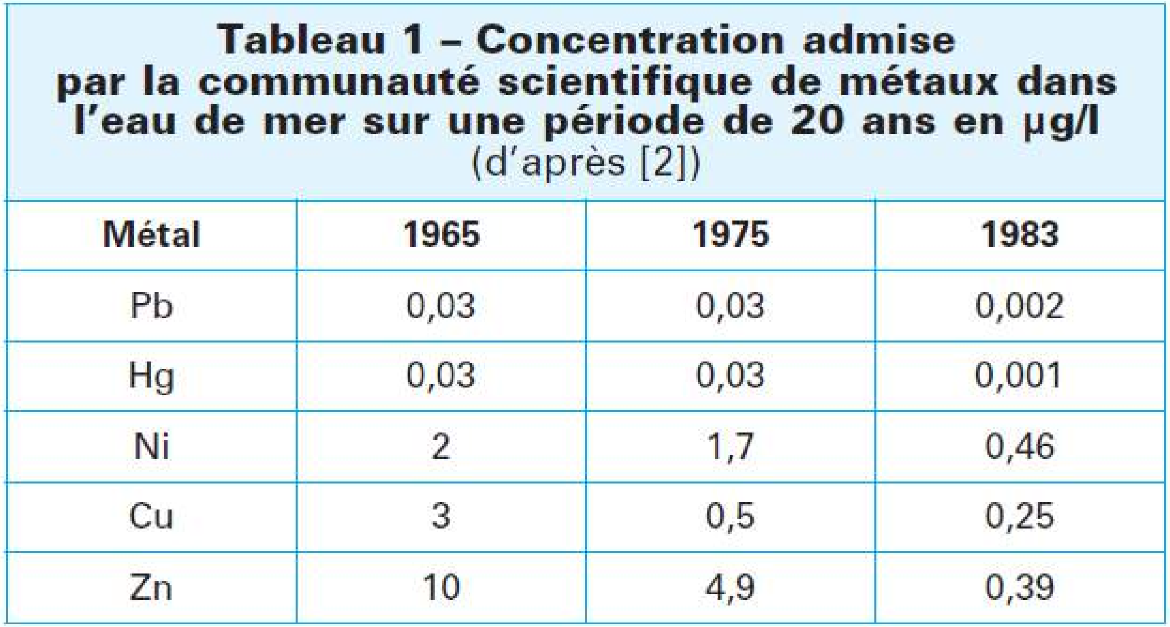


Tableau 1 – Concentration admise par la communauté scientifique de métaux dans l'eau de mer sur une période de 20 ans en µg/l
(d'après [2])

Métal	1965	1975	1983
Pb	0,03	0,03	0,002
Hg	0,03	0,03	0,001
Ni	2	1,7	0,46
Cu	3	0,5	0,25
Zn	10	4,9	0,39

Importance of quality control in analytical chemistry

What is analytical chemistry applied to the environment?

Environmental matrices: water, air, soil, sediments, plants…

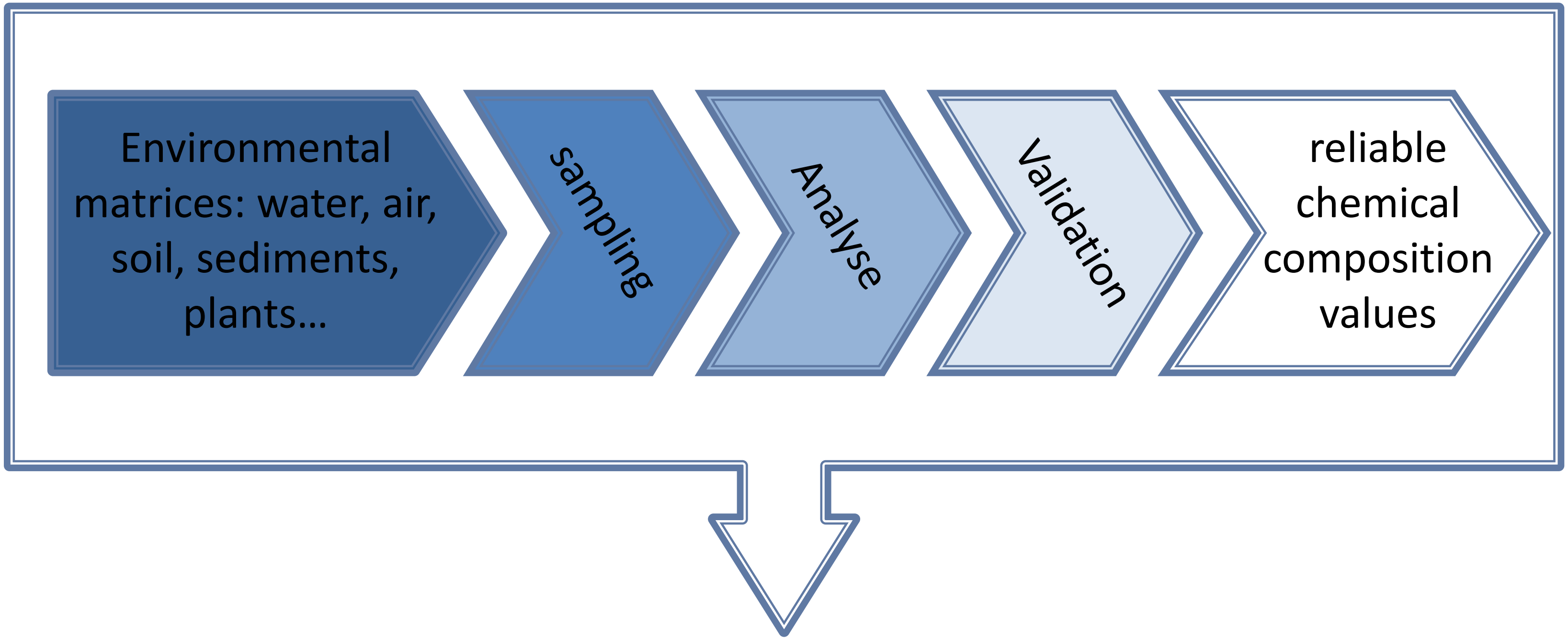
sampling

Analyse

Validation

reliable chemical composition values

What is analytical chemistry applied to the environment?



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Metrology

= science of measurement (chemical, physical, biological) at any level of uncertainty in any field of science and technology

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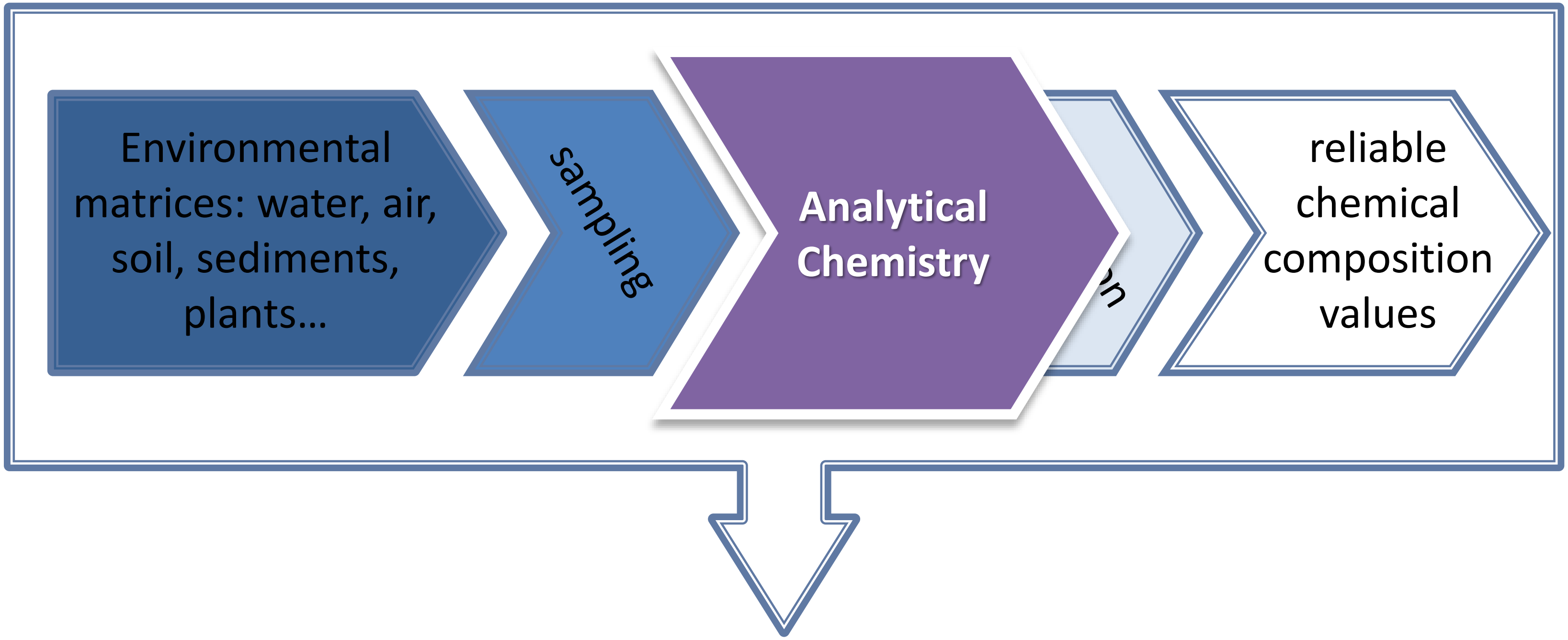

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Analytical Chemistry

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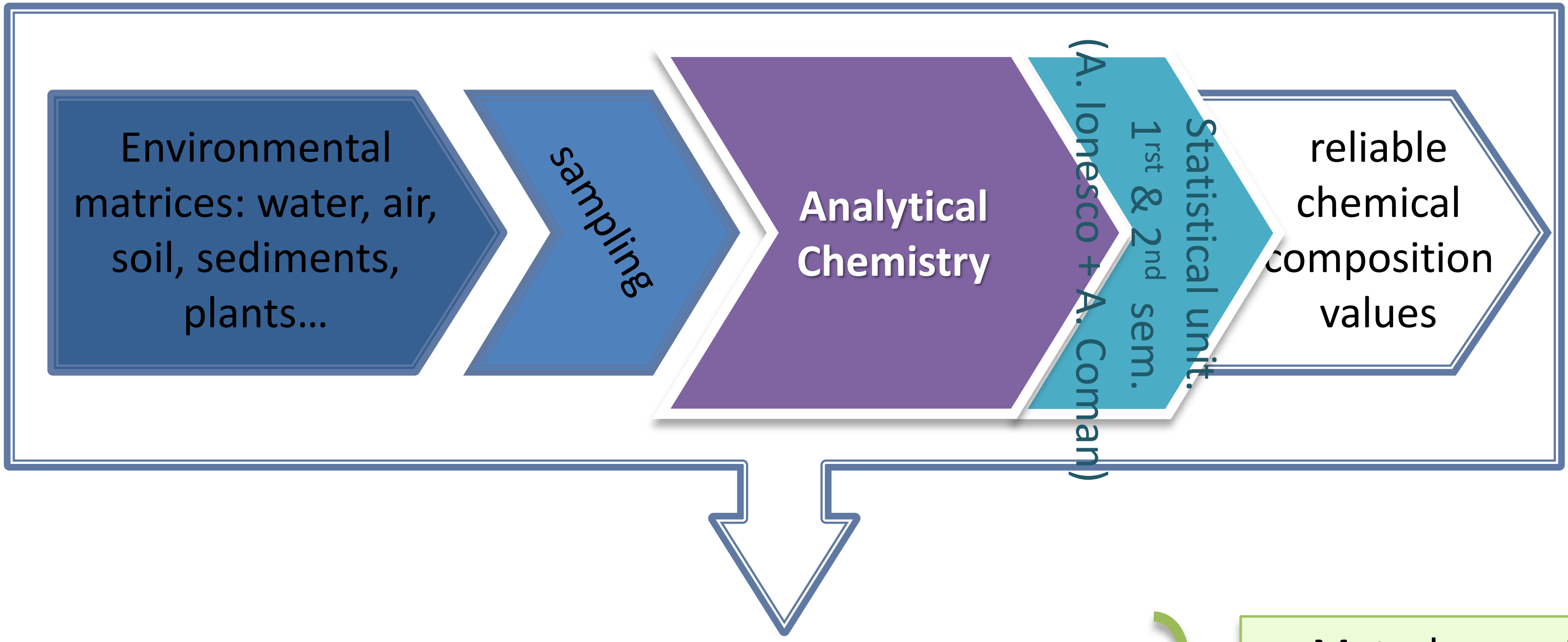


Environmental matrices: water, air, soil, sediments, plants…

sampling

Analytical Chemistry

Statistical unit:
1rst & 2nd sem.
(A. Ionesco + A. Coman)

reliable chemical composition values

Metrology

= science of measurement (chemical, physical, biological) at any level of uncertainty in any field of science and technology

Metrology unit
2nd semester
(B. Picquet-Varrault)
+
Field campaign

Course Outline

1. **General informations on chemical analysis**
2. Sample preparation
3. Metals analysis
4. Soluble inorganic pollutants analysis
5. Organic pollutants analysis
6. Quality assurance

1. General informations on chemical analysis: *Terminology*

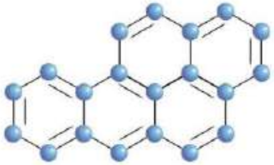
- Sample (*Echantillon*) = representative part or a single item from a larger whole to analyse
- Analyte(s) (*analyte*) = a chemical substance that is the subject of chemical analysis.
  - Solute (*solutés*)= analyte that is dissolved in a solution.
- Matrix (*matrice*)= substance in which other things are fixed, buried, dissolved..
  - Solvant (*solvant*)= Liquid matrix
  - Aqueous matrix (*Matrice aqueuse*)= when the solvant is water
  - Organic matrix (*Matrice organique*)= when the solvant or the matrix is organic (oil, leaves,..)
- Organic vs inorganic?
  - Organic = containing carbon **and** hydrogen (H-C)
  - Inorganic = containing no carbon or hydrogen (N, S, …)
    - Mineral = containing no carbon

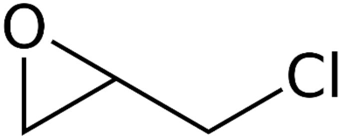
1. General informations on chemical analysis: *Why measure chemical species in different environments?*

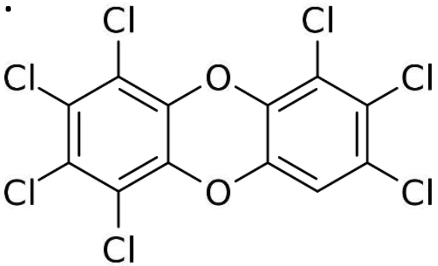
- Monitoring of regulated substances (= pollutants = *polluants*) for their environmental or health impacts
  - Generally automated analysis methods
  - Standardized procedures
    - Standard ISO 17381:2003 = Water quality : Selection and application of ready-to-use test kit methods in water analysis
    - Standard ISO 17294-2:2016 = Application of ICP-MS - Determination of selected elements including uranium isotopes in water, sludges and sediments.
- Monitoring of markers of sources
- Monitoring of reactive species to study the chemistry in the various environmental matrices.
  - "Homemade" procedures

What are the species to be analyzed = regulated substances?

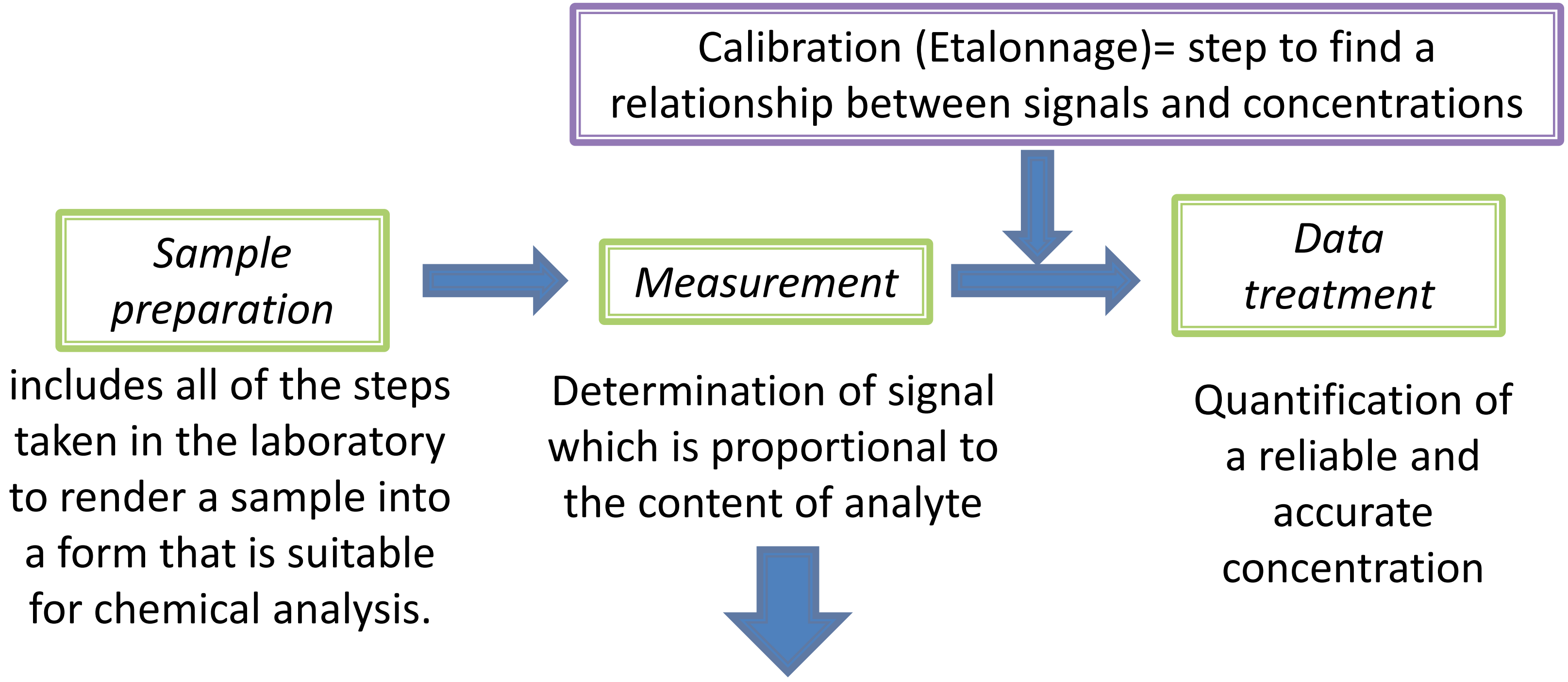
- Inorganic species:
  - Soluble compounds: nitrates (nitrates), sulphates (sulfates), chlorides (chlorures), fluorides (fluorures)…
  - Metals and heavy metals : Cd, Cr, Cu, Fe, Pb, Mo, Ni…
- Organic species:
  - Hydrocarbons (hydrocarbures): benzene, dichloroethane, …
    - Carbonyl compounds : formaldehyde, acetone…
  - PAH (HAP): Polycyclic Aromatic Hydrocarbons
    - Benzo(a)pyrene
  - Pesticide/Herbicide (glyphosate, triazine..)
    - Organochlorines: epichlorhydrin, dioxins…


Benzopyrene





1. General informations on chemical analysis: *The different stages of an analysis*



Calibration (Etalonnage)= step to find a relationship between signals and concentrations

Sample preparation

includes all of the steps taken in the laboratory to render a sample into a form that is suitable for chemical analysis.

Measurement

Determination of signal which is proportional to the content of analyte

Data treatment

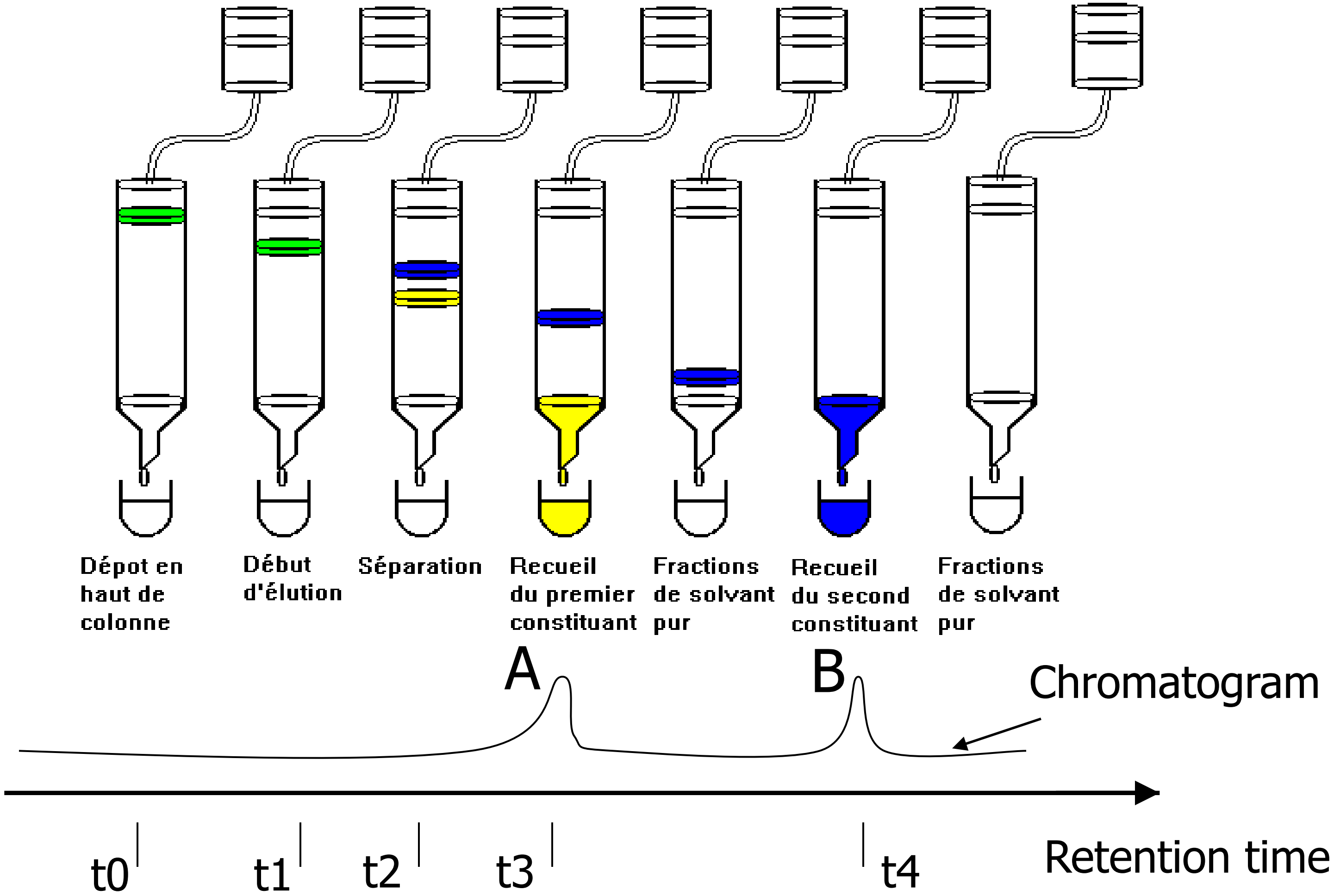
Quantification of a reliable and accurate concentration

Various analytical techniques:

- Chromatography
- Spectrometry
- Electrochemistry

1. General informations on chemical analysis: *Chromatographic Techniques*

Definition : Chromatography is a **method of separating** the constituents of a solution or a gas, based on one or more of its chemical properties.



1. General informations on chemical analysis: *Chromatographic Techniques*

Background

1906 The chemist Tswett separates colored plant pigments on a column filled with calcium carbonate. The pigments were carried with petroleum ether.

→Band formation of different colors on the column (green, orange, yellow,…)

Technique is called **CHROMATOGRAPHY** *(color writing)*

1940 Martin et Synge : Practice and theory of chromatography (Nobel Price in 1952)

1952 Gas Chromatography (GC *or CPG in french*)

1968 High performance liquid chromatography (HPLC)

1. General informations on chemical analysis: *Chromatographic Techniques*

Injection

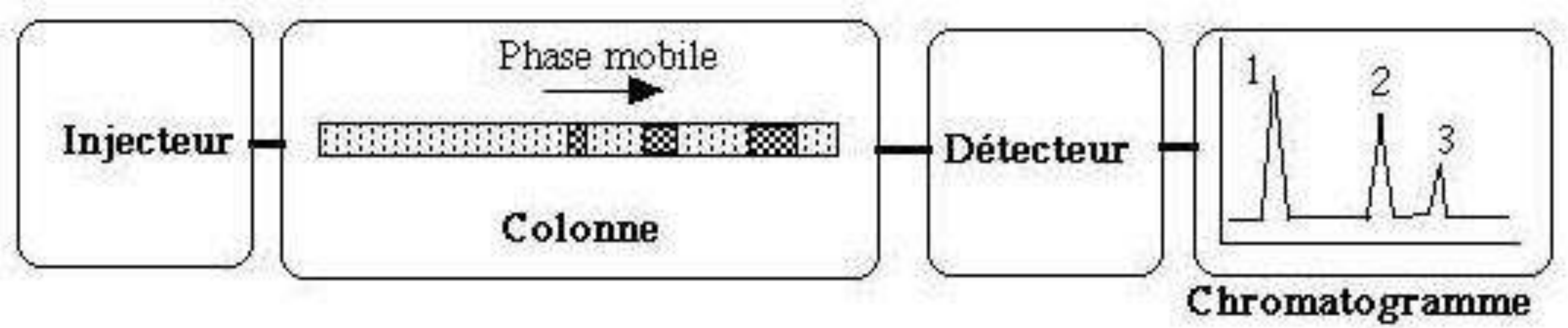
Introduction of the sample into the analytical system.

Separation

Separation of the different compounds according to their affinity with the column → Different retention times

Detection

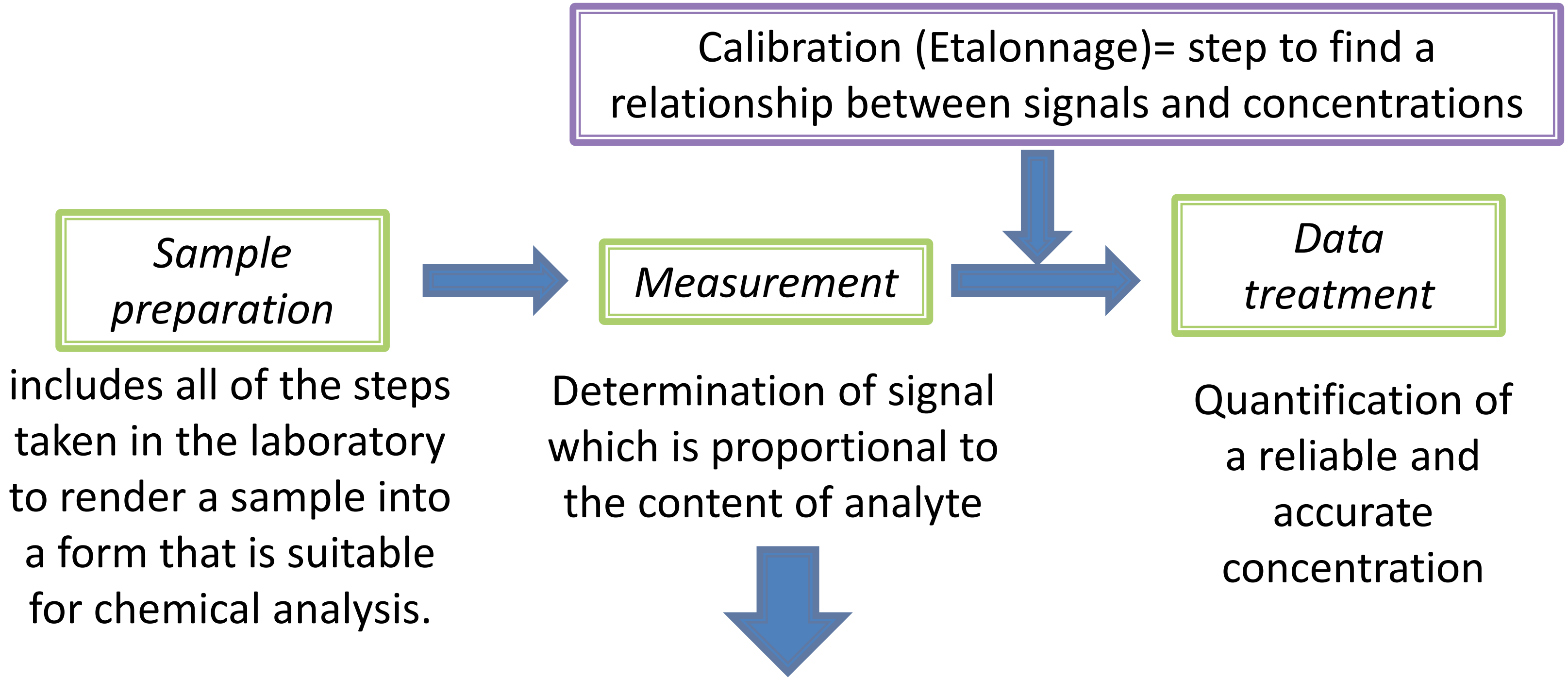
Depending on the type of compounds to be characterized, concentration thresholds to be reached.



- Two major types of chromatography for environnemental application:
  - Liquid Chromatography (LC)
  - Gaseous Chromatography (GC)

As a function of mobile phase

1. General informations on chemical analysis: *The different stages of an analysis*



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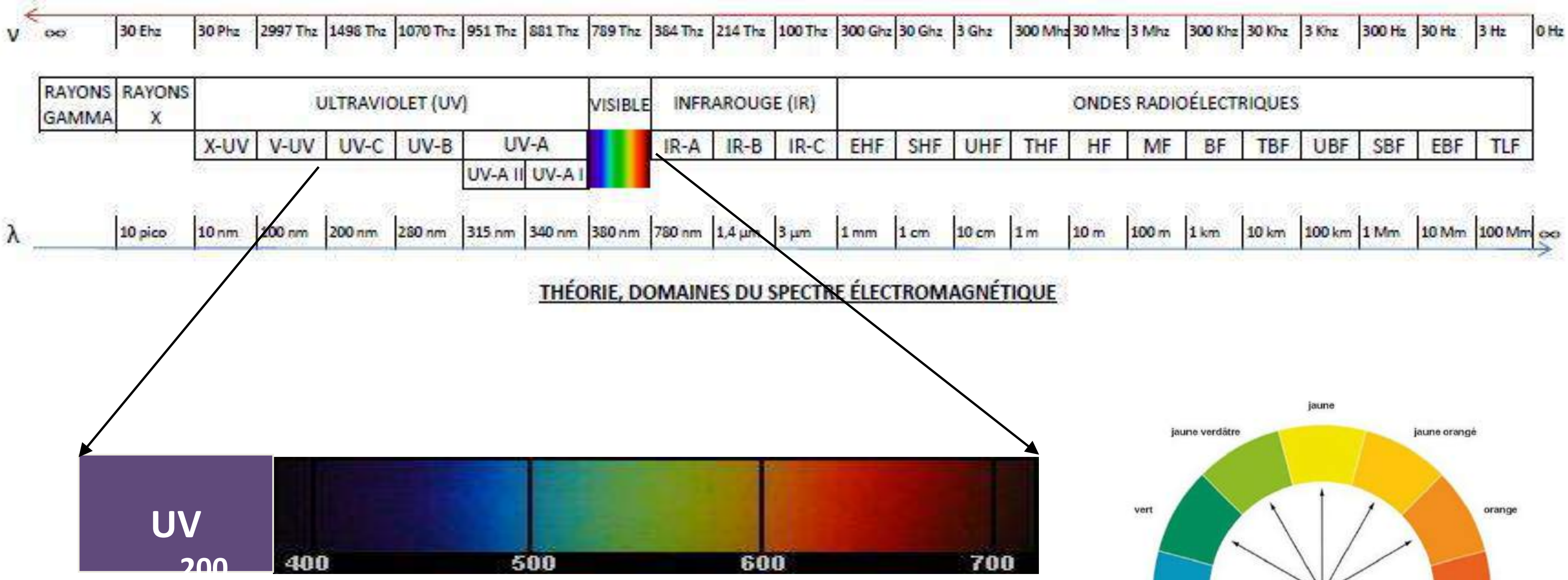
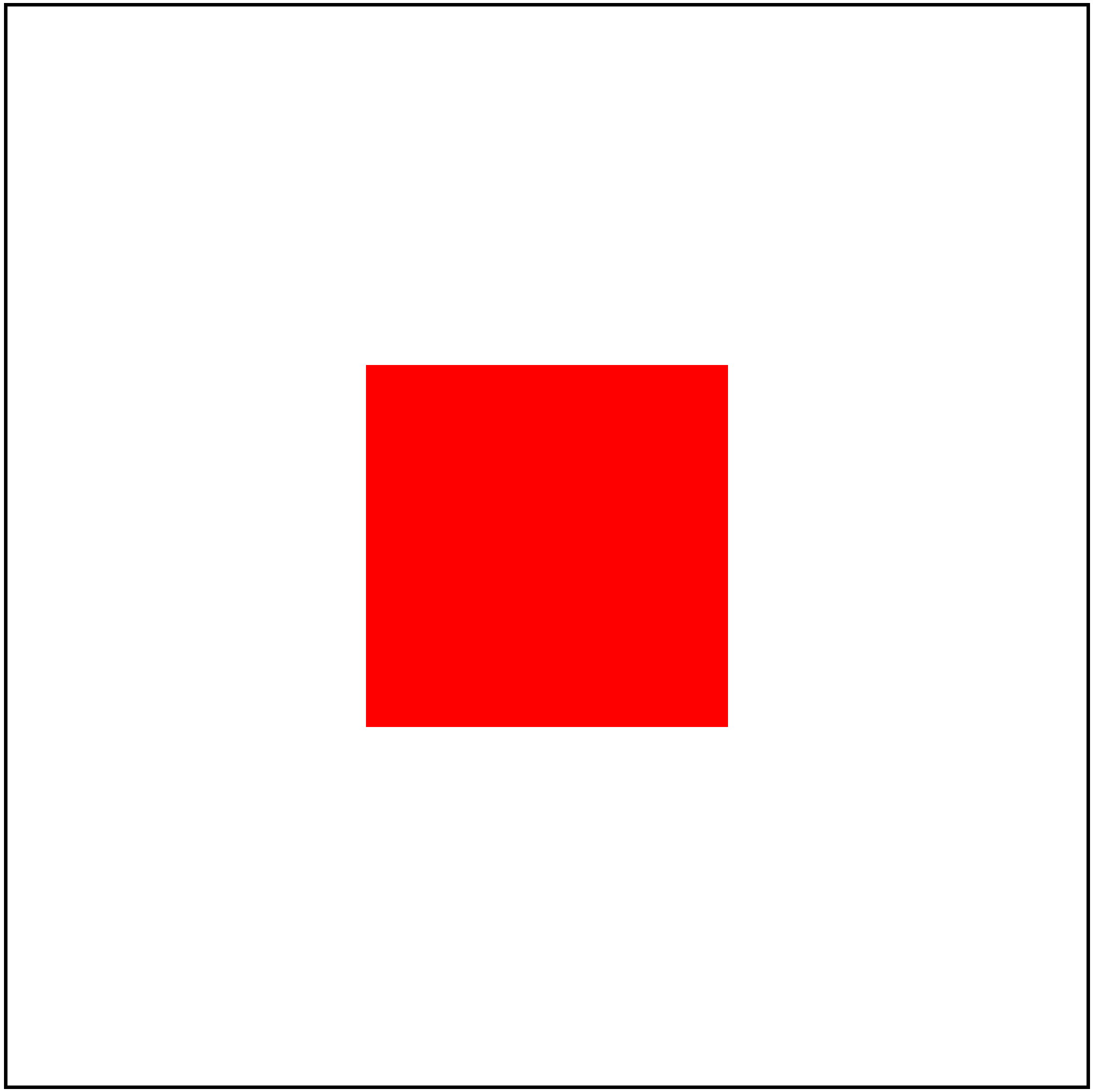
Definition : Spectrometry provides access to the composition of a sample by **measuring light** (absorption or transmission)



THÉORIE, DOMAINES DU SPECTRE ÉLECTROMAGNÉTIQUE



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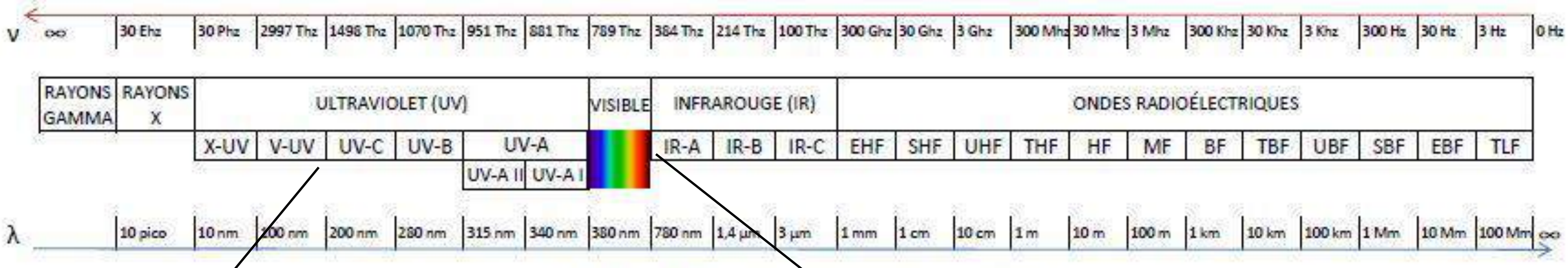

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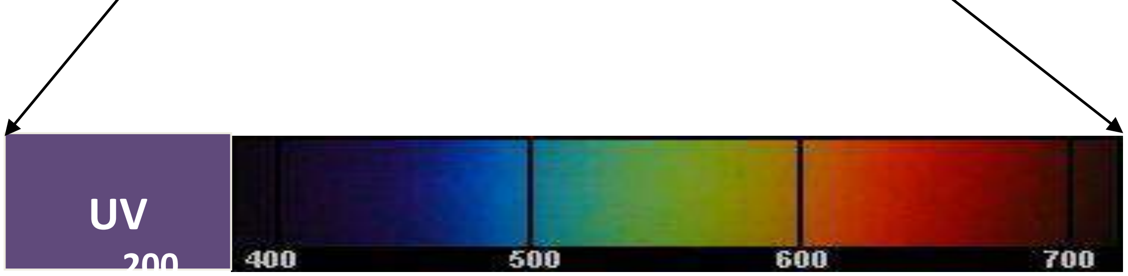

1. General informations on chemical analysis: *Spectrometry Techniques*

- For electromagnetic radiation, we measure:
  - The energy absorbed by an atom or a molecule:
    - UV-Visible Spectrometry
    - Atomic Absorption Spectrometry (AAS)
    - Nuclear magnetic resonance spectroscopy (RMN)
  - The energy emitted by an atom or a molecule
    - Atomic Emission spectrometry (AES)
    - Spetrofluorimetry (Fluorescence spectrometry)
    - Luminescence spectrometry

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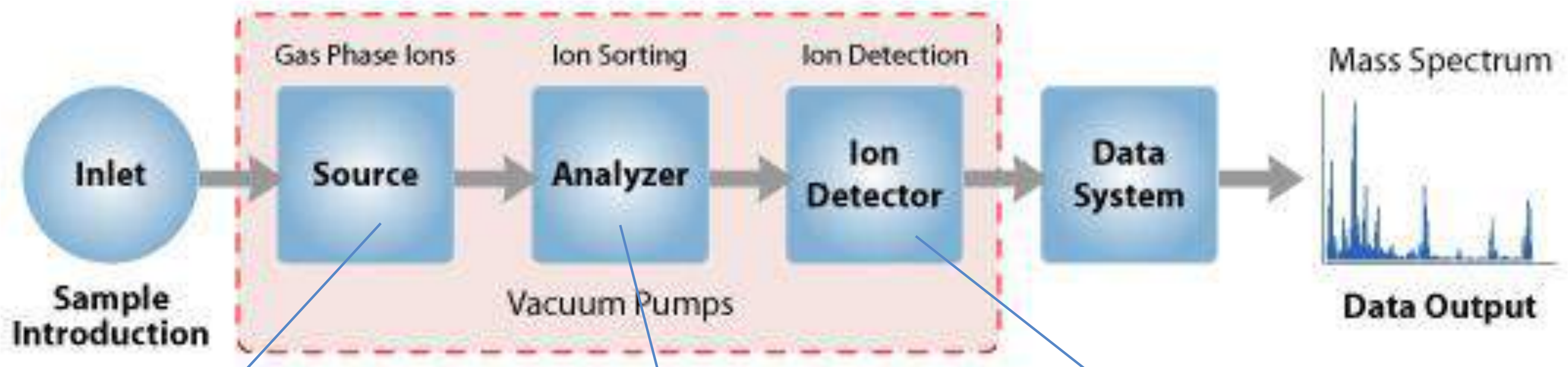
- For ions or ionized molecules, we measure:
  - Their mass-to-charge ratio
    - Mass spectrometry

Mass Spectrometry : Ions Separations

- History:
  - 1898: J. J. Thomson measures the mass-to-charge ratio of electrons. (Nobel prize in 1906)
  - 1912-1960: Analysis of elements (isotopes) and increase of resolving power
  - 1960-1980: Analysis of organic compounds and increase of mass range + increase of resolving power to find the precise mass of ions
  - 1980- : Analysis of organic macromolecules
  - un essor spectaculaire au cours des années 90 avec l’avènement des spectromètres de masse (un développement technologique récompensé par un prix Nobel de chimie, attribué en 2002 à John Fenn et Koichi Tanaka)

Mass Spectrometry : Ions Separations

- The instrument consists of three major components:

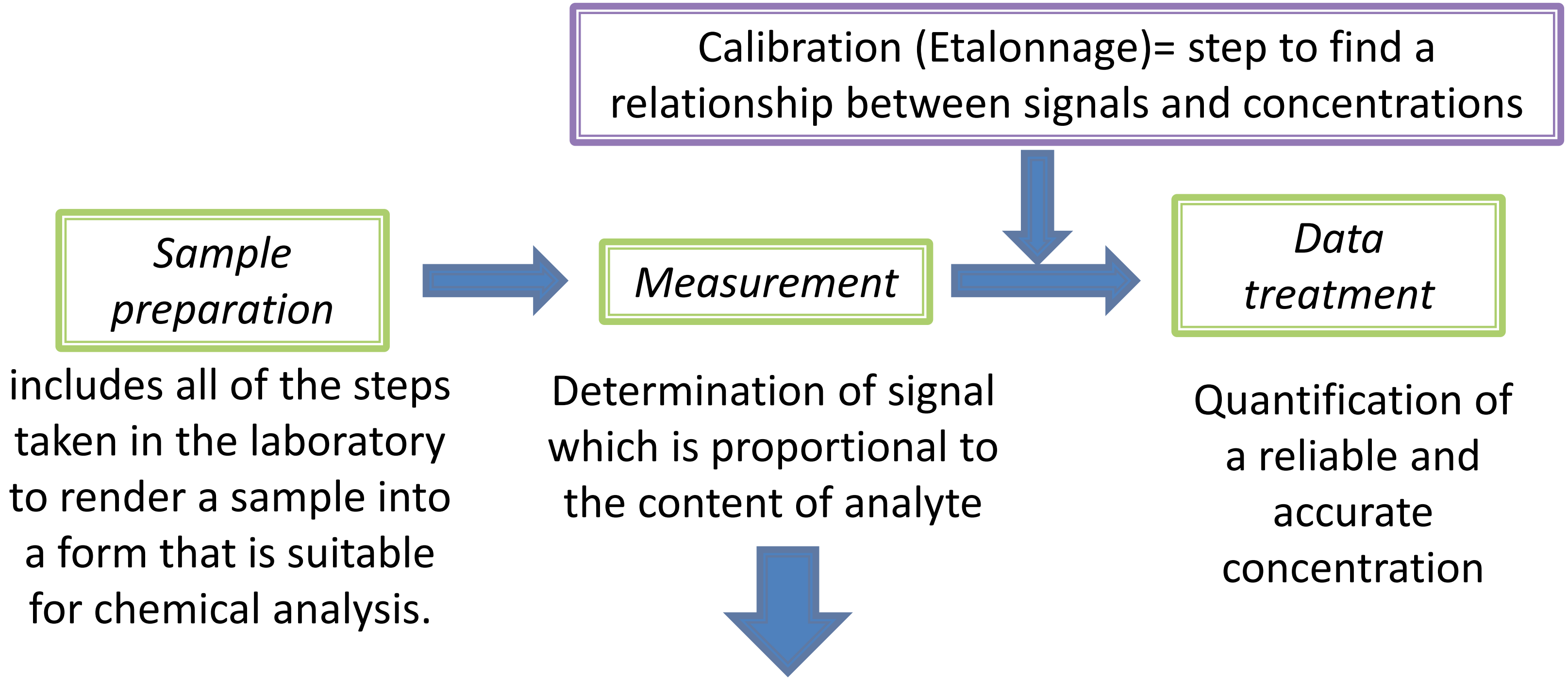


For producing gaseous ions from the matrix

For separating the ions according to their mass-to-charge ratio.

For detecting and counting the ions

1. General informations on chemical analysis: *The different stages of an analysis*



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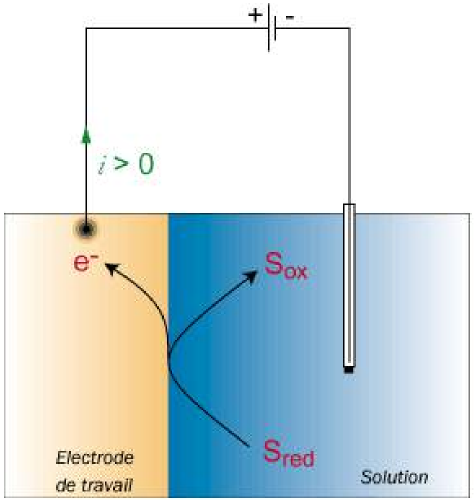
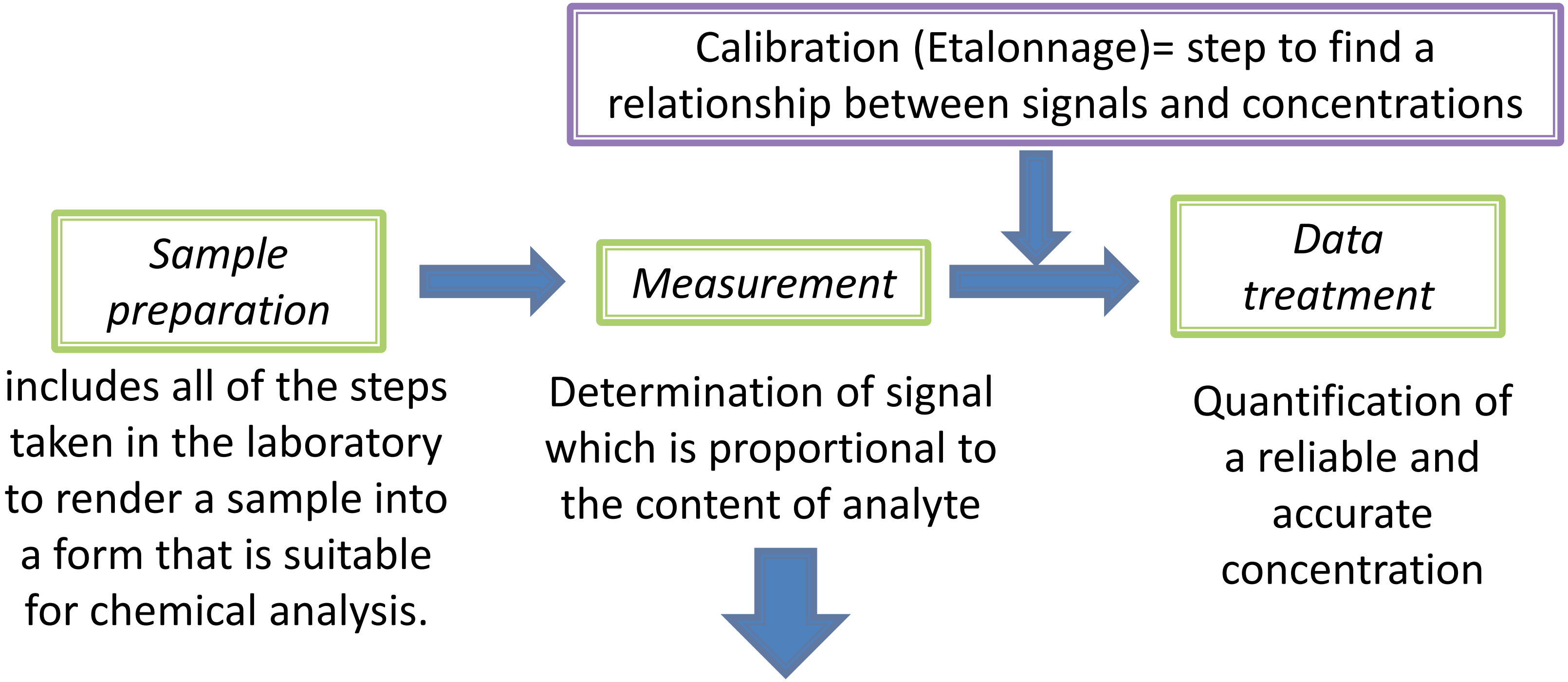
1. General informations on chemical analysis: *Electrochemistry*

Definition : the electrochemical methods give information about the species involved in **an oxidation or reduction reaction**



- In an oxidation or reduction reaction, we measure:
  - Exchange of charges → Coulometry
  - Potential of redox couple→ Potentiometry (pHmetry)
  - Resulting current→ Voltammetry/Polarography

1. General informations on chemical analysis: *The different stages of an analysis*



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1. General informations on chemical analysis
2. **Sample preparation**
3. Metals analysis
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5. Organic pollutants analysis
6. Quality assurance

2. Sample preparation

- In order to adapt the analyte at a concentration appropriate to the method of analysis:
  - Dilution
  - Preconcentration
- In order to isolate it from the other constituents (Purification):
  - Precipitation
  - Extraction
  - Filtration/ultrafiltration/dialyse
- In order to change the matrix:
  - Extraction
  - Mineralisation
- In order to make it detectable (transmitter of a signal) by the method of analysis:
  - Complexation (coloured species)
  - Derivatisation

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- In order to adapt the analyte at a concentration appropriate to the method of analysis:

2.1. Solid matrices: Decomposition into soluble forms

- Mineralisation
- Extraction

2.2 Liquid matrices

- Extraction SPE / Preconcentration
- Derivatisation

  - Complexation (coloured species)
  - **Derivatisation**

2.1. Decomposition into soluble forms:

- **Objective:** To dissolve and homogenize the species to be analysed from a solid matrix
- **Principle:** Method based on:
  - Total digestion of solid matrix → Mineralisation
  - Extraction of analytes in a liquid phase from the solid matrix.

- **Applications:**
  - Analyse des métaux dans des échantillons solides (boues, sols, aérosols): par des méthodes en voie liquide (ICP)
  - Analyse des composés organiques (HAP, pesticides, herbicides) dans des échantillons solides (boues, sols, aérosols) par des méthodes en voie liquide (LC)

2.1.1. Mineralisation

- For **element** analysis
  - If sample is already mineral :
    - Mineralisation= dissolution of mineral matrix
  - If sample is organic or mixt (Case of environmental samples):
    - Mineralisation = decomposition of organic matter in mineral matter
    - Dissolution into soluble forms
    - According the protocol, the two steps are simultaneous or not

2.1.1. Mineralisation

- Two different ways of mineralisation
  - Dry mineralisation (*par voie sèche*):
    - By ashing (calcination)
  - Wet mineralisation (*par voie humide*):
    - by oxidation and hot digestion

- Major heating devices:
  - Oven
  - Block digestion systems
  - Microwave heating
    - Temperature control
    - Pression control

2.1.1. Mineralisation

Dry mineralisation

- Protocol
  - Ashing in several steps:
    1. Drying (103-105°C) to remove water (+ crushing and sieving)
    2. Weighing of dry matter (résidu sec)
    3. Heating at 450-500°C during some hours

    → Yield of Ashes (consisting of carbonates and oxides)
  - Dissolution of ashes in a mixture of acids (e.g. nitric acid, chlorhydric acid..)
- Critical points:
  - Complete decomposition of organic matter but losses by volatilisation (Hg, As, Se, P)

2.1.1. Minéralisation

Wet mineralisation

- Protocol
  - Oxidation/digestion of sample
    1. Drying (103-105°C) to remove water (+ crushing and sieving)
    2. Weighing of dry matter (résidu sec)
    3. Decomposition of matrix with the aid of strong minerals acids/oxidising agents with heating
    4. Evaporation of reactive agents, if necessary
    5. Dilution in adapted solvent for analysis

→ Multitude of procedures (kind and mixture of reactives, temperature, time contact...) depending on the target element and the material analysed.

- Main problem: The mineralisation is sometimes incomplete!

2.1.1. Minéralisation

Wet mineralisation

- Main acids and oxiding agents:
    - H_2O_2: oxidant
    - $HClO_4$, H_2SO_4 /HNO_3: acids with an oxidising effect
    - HF: only acid to digest silicated matrix
    - Aqua regia (*Eau régale*) : 3 HCl/ 1 HNO_3 (méthode normalisée)

- Caution to used materials:
    - Don't use HF with glass, borosilicates or quartz
    - PTFE is the only "plastic" material which can be used with the sulfuric acid (vs polycarbonate, polyethylene, polypropylene..)

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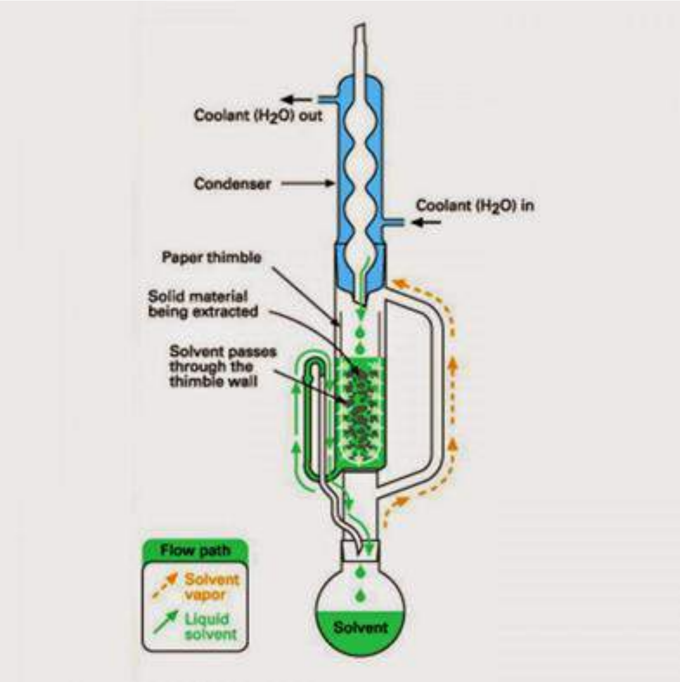
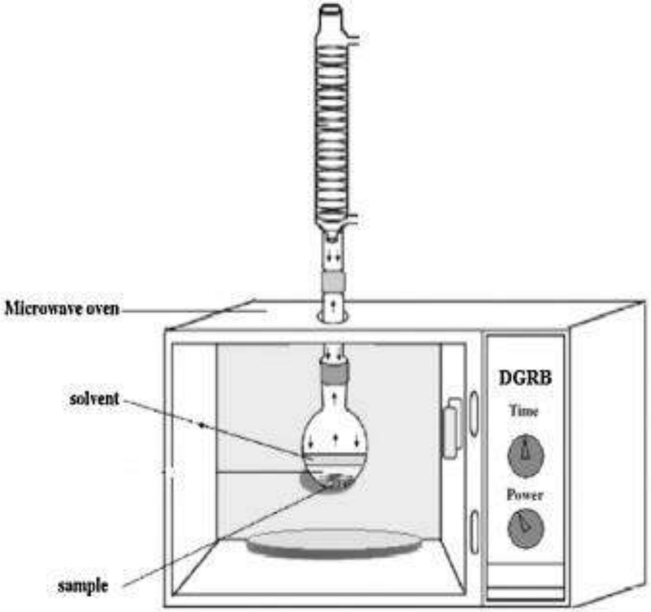
2.1.2. Extraction

- For **molecular** analysis:
  - Two main extraction systems:
    - Soxhlet system
    - Microwave-assisted extraction (MAE)





2.1.2. Extraction

- Protocol:

1. Extraction = sample in organic solvent adapted for solubilisation of target species with heating

2. Purification:
   - → Evaporation of the solvent used for extraction (Rotary evaporator)
   - → Purification on micro-columns (alumina, silica, copper ..) to remove artefacts compounds (e.g. polar / apolar compounds, sulfur species ..) or by chromatography (HPLC)

3. Pre-concentration: Recovery in a lower solvent volume adapted to the analysis method used later

2. Sample preparation

- In order to adapt the analyte at a concentration appropriate to the method of analysis:

2.1. Solid matrices: Decomposition into soluble forms

- Mineralisation
- Extraction

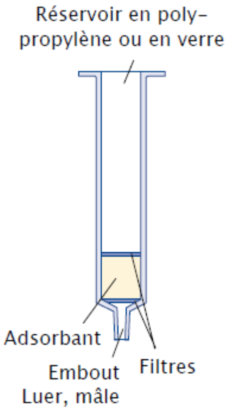
2.2 Liquid matrices

- Extraction SPE / Preconcentration
- Derivatisation

  - Complexation (coloured species)
  - **Derivatisation**

2.2.1. Solid Phase Extraction (SPE)

- **Aim:** To concentrate or isolate from a liquid or gaseous matrix a target specie
- **Principle:** Method based on the adsorption on a solid phase (adsorbent, *adsorbant*) of target compounds present in the sample (liquid or gaseous)
- **Applications:**
  - Analyse des herbicides/pesticides/hydrocarbures/HAP dans les eaux de surface: pour les concentrer avant analyse en HPLC ou LC-MS
  - Analyse des métaux/polluants organiques dans l'eau de mer: pour les isoler de la matrice « salée » (effet de matrice) avant analyse….
  - Analyse des composés organiques volatiles dans l'air : pour les capturer et les concentrer avant analyse



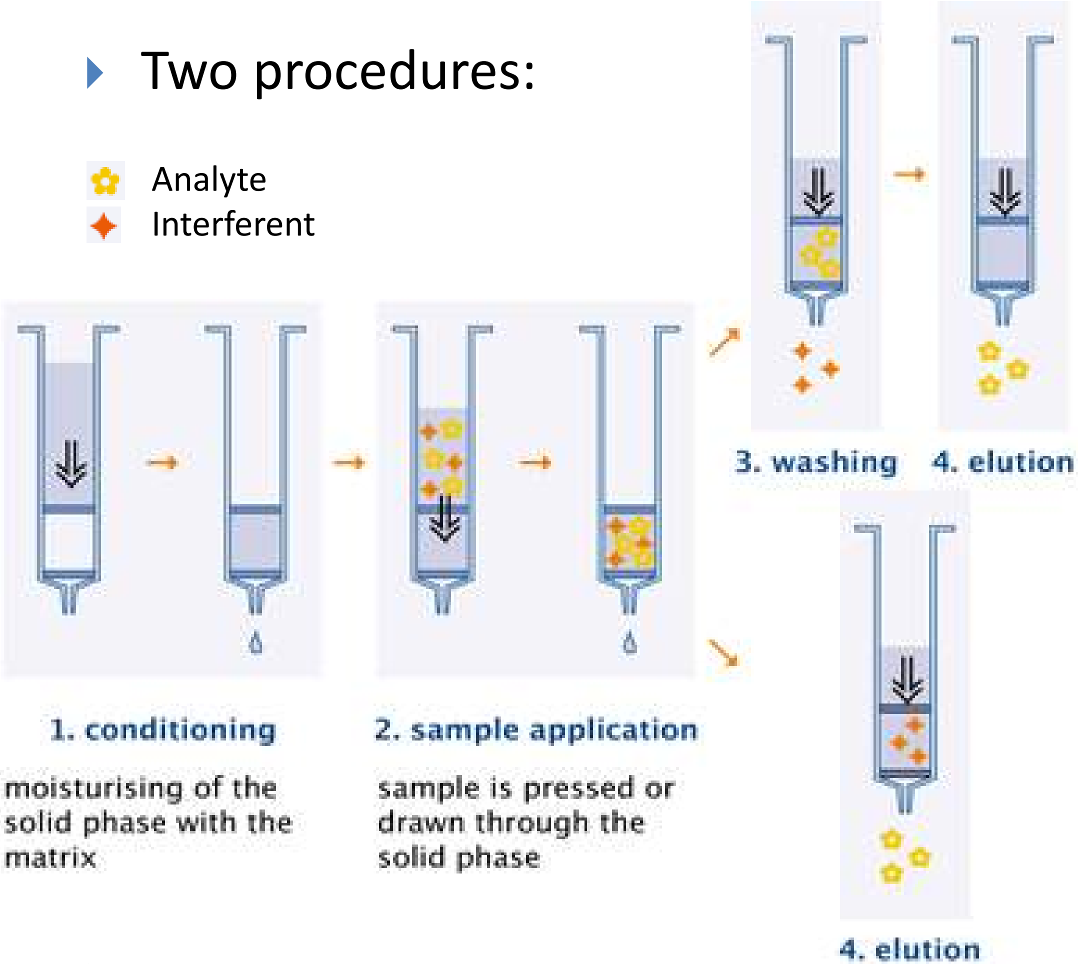
SPE cartridge

Module of SPE

2.2.1. Solid Phase Extraction (SPE)

- Two procedures:

✿ Analyte
✦ Interferent



moisturising of the solid phase with the matrix

sample is pressed or drawn through the solid phase

A. Retention fo analyte

- **Washing:** This step purposes to remove interfering compounds and solvent molecules.
- **Elution**: the analyte is removed from the adsorbent by elution with a suitable solvent

B. Retention of interferents

- **Direct Elution** of analyte molecules which show no interaction with the adsorbent (SPE acts as a filter).

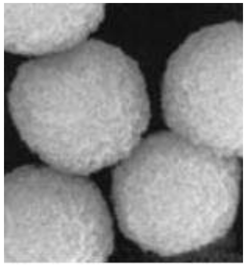
➡ Analyte is isolated
if eluent volume < sample volume → Pre-concentration of the analyte

(ref: Marchery and Nagel guide)

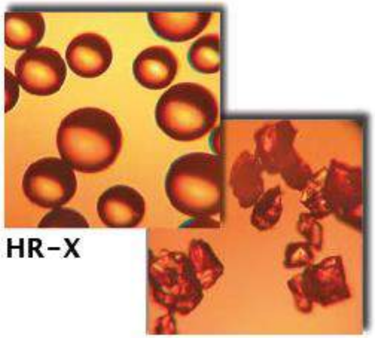
2.2.1. Solid Phase Extraction (SPE) :

Adsorbents

- Adsorbents = selectivity of SPE for target compounds
- Adsorbents = balls of gel to enable percolation.
- Two main types:
  - **Unbonded or bonded silica gel (*Silices vierges ou greffées*** (85% of cases): hard material, stable in almost all organic solvents but low capacity of adsorption
  - **Polymer resins:** low selectivity but high capacity of adsorption (vs silica)→ Amberlite (XAD)
  - **(Carbon nanotubes)**



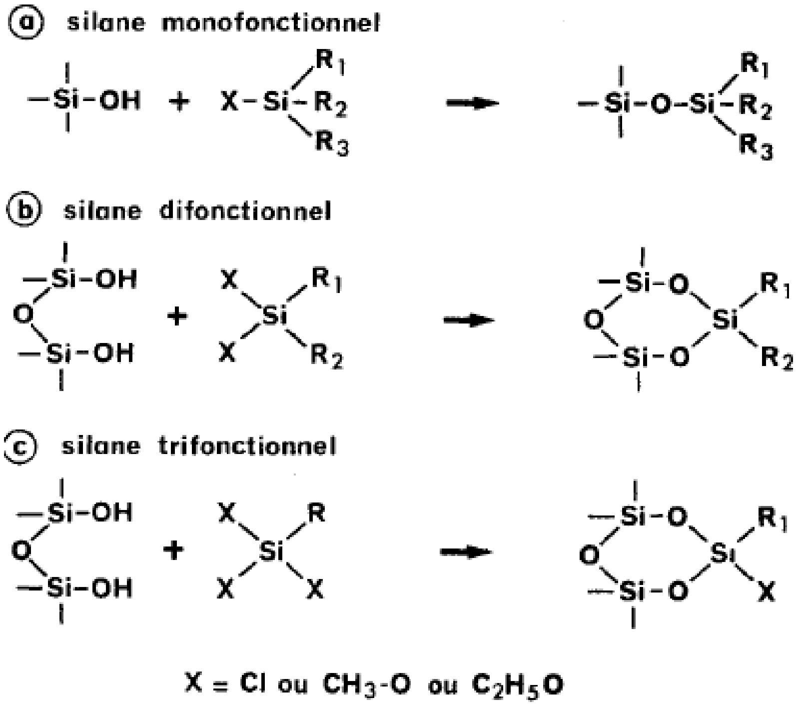
Sicila gel



copolymère PS/DVB conventionnel

2.2.1. Solid Phase Extraction (SPE)

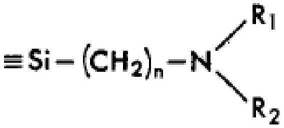
- Case of bonded silica (*silices greffées*):
  - SiOH = silanols group
  - The bonding= **Silanization (silanes = XSiR)**



usual XX- bonded silica

$\equiv Si-C_8H_{17}$ $\equiv Si-C_{18}H_{37}$

octyle octadécyle

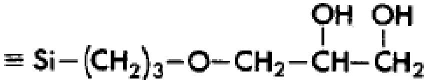


amino

nitro

$\equiv Si-(CH_2)_n-CN$

nitrile



$\equiv Si-(CH_2)_3-O-CH_2-\overset{OH}{CH}-\overset{OH}{CH_2}$

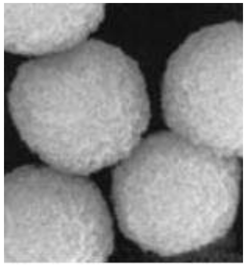
diol

Rq: Instead silica, **Alumina or Florisil (Mg silicate) can be used**

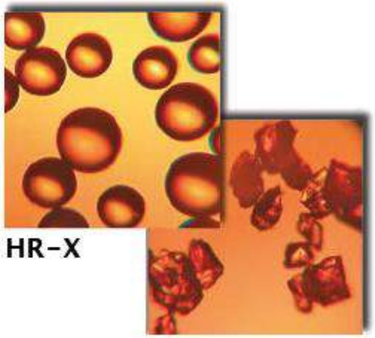
2.2.1. Solid Phase Extraction (SPE) :

Adsorbents

- Adsorbent = selectivity of SPE for target compounds
- Adsorbents = balls of gel to enable percolation.
- Two main types:
  - **Unbonded or bonded silica gel (*Silices vierges ou greffées*** (85% of cases): hard material, stable in almost all organic solvents but low capacity of adsorption
  - **Polymer resins:** low selectivity but high capacity of adsorption (vs silica)→ Amberlite (XAD)
  - **(Carbon nanotubes)**



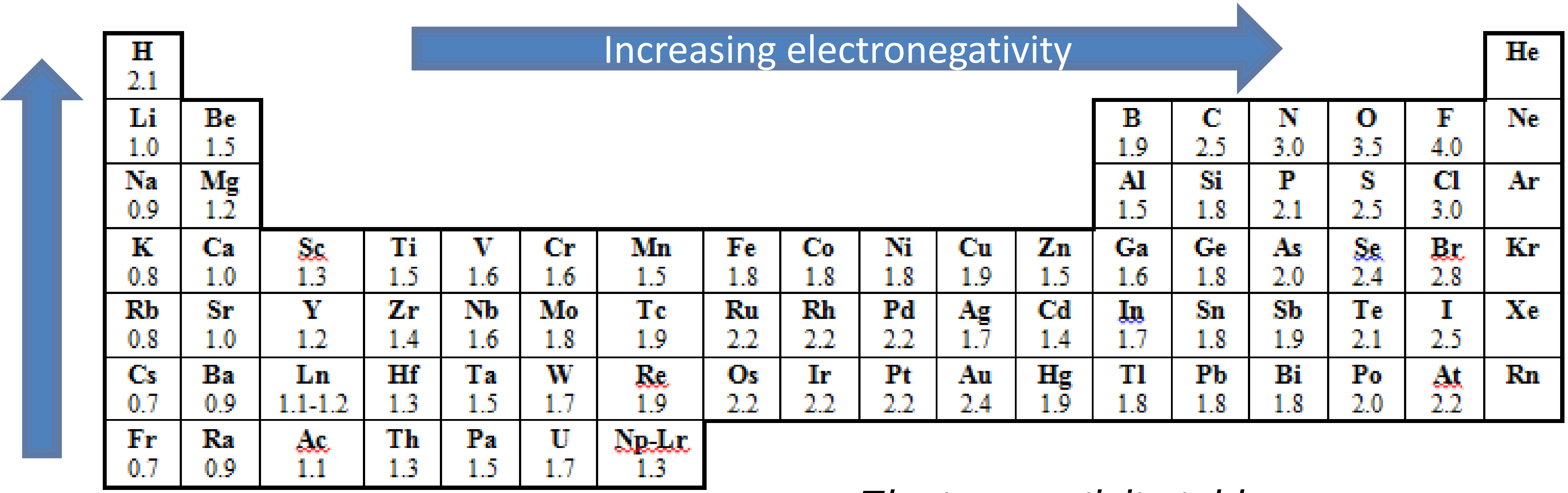
Sicila gel



copolymère PS/DVB
conventionnel

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of polarity or charges
  - Polarity = distribution of electronic charges within a molecule
    - Electronegativity scale:
      - ☐ Decreases when z increases in a same column
      - ☐ Increases when z increases in a same line

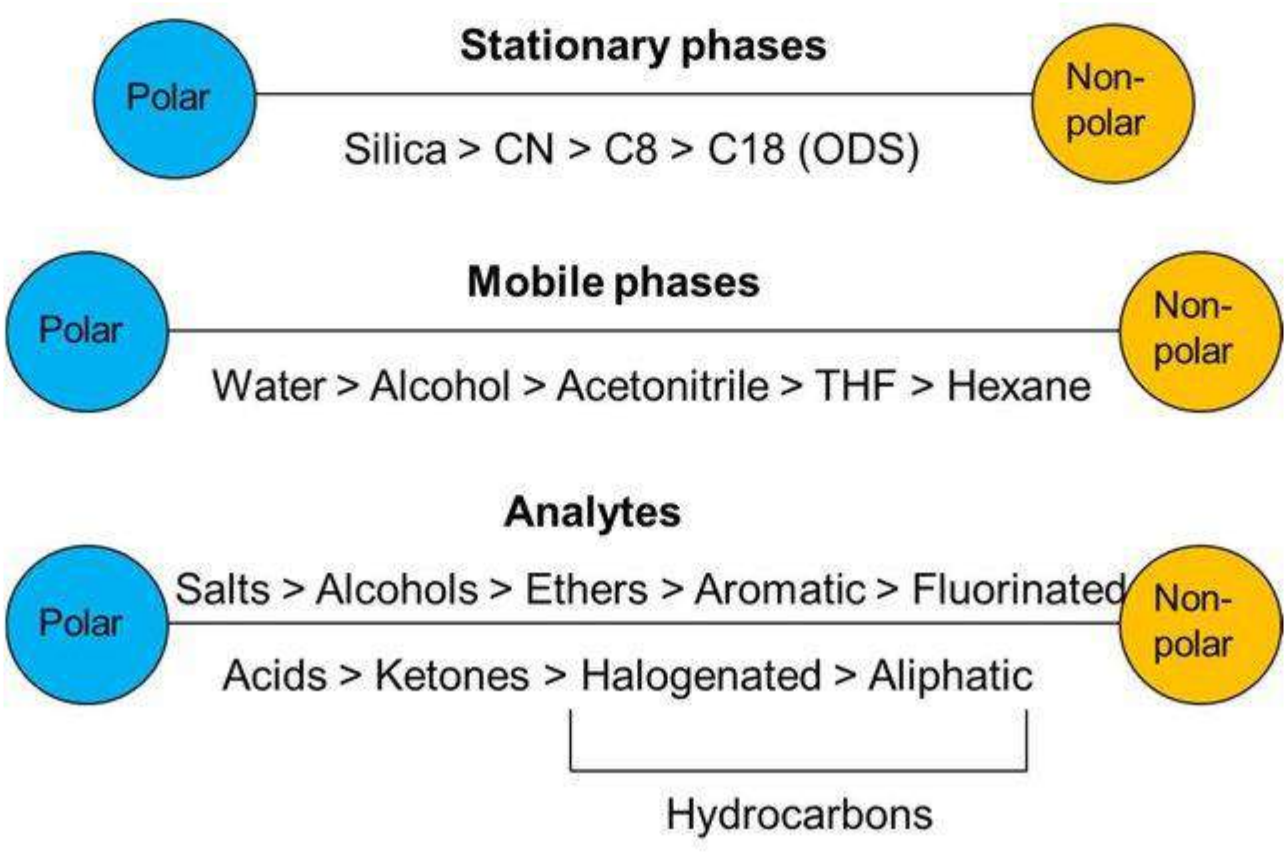


H 2.1																	**He**
Li 1.0	**Be** 1.5											**B** 1.9	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	**Ne**
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	**Ar**
K 0.8	**Ca** 1.0	**Sc** 1.3	**Ti** 1.5	**V** 1.6	**Cr** 1.6	**Mn** 1.5	**Fe** 1.8	**Co** 1.8	**Ni** 1.8	**Cu** 1.9	**Zn** 1.5	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8	**Kr**
Rb 0.8	**Sr** 1.0	**Y** 1.2	**Zr** 1.4	**Nb** 1.6	**Mo** 1.8	**Tc** 1.9	**Ru** 2.2	**Rh** 2.2	**Pd** 2.2	**Ag** 1.7	**Cd** 1.4	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5	**Xe**
Cs 0.7	**Ba** 0.9	**Ln** 1.1-1.2	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.8	**Bi** 1.8	**Po** 2.0	**At** 2.2	**Rn**
Fr 0.7	**Ra** 0.9	**Ac** 1.1	**Th** 1.3	**Pa** 1.5	**U** 1.7	**Np-Lr** 1.3											

Electronegativity table

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of polarity or charges
  - Polarity = distribution of electronic charges within a molecule



Anita Ketola, 2016

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of **polarity or charges.**
- 2 principles of extraction:

Adsorption

⚠ **the polar molecules attract and vice versa!**

Normal

Polar analytes in non-polar matrix + Polar solid phase

Reverse

Non-polar analytes in polar matrix + Non-polar solid phase

Ion Exchange

the inverse charge attract (+/-)

Cation

Analytes with (+) charge in water + solid phase with (-) charge

Anion

Analytes with (-) charge in water + solid phase with (+) charge

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of polarity or charges.
- 2 principles of extraction:

Adsorption

⚠ **the polar molecules attract and vice versa!**

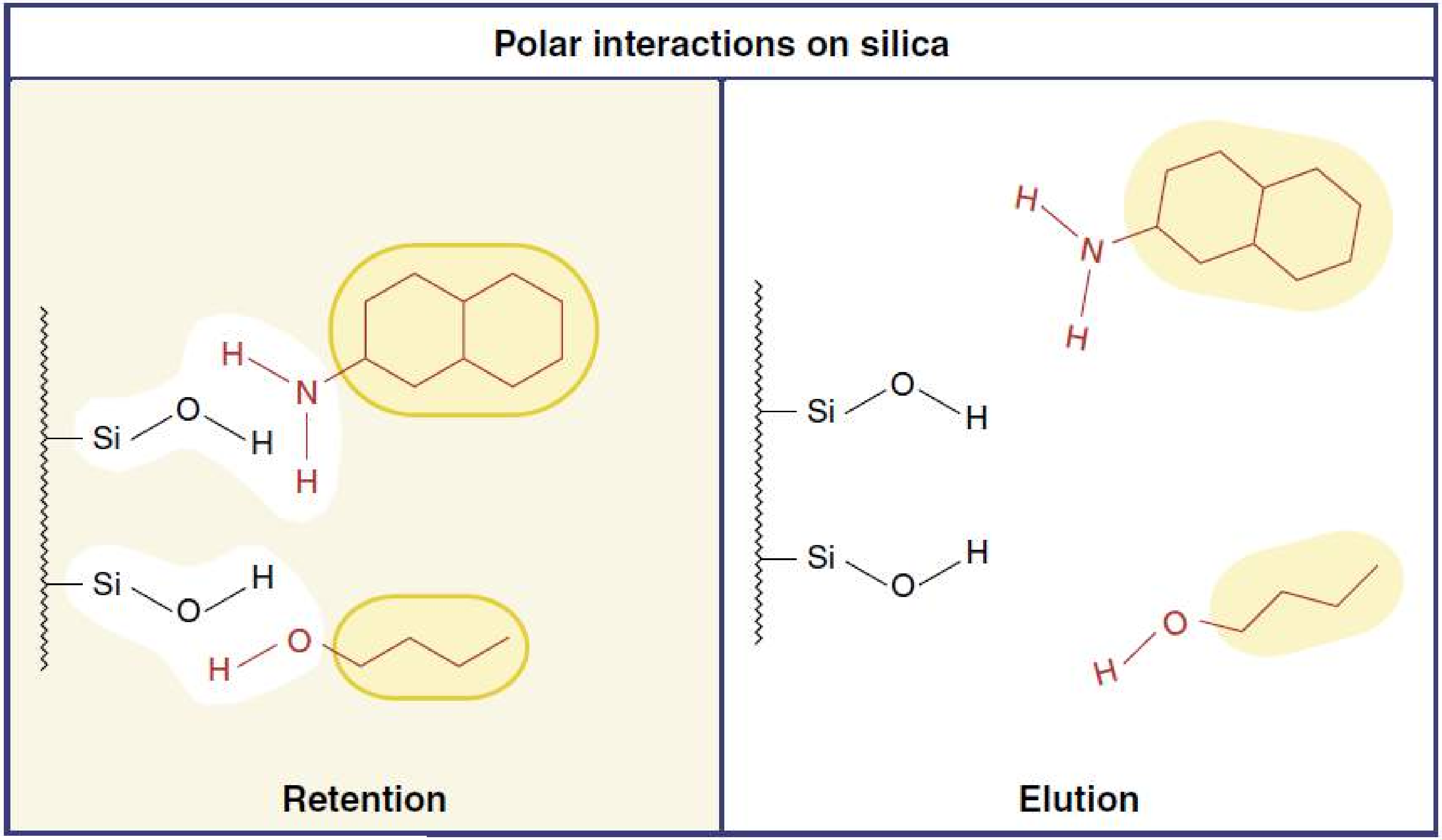
Normal

Polar analytes in non-polar matrix + Polar solid phase

- Normal phase: Typically for high polarity compounds: some pesticides or some PAH
  - Liquid non-polar matrix samples (oils, organic solvents, non-aqueous samples…)
  - Solid phase = polar (bonded Si with –CN, -NH_2 et –diol, non-bonded silica, alumina, florisil)
  - Eluent = polar solvent or more polar solvent than the matrix (e.g. methanol/water, acetonitrile..)

2.2.1. Solid Phase Extraction (SPE) :

Normal phase



🟨 **nonpolar (relative)**

⬜ **polar (relative)**

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of polarity or charges.
- 2 principles of extraction:

Adsorption

⚠ **the polar molecules attract and vice versa!**

Reverse

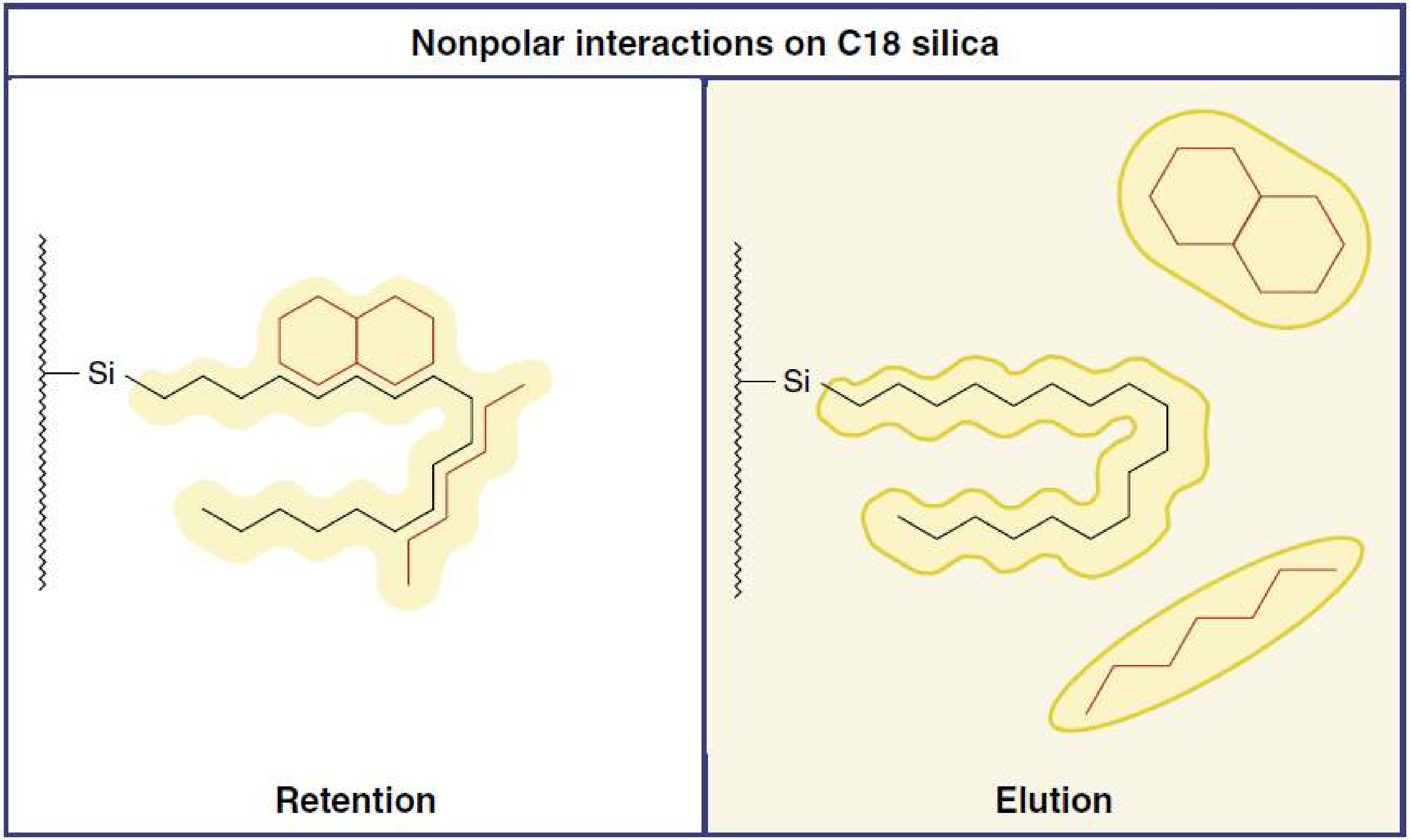
Non-polar analytes in polar matrix + Non-polar solid phase

The most commonly employed!

- Reversed phase: for low polar or non polar compounds: hydrocarbon, some PAH, Pesticides..
  - Typically aqueous matrix
  - Solid phase = non polar (C18, C8, XAD)
  - Eluent = non polar solvent or less polar than water (acetonitrile, dichloromethane..)

2.2.1. Solid Phase Extraction (SPE) :

Reversed phase



🟨 **nonpolar (relative)**

⬜ **polar (relative)**

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of polarity or charges.
- 2 principles of extraction:

Ion Exchange

the inverse charge attract (+/-)

- Extraction of charged compounds: metals, acids, bases, some herbicides..
  - Aqueous samples or liquid organic samples
  - Solid Phase = charged (bonded Si with $–SO_3^-$ and $–N^+(CH_3)_3$)
  - Eluent = aqueous solution with various pH or containing a more selective counter-ion to compete for ion-exchange binding sites

Cation

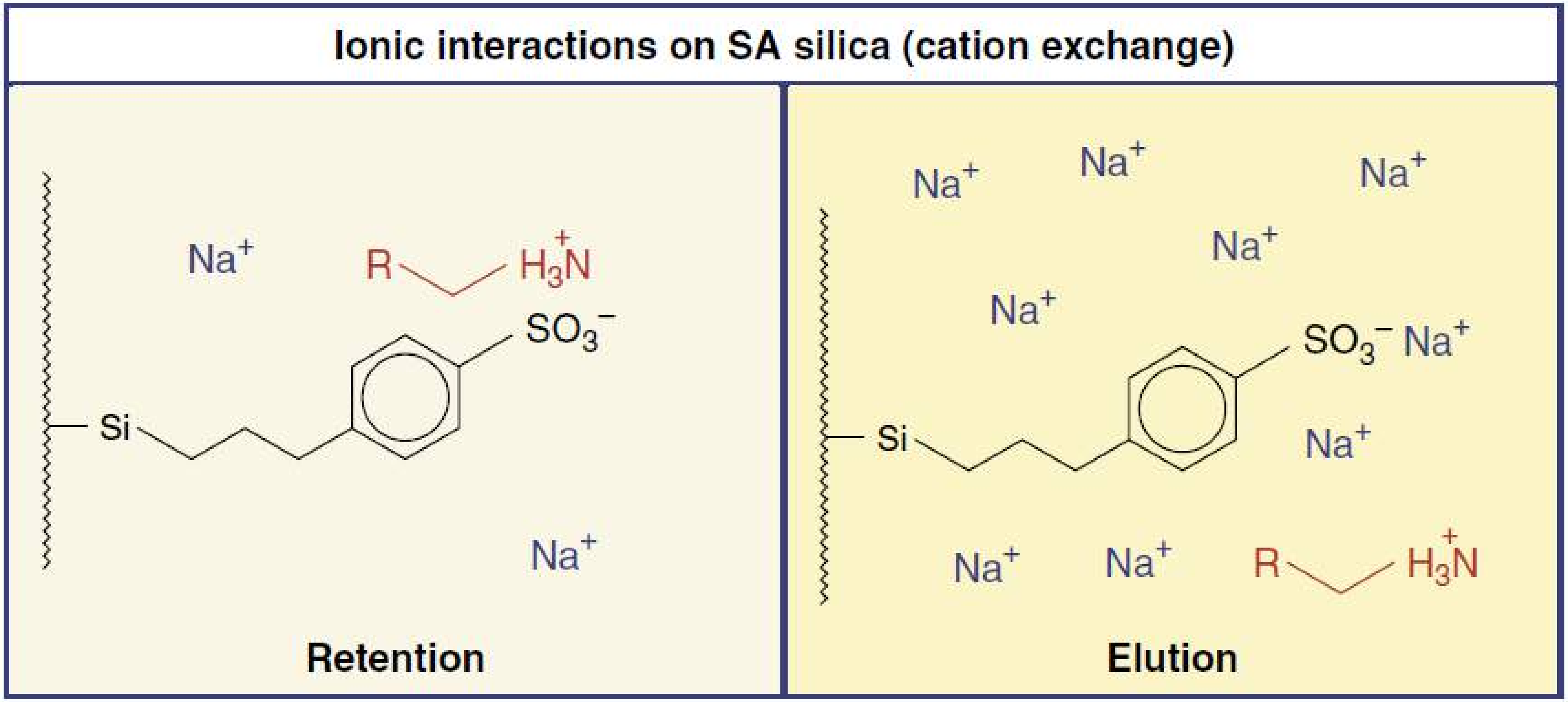
Analytes with (+) charge in water + solid phase with (-) charge

Anion

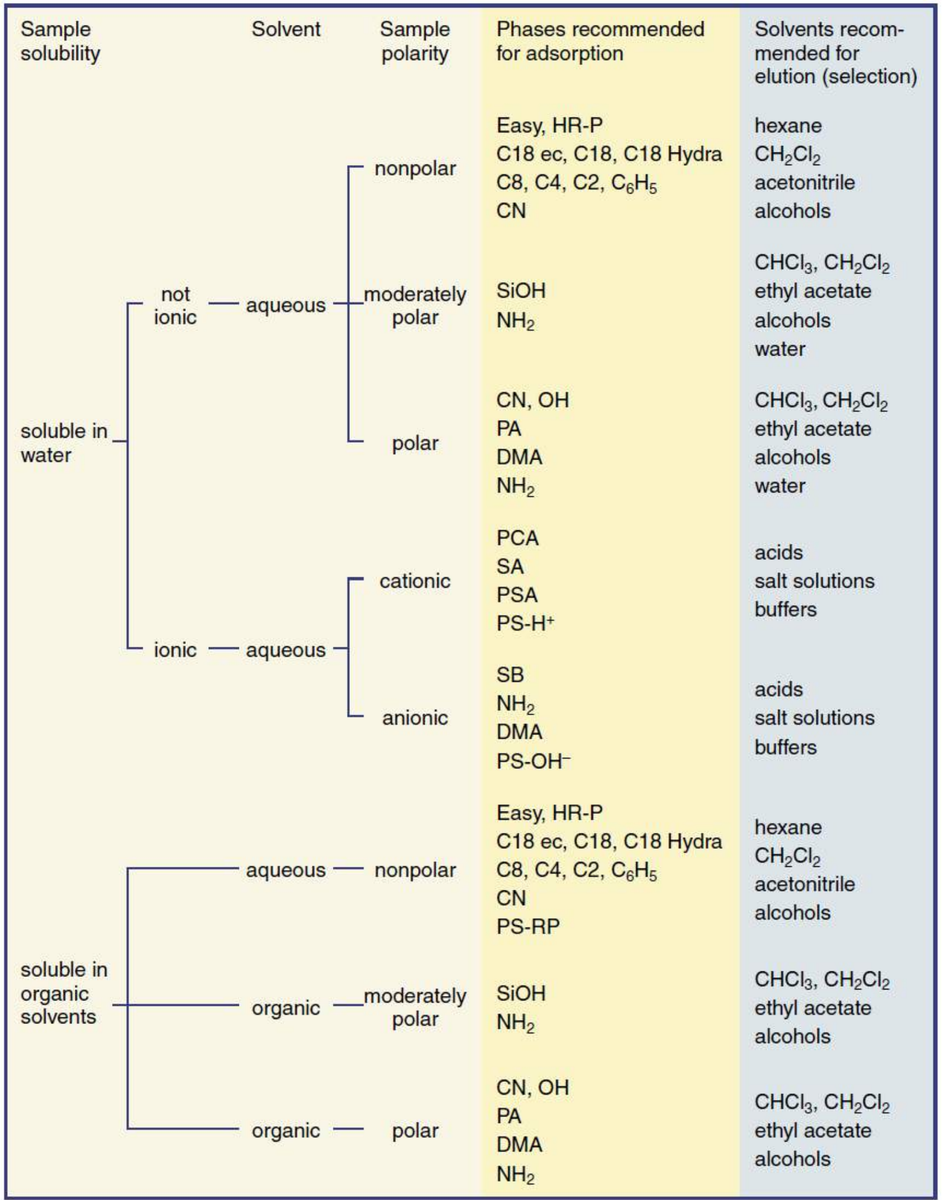
Analytes with (-) charge in water + solid phase with (+) charge

2.2.1. Solid Phase Extraction (SPE) :

Ion Exchange



2.2.1. Solid Phase Extraction (SPE) :



Sample solubility		Solvent	Sample polarity	Phases recommended for adsorption	Solvents recommended for elution (selection)
soluble in water	not ionic	aqueous	nonpolar	Easy, HR-P C18 ec, C18, C18 Hydra C8, C4, C2, C_6H_5 CN	hexane CH_2Cl_2 acetonitrile alcohols
			moderately polar	SiOH NH_2	$CHCl_3$, CH_2Cl_2 ethyl acetate alcohols water
			polar	CN, OH PA DMA NH_2	$CHCl_3$, CH_2Cl_2 ethyl acetate alcohols water
	ionic	aqueous	cationic	PCA SA PSA PS-H^+	acids salt solutions buffers
			anionic	SB NH_2 DMA PS-OH^-	acids salt solutions buffers
soluble in organic solvents		aqueous	nonpolar	Easy, HR-P C18 ec, C18, C18 Hydra C8, C4, C2, C_6H_5 CN PS-RP	hexane CH_2Cl_2 acetonitrile alcohols
		organic	moderately polar	SiOH NH_2	$CHCl_3$, CH_2Cl_2 ethyl acetate alcohols
		organic	polar	CN, OH PA DMA NH_2	$CHCl_3$, CH_2Cl_2 ethyl acetate alcohols

2.2.1. Solid Phase Extraction (SPE) :

- SPE extraction is essentially based on the notions of polarity or charges.
- 2 principle

Similar principles for separation in the column of Chromatography

Adsor

change

⚠ **the polar**
attract and

charge attract
+/-)

Normal

Polar

matrix +
Polar solid
phase

Reverse

Non-polar

Non-polar
solid
phase

Liquid Chromatography and gasesous chromatography

Cation

Analytes

solid phase
with (-)
charge

Anion

Analytes

solid phase
with (+)
charge

Ion chromatography

2. Sample preparation

- In order to adapt the analyte at a concentration appropriate to the method of analysis:

2.1. Solid matrices: Decomposition into soluble forms

- Mineralisation
- Extraction

2.2 Liquid matrices

- Extraction SPE / Preconcentration
- Derivatisation

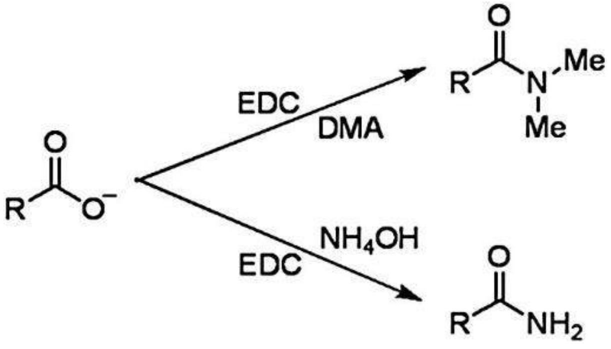
  - Complexation (coloured species)
  - **Derivatisation**

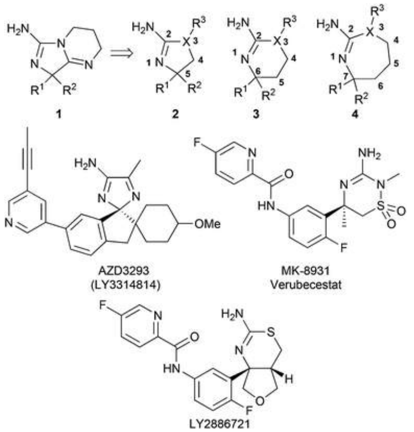
2.2.2 Derivatisation

- **Objective:** to render detectable by spectrometry a specie in a liquid (gaseous) matrix (absorbing or coloured) or to modify the volatility of species for GC analysis

- **Principle:** method based on the complexation of the species to be analyzed in order to make it absorbing radiation or to change temperature of ebullition

- **Applications:**
  - Analysis of carbonyl species by HPLC in aqueous matrices or after extraction in the liquid phase





Course Outline

1. General informations on chemical analysis
2. Sample preparation
3. **Metals analysis**
4. Soluble inorganic pollutants analysis
5. Organic pollutants analysis
6. Quality assurance

3. Metals analysis

- Heavy metals or other metals
  - = trace metals (Ag, Cd, Cr, Cu, Pb, Hg, Ni ..) + non-metallic elements (As, Se ..), which are classified as hazardous substances

  - Often oligo-elements but toxic for high doses (Cu, Ni,..) or only toxic (Pb, Cd, Sb..)
    - Toxicity depend on chemical forms :
      - Hexavalent chromium : Cr^{6+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, CrO_3, ...
      - Mercury: Hg^0, Hg_2Cl_2, $(CH_3)_2Hg$…
    - Labile fraction = Bioavailable fraction

  - Ubiquitous in different environments: soil, water, air (particles)
    - Problem of accumulation
  - Sources: fossil fuel combustion + power and incineration plant + mining industries

3. Metals analysis:

- **But**: heavy and trace metals analysis
- **Techniques applicable to liquid and solid phases (after dissolution):**
  - Atomic Absoprtion Spectrometry
  - Atomic Emission Spectrometry
  - Mass Spectrometry

In coupling with plasma technology:
ICP-AES et ICP-MS

- **Techniques applicable to soild phases**:
  - X-ray Spectrometry

3.1. Elemental analysis: ICP methods

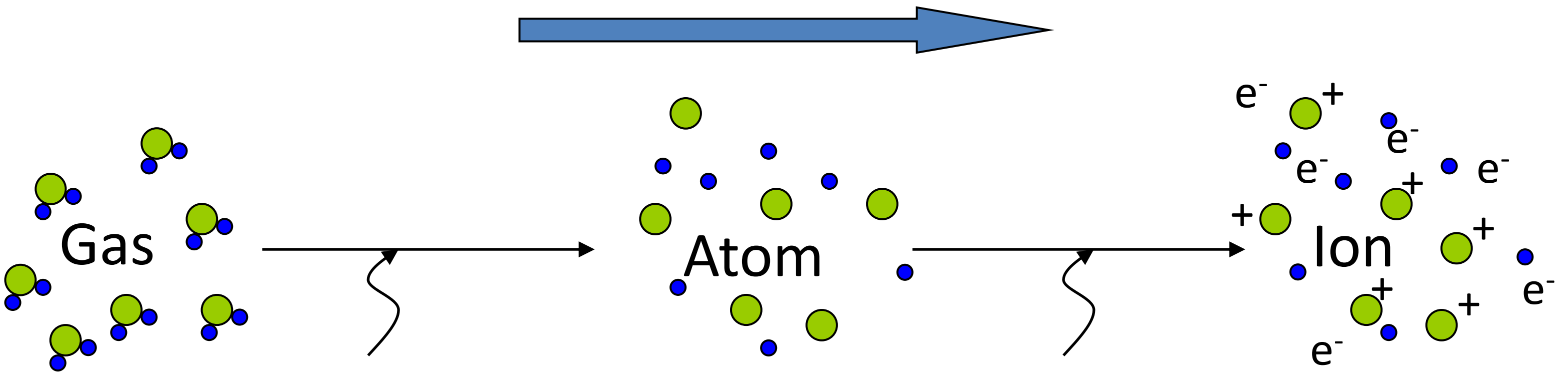
- **ICP:** Inductively Coupled Plasma
  - Techniques based on plasma technology
  - aim: Atomisation of all the molecules which are in the sample
  - Principle: Detection of atoms thanks to spectrometry methods

- **ICP-AES: ICP-Atomic Emission Spectrometry**
  - Coupling with Atomic Emission Spectrometry

- **ICP-MS: ICP-Mass Spectrometry**
  - Coupling with Mass Spectrometry

3.1. What is a plasma?

- Formation:



Heating

Atomisation energy

(2 -6 eV)

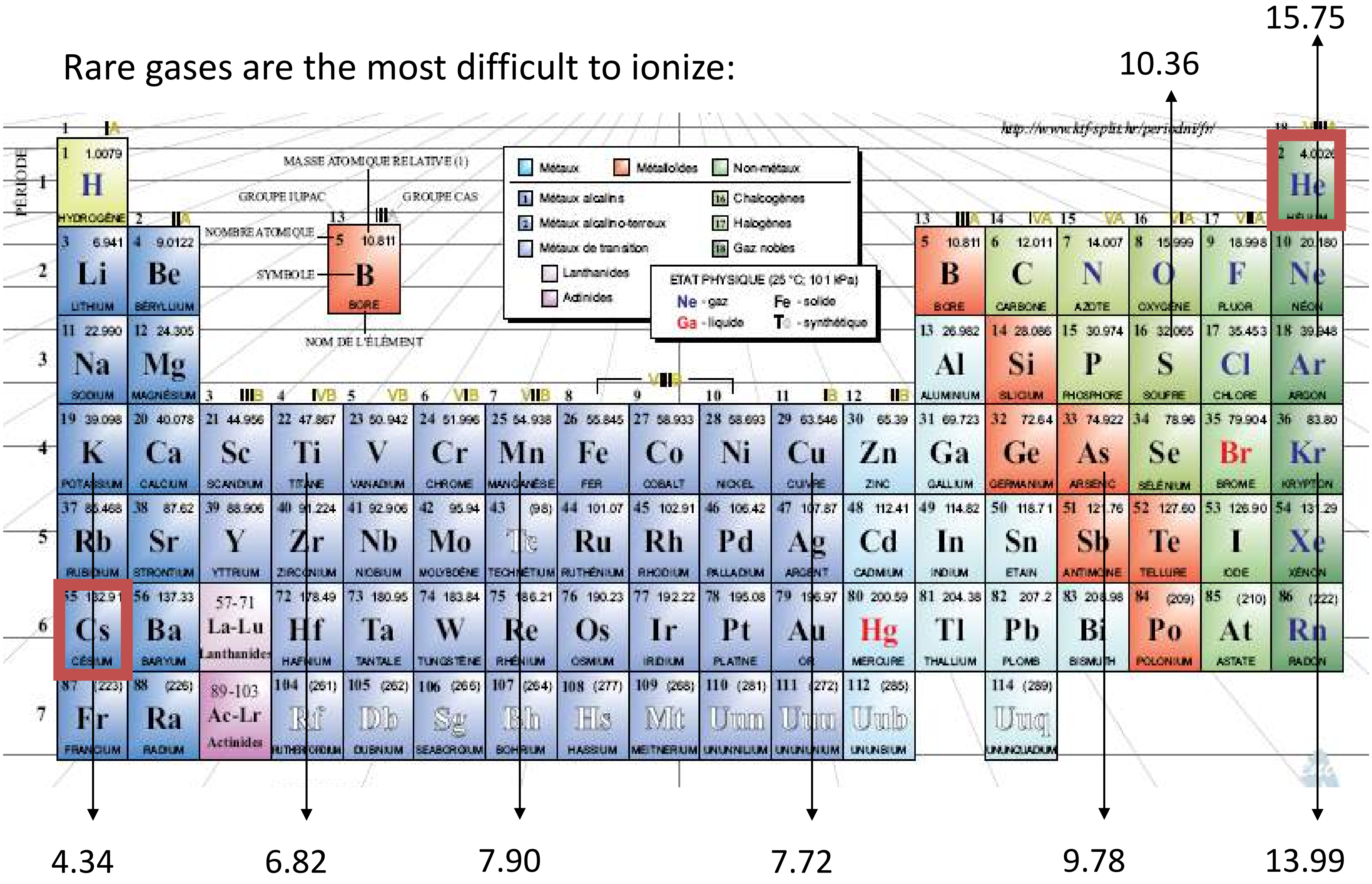
Ionisation energy

(4 -24 eV)

Hot ionized gas with equal numbers of positively charged ions and negatively charged electrons.

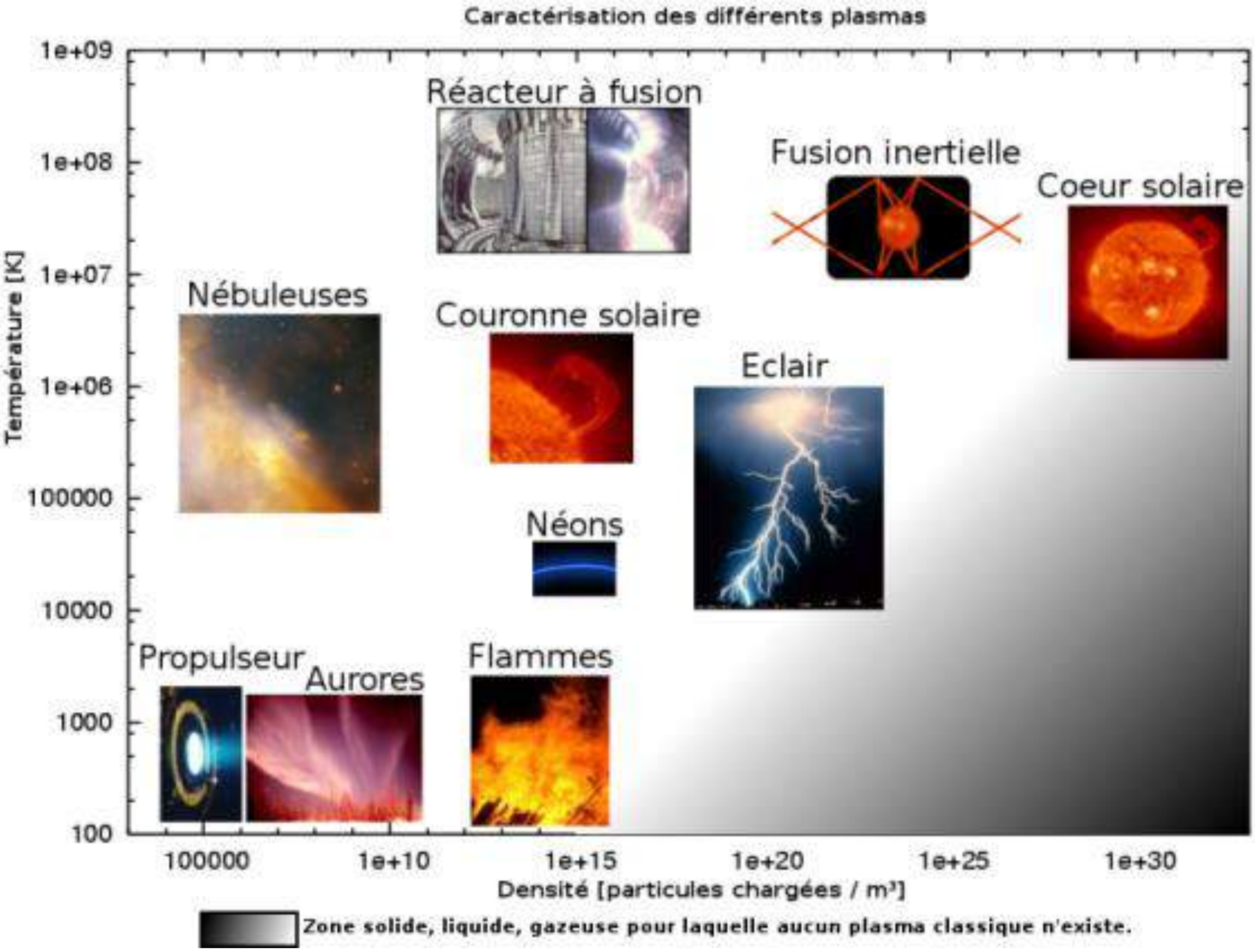
3.1. Ionisation energy (eV)

Rare gases are the most difficult to ionize:



3.1. Practically…

- Ignition temperature depends on the gas to ionize :
    - 4 000 K for the element which are easy to ionize (Cs)
    - 20 000K for the elements which are hardly to ionize (He, rare gases..)
- In practice, ignition is done by electric discharge or laser
- Plasma exists over a wide range of temperature or density


Caractérisation des différents plasmas
Température [K]
1e+09
1e+08
1e+07
1e+06
100000
10000
1000
100
100000
1e+10
1e+15
1e+20
1e+25
1e+30
Densité [particules chargées / m³]
Réacteur à fusion
Fusion inertielle
Coeur solaire
Nébuleuses
Couronne solaire
Eclair
Néons
Propulseur
Aurores
Flammes
Zone solide, liquide, gazeuse pour laquelle aucun plasma classique n'existe.

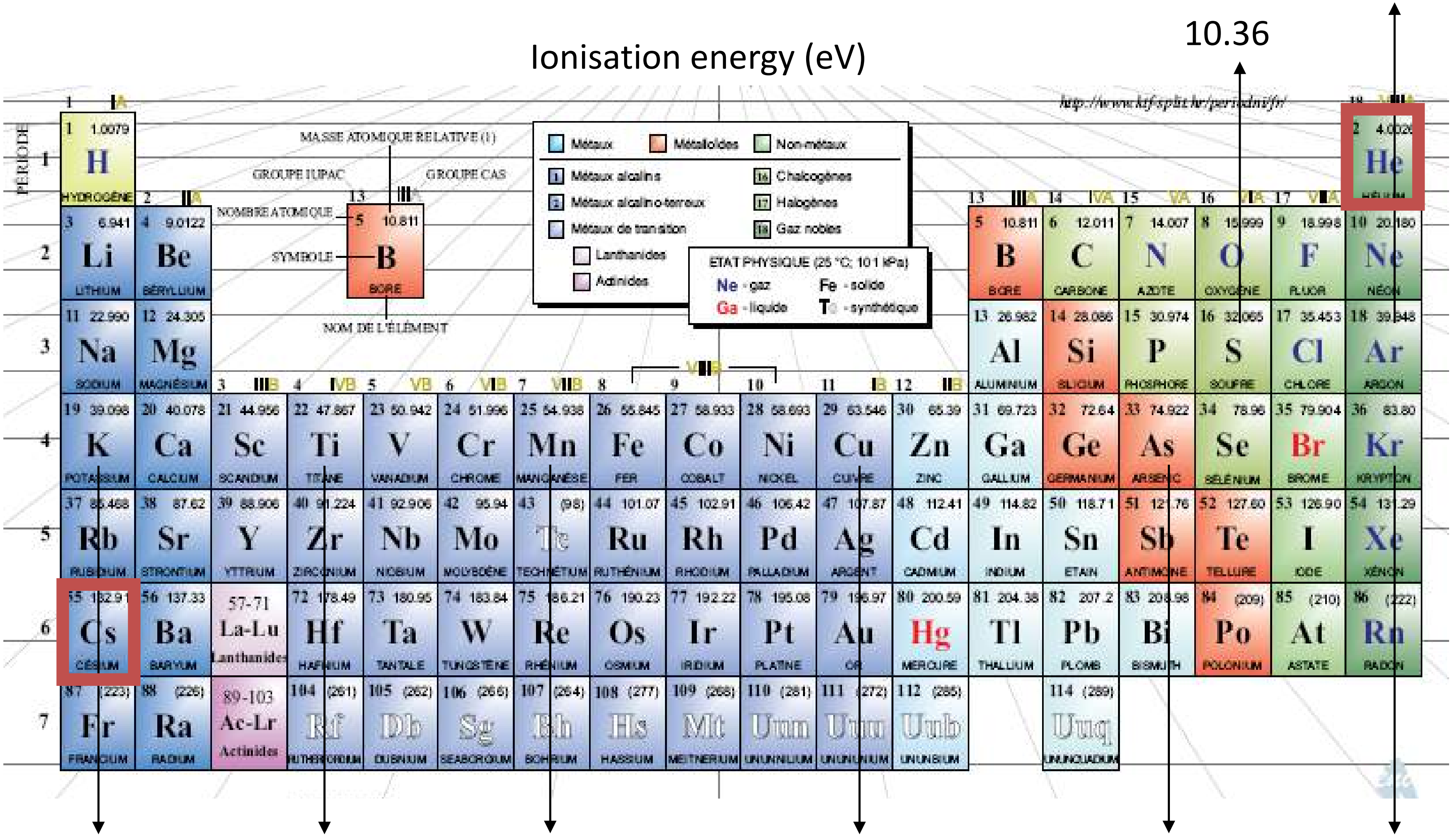
3.1. Application in Analytical Chemistry

- Ver hot source
  - Higher temperature than that produced by flames or electric discharges (arc / spark), therefore more efficient for atomisation

Method	Temperature (°C)
Flame	1700-3150
Electrothermy	2200-3000
Plasma	6500-10000
Electrique Arc	4000-5000

3.1. Practically: *Which gas?*

Ionisation energy (eV)



15.75

10.36

4.34

6.82

7.90

7.72

9.78

13.99

http://www.ktf-split.hr/periodni/fr/

MASSE ATOMIQUE RELATIVE (1)

GROUPE IUPAC

GROUPE CAS

NOMBRE ATOMIQUE

SYMBOLE

NOM DE L'ÉLÉMENT

13 IIIA — 5 10.811 B BORE

- ☐ Métaux
- ☐ Métalloïdes
- ☐ Non-métaux
- 1 Métaux alcalins
- 2 Métaux alcalino-terreux
- ☐ Métaux de transition
  - ☐ Lanthanides
  - ☐ Actinides
- 16 Chalcogènes
- 17 Halogènes
- 18 Gaz nobles

ETAT PHYSIQUE (25 °C; 101 kPa)

Ne - gaz
Fe - solide
Ga - liquide
Tc - synthétique

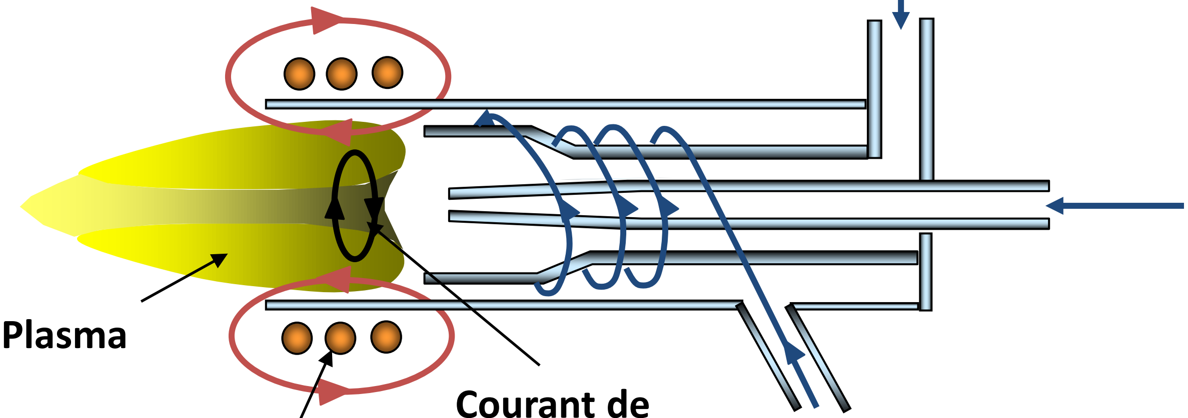
PÉRIODE	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGÈNE																	2 4.0026 He HÉLIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BÉRYLLIUM											5 10.811 B BORE	6 12.011 C CARBONE	7 14.007 N AZOTE	8 15.999 O OXYGÈNE	9 18.998 F FLUOR	10 20.180 Ne NÉON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNÉSIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICIUM	15 30.974 P PHOSPHORE	16 32.065 S SOUFRE	17 35.453 Cl CHLORE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANE	23 50.942 V VANADIUM	24 51.996 Cr CHROME	25 54.938 Mn MANGANÈSE	26 55.845 Fe FER	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu CUIVRE	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SÉLÉNIUM	35 79.904 Br BROME	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDÈNE	43 (98) Tc TECHNÉTIUM	44 101.07 Ru RUTHÉNIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag ARGENT	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn ETAIN	51 121.76 Sb ANTIMOINE	52 127.60 Te TELLURE	53 126.90 I IODE	54 131.29 Xe XÉNON
6	55 132.91 Cs CÉSIUM	56 137.33 Ba BARYUM	57-71 La-Lu Lanthanides	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALE	74 183.84 W TUNGSTÈNE	75 186.21 Re RHÉNIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINE	79 196.97 Au OR	80 200.59 Hg MERCURE	81 204.38 Tl THALLIUM	82 207.2 Pb PLOMB	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinides	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

3.1. Practically: *Which gas?*

- Argon is the most used gas for plasmas in analytical chemistry because
  - Ionisation energy ~16 eV : rare gases are used because the most difficult to ionize so plasma with a very high temperature

    Temperatures around 10000 K
  - Ar rare gas the most abundant in the Earth's atmosphere… He : OK, but expensive
  - Monoatomic Rare gas : Simple emission spectra, does not recombine with the chemical species in a stable way
  - Disadvantage: poor thermal conductivity therefore unstable
    - Need to disturb as little as possible if you want to have repeatable conditions, including temperature

3.1. Practically: *Which gas?*



Champ Magnétique

Argon auxiliaire

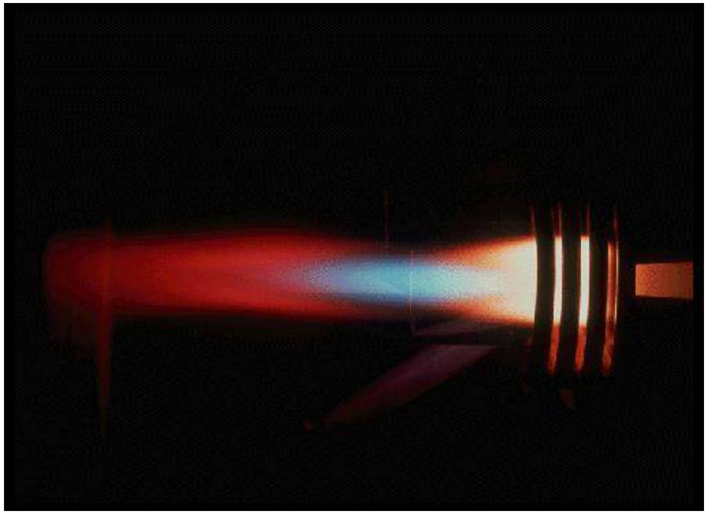
Introduction de l'échantillon

Plasma

Courant de Foucault

Argon pour le plasma

Bobine RF

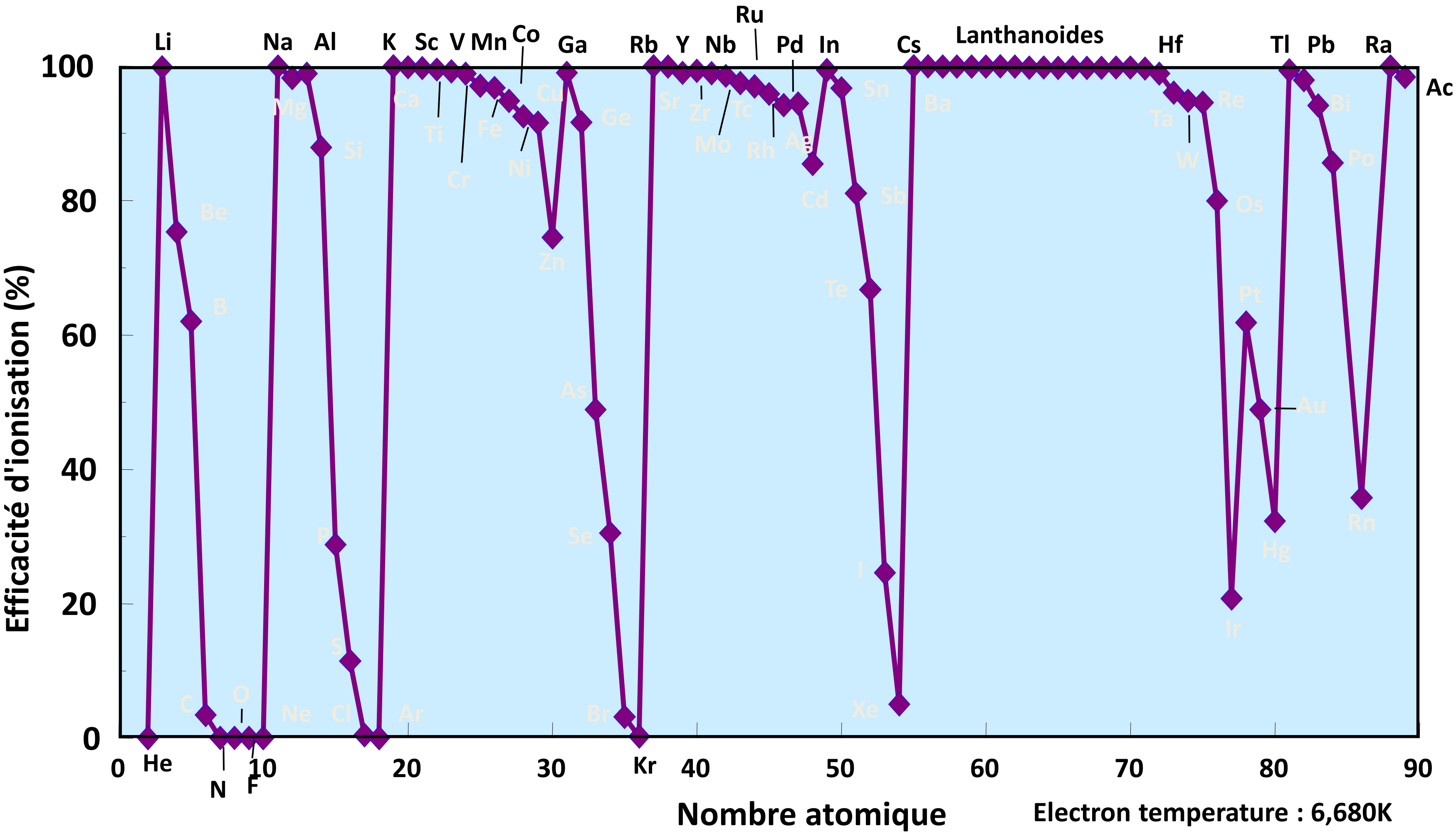


3.1. Application in Analytical Chemistry

- Ver hot source
  - Higher temperature than that produced by flames or electric discharges (arc / spark), therefore more efficient for atomization

- So very energy source:
  - it is easy to reach the heats of atomization of molecules and the energy of ionization and excitation of atoms

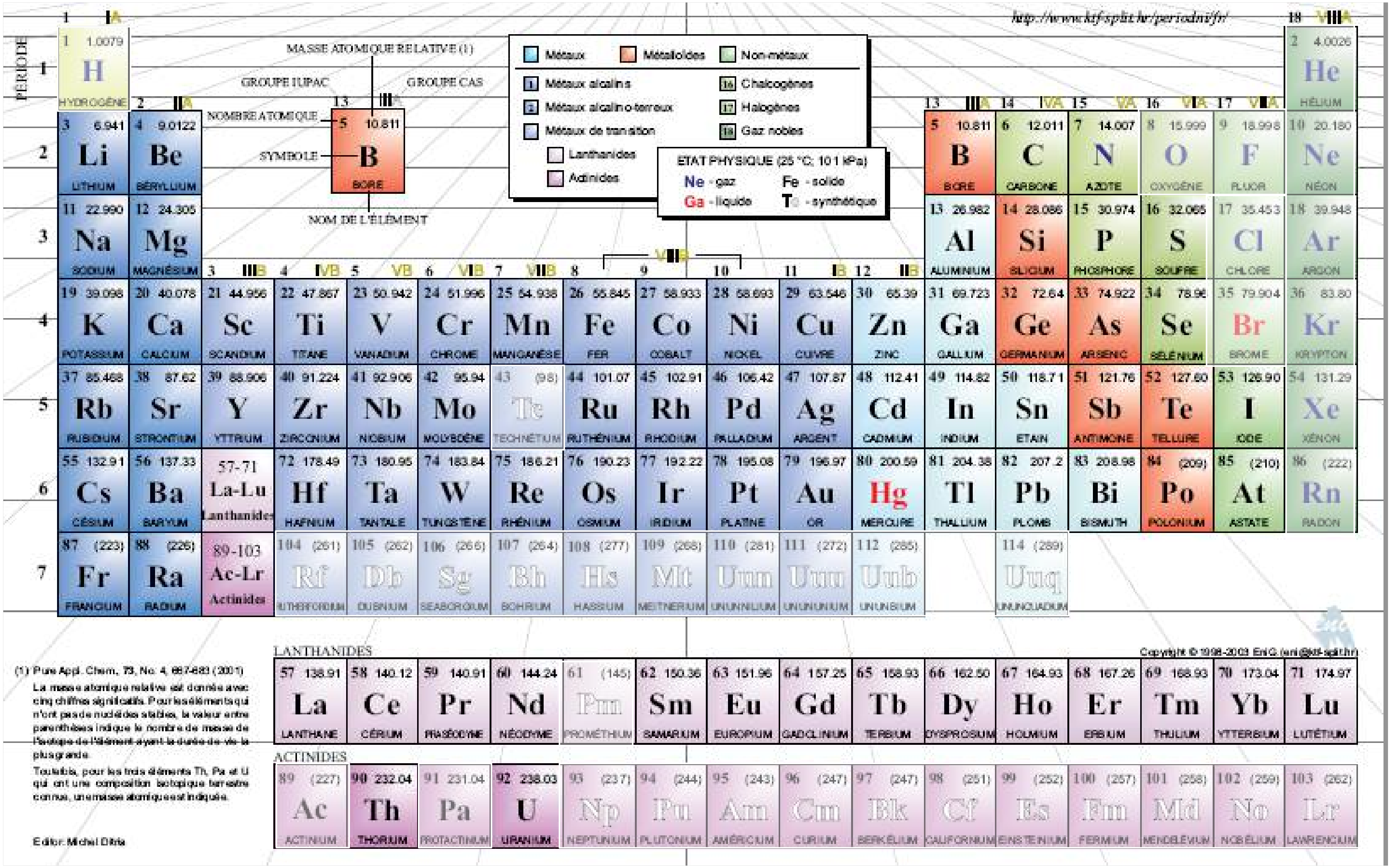
Ionsation energy for Argon plasma



Electron temperature : 6,680K

Electron density : 1.47^{14} x 10 cm^{-1}

Elements peu ou pas ionisables en plasma d'Ar



http://www.ktf-split.hr/periodni/fr/

MASSE ATOMIQUE RELATIVE (1)
GROUPE IUPAC
GROUPE CAS
NOMBRE ATOMIQUE
SYMBOLE
NOM DE L'ÉLÉMENT

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🟥 Métalloïdes
🟩 Non-métaux
1 Métaux alcalins
2 Métaux alcalino-terreux
☐ Métaux de transition
☐ Lanthanides
☐ Actinides
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17 Halogènes
18 Gaz nobles

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3	11 22.990 Na SODIUM	12 24.305 Mg MAGNÉSIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICIUM	15 30.974 P PHOSPHORE	16 32.065 S SOUFRE	17 35.453 Cl CHLORE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANE	23 50.942 V VANADIUM	24 51.996 Cr CHROME	25 54.938 Mn MANGANÈSE	26 55.845 Fe FER	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu CUIVRE	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SÉLÉNIUM	35 79.904 Br BROME	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDÈNE	43 (98) Tc TECHNÉTIUM	44 101.07 Ru RUTHÉNIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag ARGENT	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn ÉTAIN	51 121.76 Sb ANTIMOINE	52 127.60 Te TELLURE	53 126.90 I IODE	54 131.29 Xe XÉNON
6	55 132.91 Cs CÉSIUM	56 137.33 Ba BARYUM	57-71 La-Lu Lanthanides	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALE	74 183.84 W TUNGSTÈNE	75 186.21 Re RHÉNIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINE	79 196.97 Au OR	80 200.59 Hg MERCURE	81 204.38 Tl THALLIUM	82 207.2 Pb PLOMB	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinides	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDES

57 138.91 La LANTHANE	58 140.12 Ce CÉRIUM	59 140.91 Pr PRASÉODYME	60 144.24 Nd NÉODYME	61 (145) Pm PROMÉTHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTÉTIUM

ACTINIDES

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMÉRICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKÉLIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDÉLÉVIUM	102 (259) No NOBÉLIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
La masse atomique relative est donnée avec cinq chiffres significatifs. Pour les éléments qui n'ont pas de nucléides stables, la valeur entre parenthèses indique le nombre de masse de l'isotope de l'élément ayant la durée de vie la plus grande.
Toutefois, pour les trois éléments Th, Pa et U qui ont une composition isotopique terrestre connue, une masse atomique est indiquée.

Editor: Michel Ditria

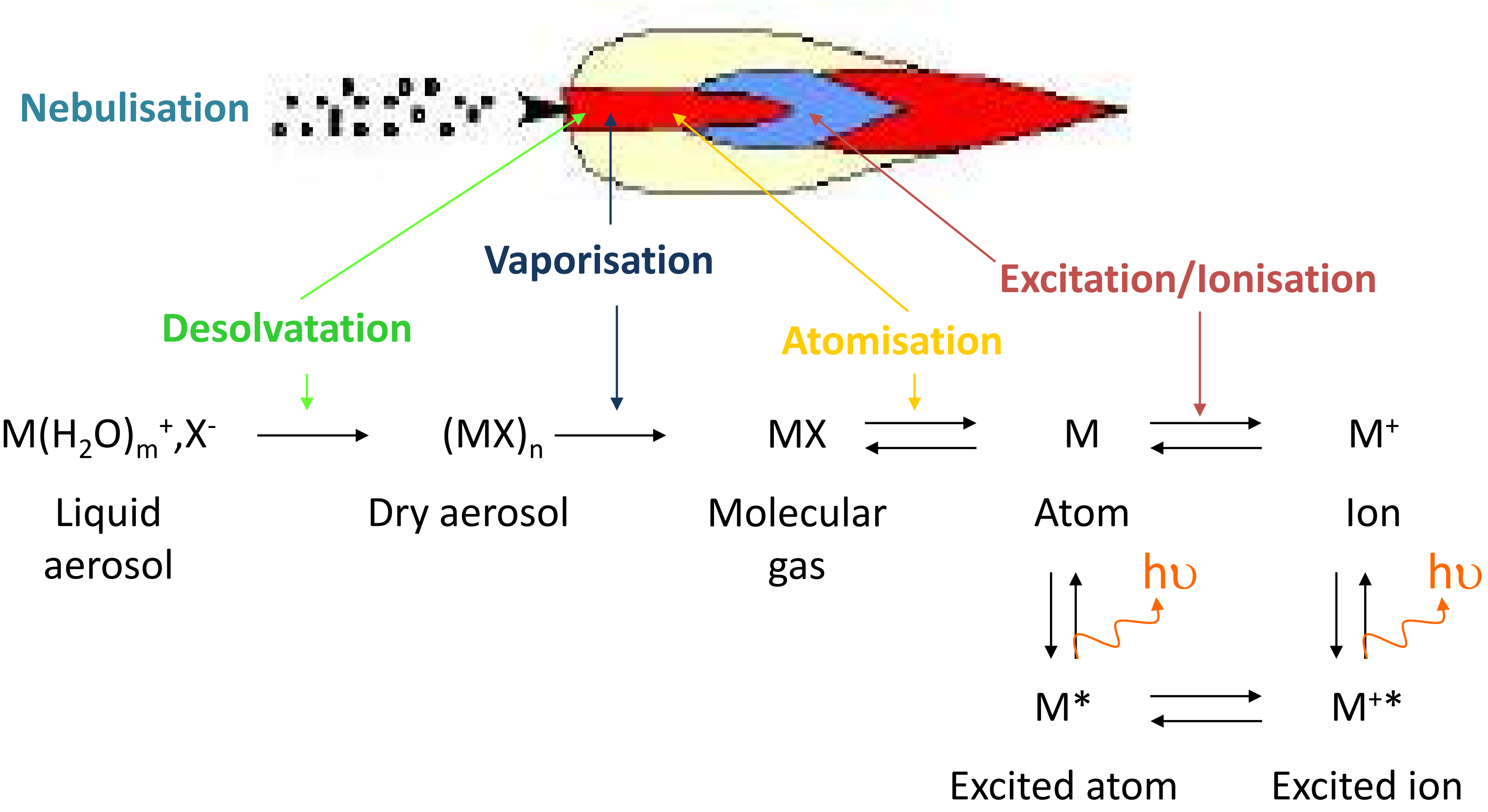
3.1. Application in Analytical Chemistry

- Ver hot source
  - Higher temperature than that produced by flames or electric discharges (arc / spark), therefore more efficient for atomization

- So very energy source:
  - it is easy to reach the heats of atomization of molecules and the energy of ionization and excitation of atoms

⇒ **Use for the determination of the elemental chemical composition**

3.1. Application in Analytical Chemistry



Nebulisation

Desolvatation

Vaporisation

Atomisation

Excitation/Ionisation

$$M(H_2O)_m^+,X^- \longrightarrow (MX)_n \longrightarrow MX \rightleftharpoons M \rightleftharpoons M^+$$

Liquid aerosol

Dry aerosol

Molecular gas

Atom

Ion

hυ

hυ

$$M^* \rightleftharpoons M^{+*}$$

Excited atom

Excited ion

3.1. Application in Analytical Chemistry

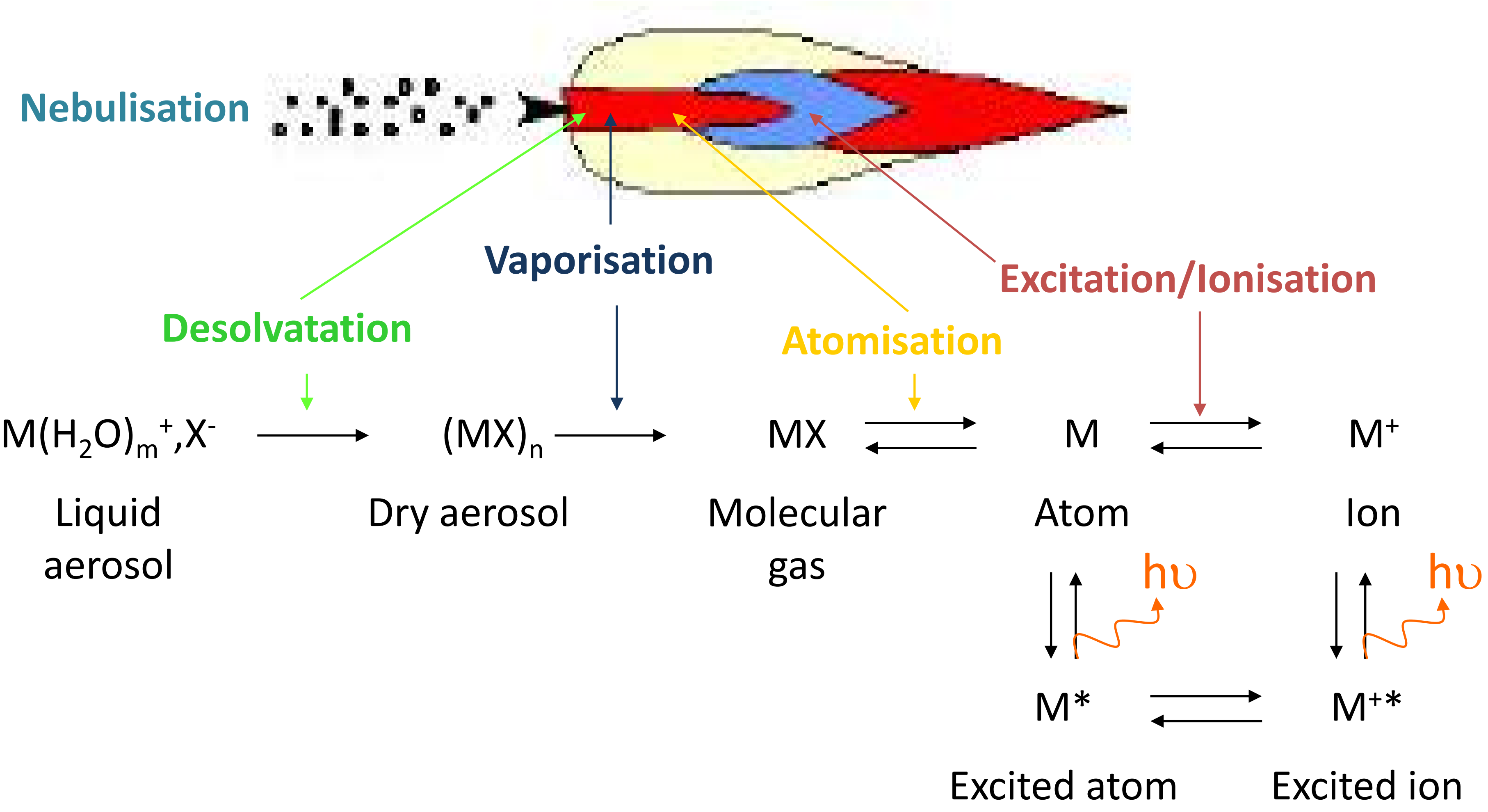
- **Plasma makes it possible to:**
  - break the molecular bonds
  - produce atoms and free ions

Ions source ➡ Mass spectrometry

  - to excite these atoms / ions

Photons source ➡ Atomic emission spectrometry

3.1. Application in Analytical Chemistry



Nebulisation

Vaporisation

Excitation/Ionisation

Desolvatation

Atomisation

$$\begin{tikzcd} M(H_2O)_m^+, X^- \arrow[r] & (MX)_n \arrow[r] & MX \arrow[r, shift left] & M \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift right] & M^+ \arrow[l, shift left] \arrow[d, shift right] \\ & & & M^* \arrow[u, shift right, "h\upsilon"'] \arrow[r, shift left] & M^{+*} \arrow[l, shift left] \arrow[u, shift right, "h\upsilon"'] \end{tikzcd}$$

Liquid aerosol

Dry aerosol

Molecular gas

Atom

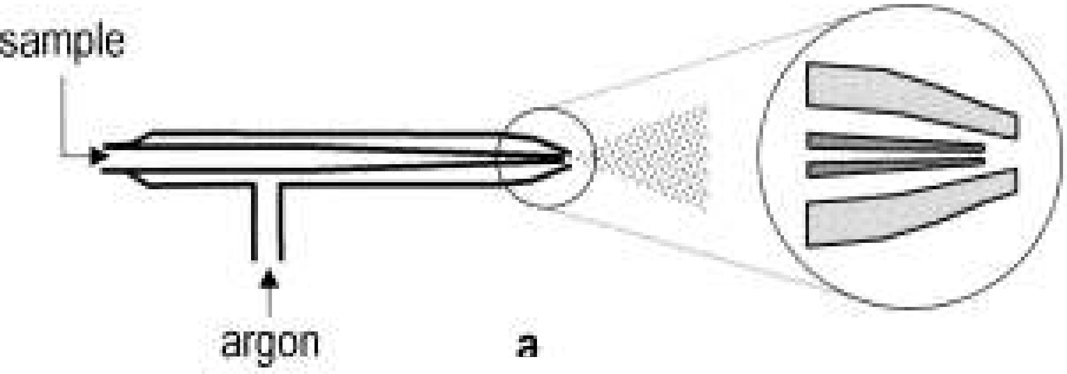
Ion

Excited atom

Excited ion

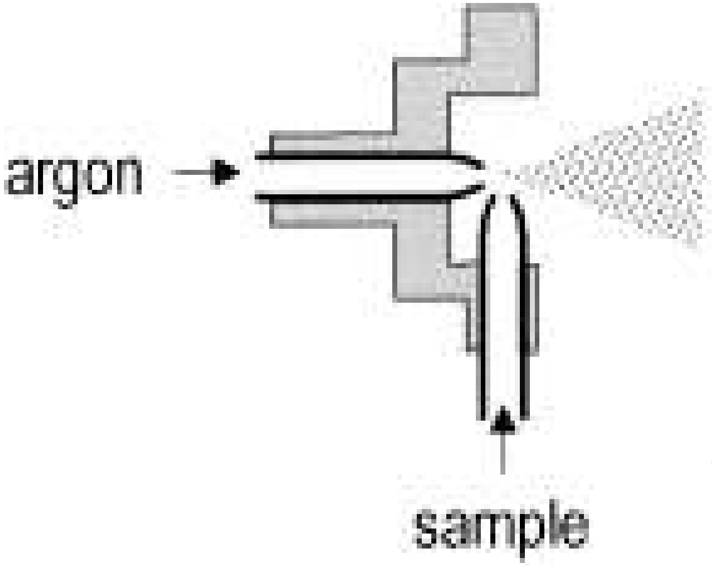
3.1. Application in Analytical Chemistry

- Introduction of sample → Nebulisation



a

Ex. of nebulisation systems



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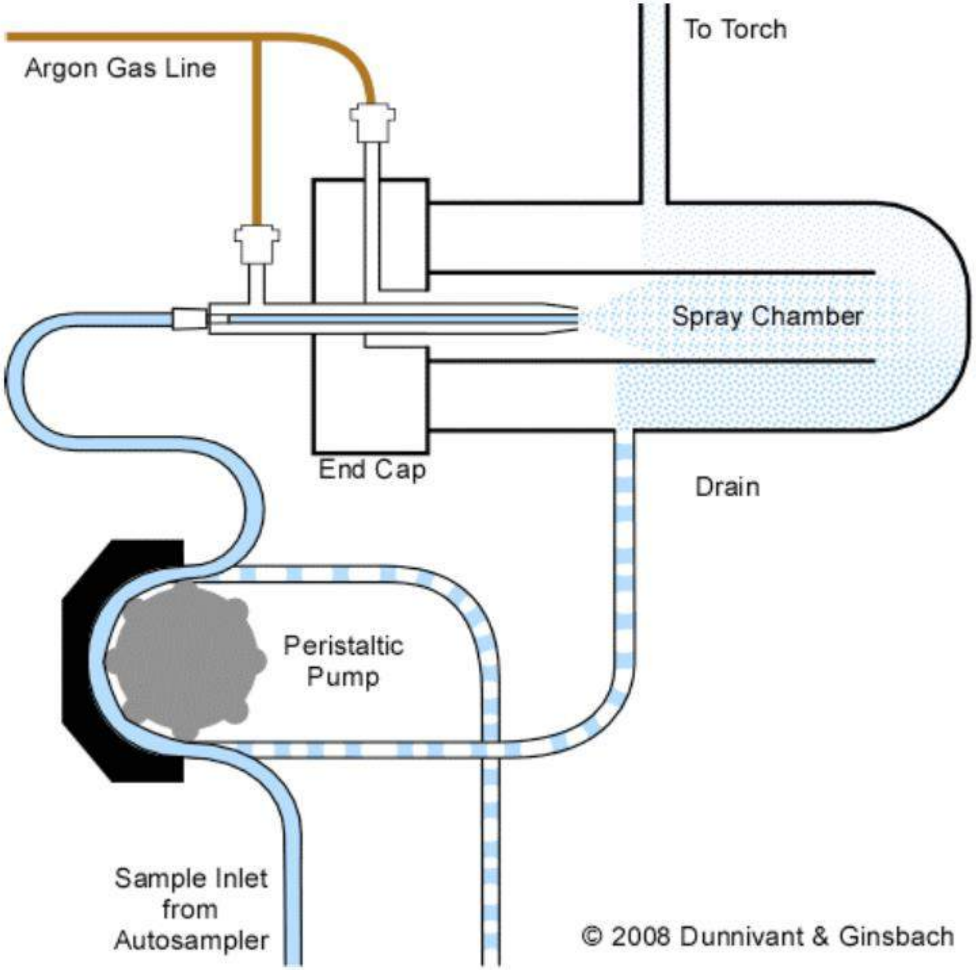
3.1. Application in Analytical Chemistry

- Introduction of sample → Nebulisation



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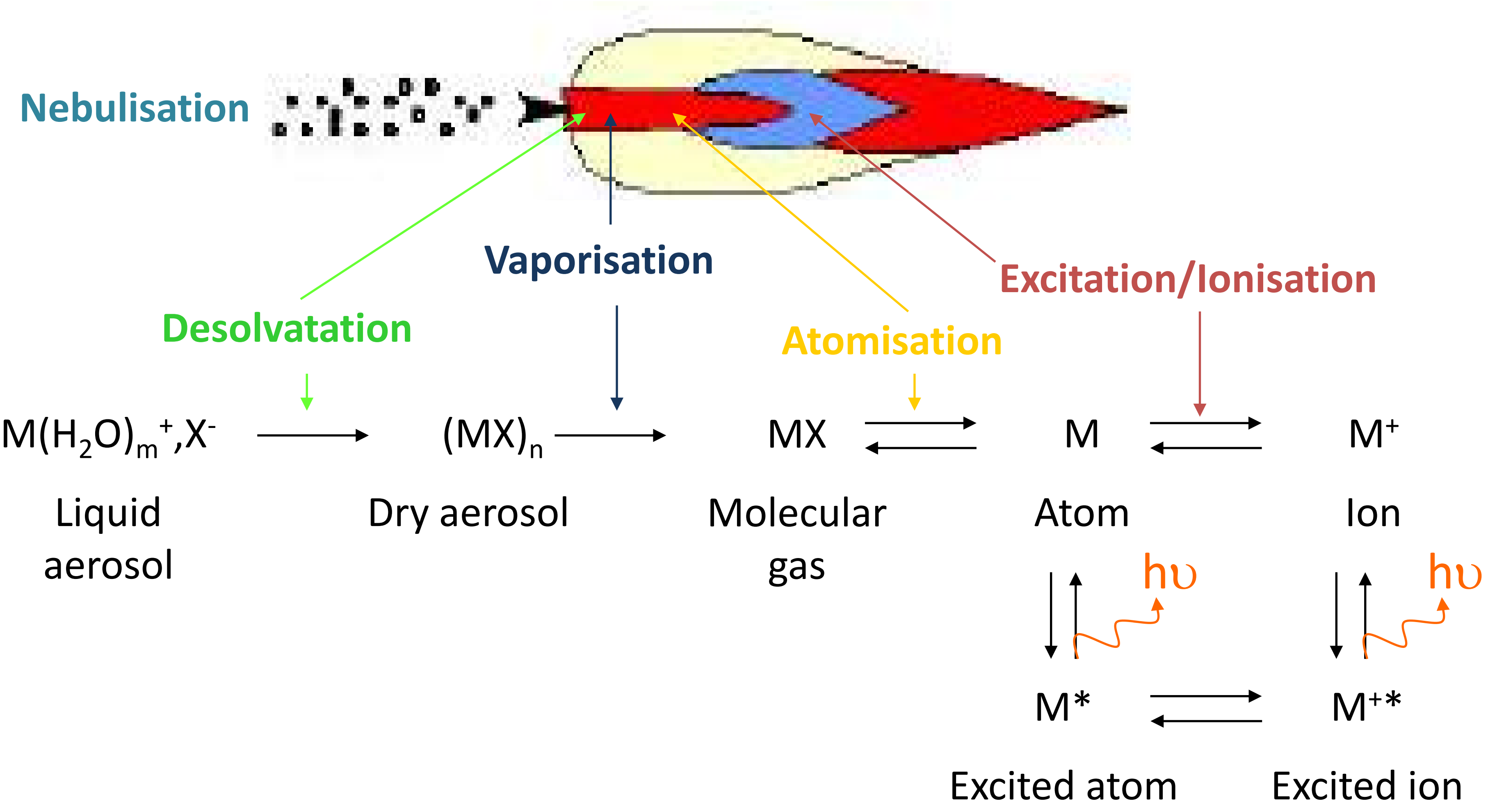
3.1. Application in Analytical Chemistry



Nebulisation

Vaporisation

Excitation/Ionisation

Desolvatation

Atomisation

$$\begin{tikzcd} M(H_2O)_m^+,X^- \arrow[r] & (MX)_n \arrow[r] & MX \arrow[r, shift left] & M \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift right] & M^+ \arrow[l, shift left] \arrow[d, shift right] \\ & & & M^* \arrow[u, shift right] \arrow[r, shift left] & M^{+*} \arrow[l, shift left] \arrow[u, shift right] \end{tikzcd}$$

Liquid aerosol

Dry aerosol

Molecular gas

Atom

Ion

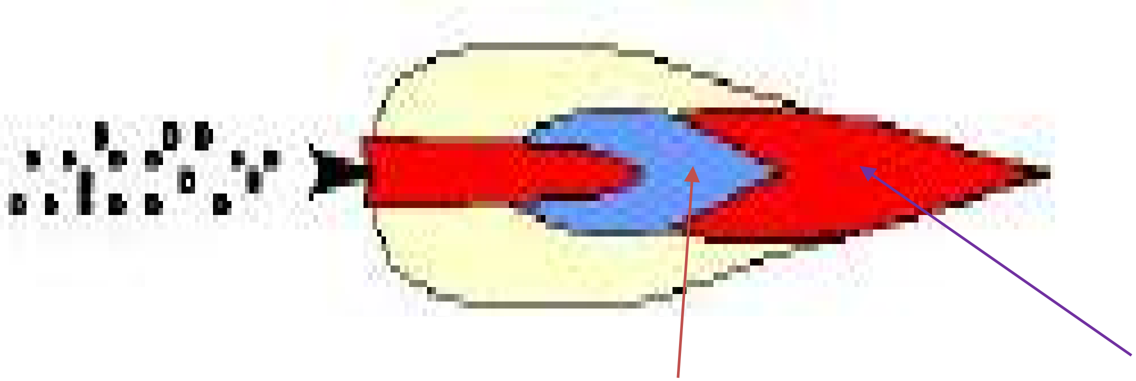
hυ

hυ

Excited atom

Excited ion

3.1. Application in Analytical Chemistry



Excitation/Ionisation

Excited atoms and ions

AES

Charge transfer

Ions

MS

A. ICP-AES

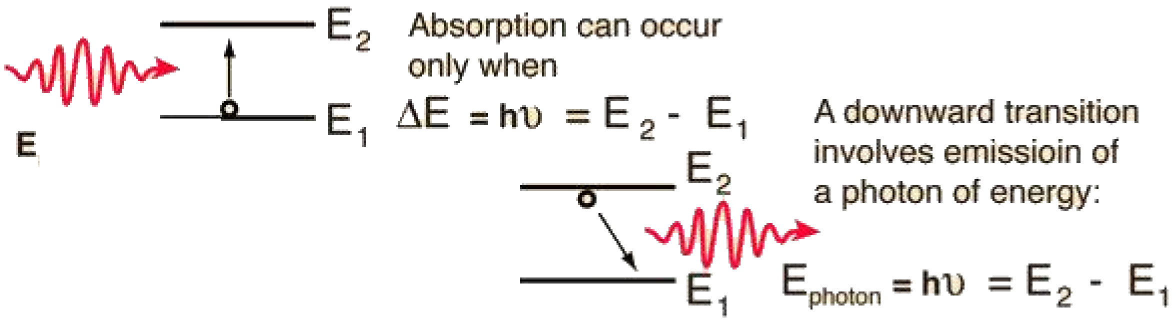
Inductively Coupled Plasma-Atomic Emission Spectrometry

3.1.1 ICP-AES:

- ICP-AES or ICP-OES, for Optical Emission, since the emission is often due to ions excitation and not only atomic excitation.
  - ICP = Photons Source
  - AES = Photons Detector

3.1.1 ICP-AES: Emission: Principle

- The photon is emitted when an electron makes the downward transition



- A unique wavelength is associated to each electronic transition and is specific of each element :

$$\boxed{E_2 – E_1 = h.\upsilon = hc/\lambda}$$

h : cte of Planck (6.63×10^{-34} J.s), c : speed of light (3×10^{8} m/s)

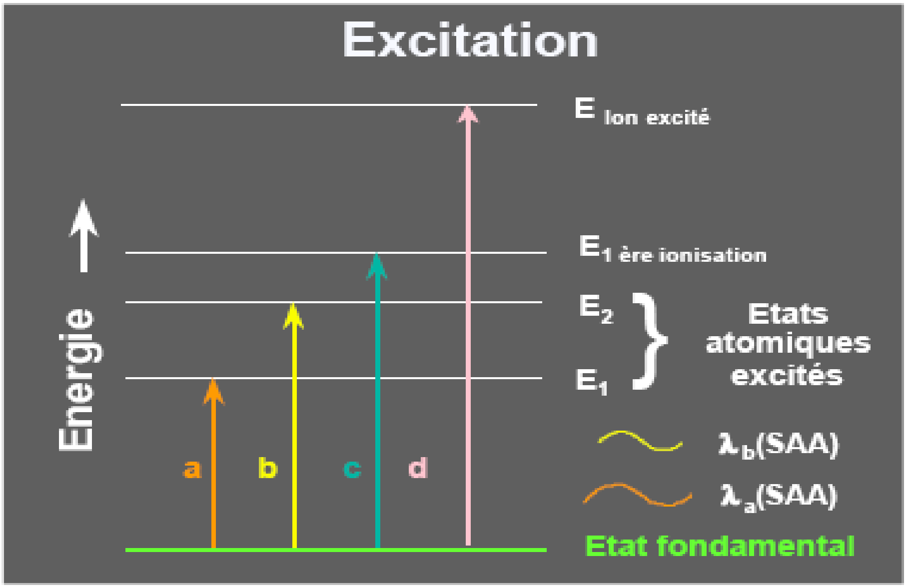
υ : frequency (Hz), λ : wavelength (m)

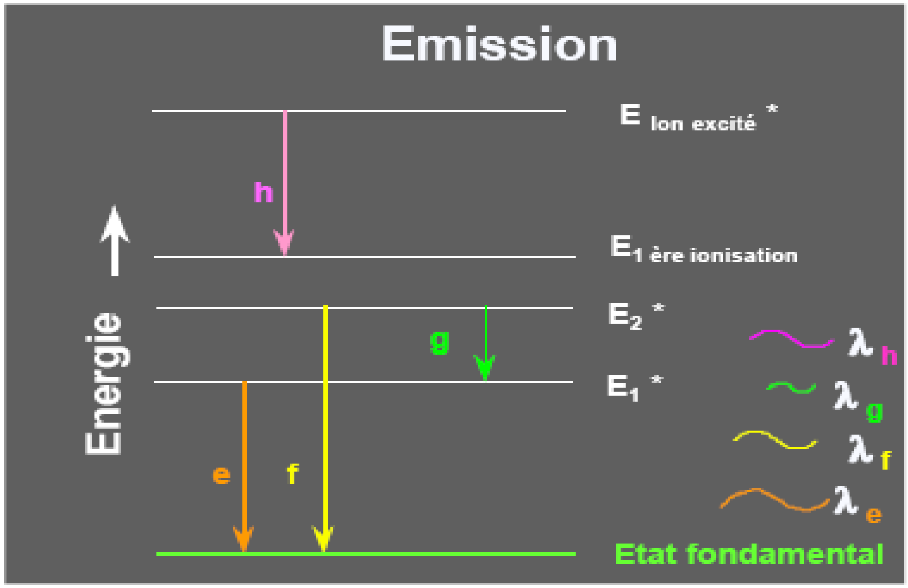
Note: The frequency that is emitted when an electron makes the downward transition is the same as the frequency absorbed by this two-level system.

The smallest wavelengths (UV) are the highest energy transitions

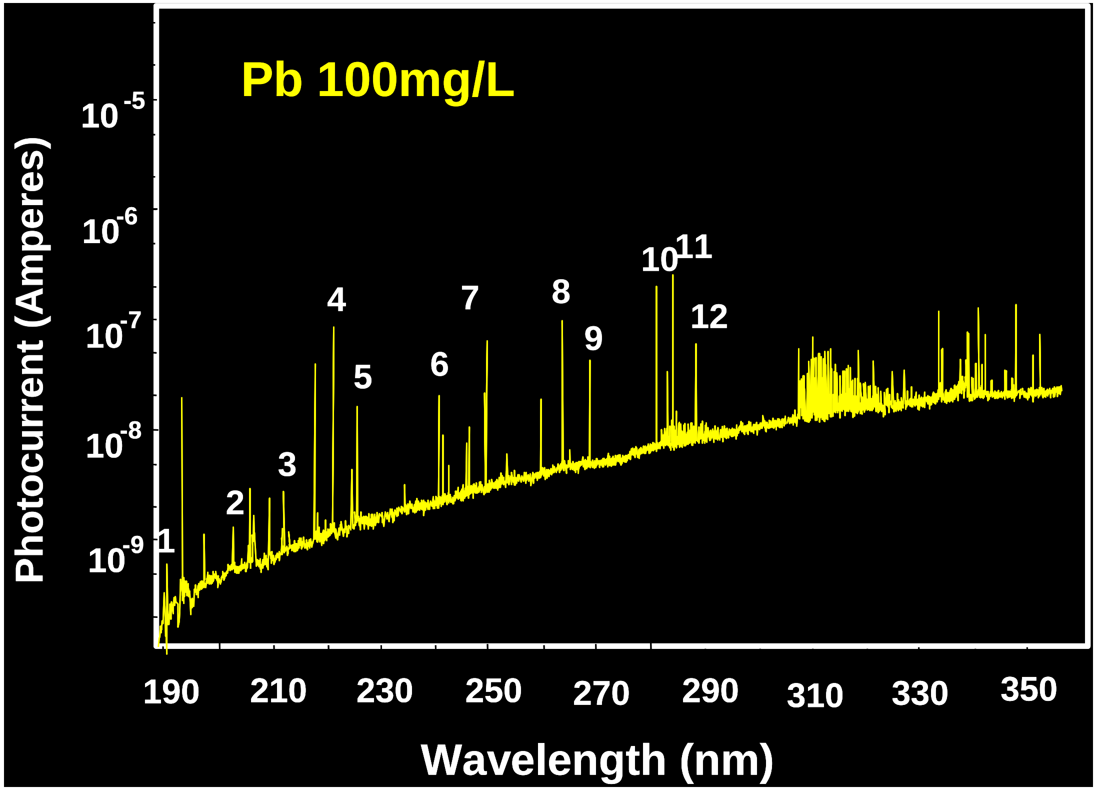
3.1.1 ICP-AES: Emission: Principle

- During excitation, several electronic transition are possible:





3.1.1 ICP-AES: Emission: Principle



Emission spectrum is specific for a given element

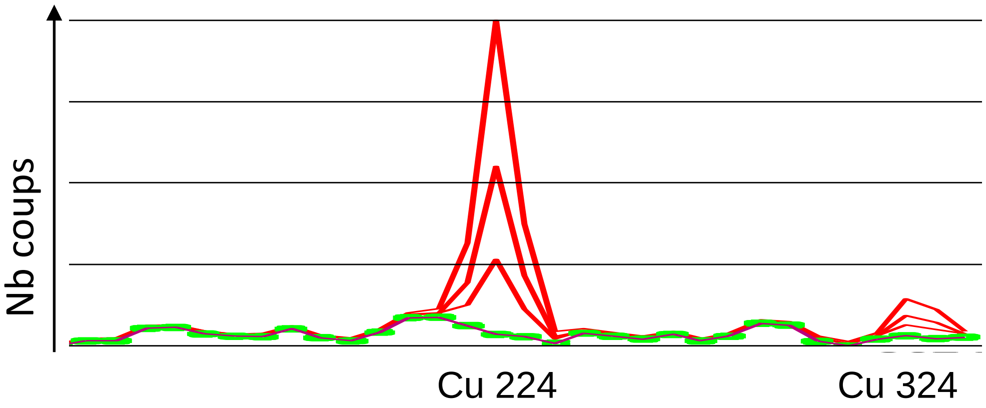
According to the element, it can be more or less rich in line: Cs: 6 lines; K: 9 lines; Cu: 77 lines ....

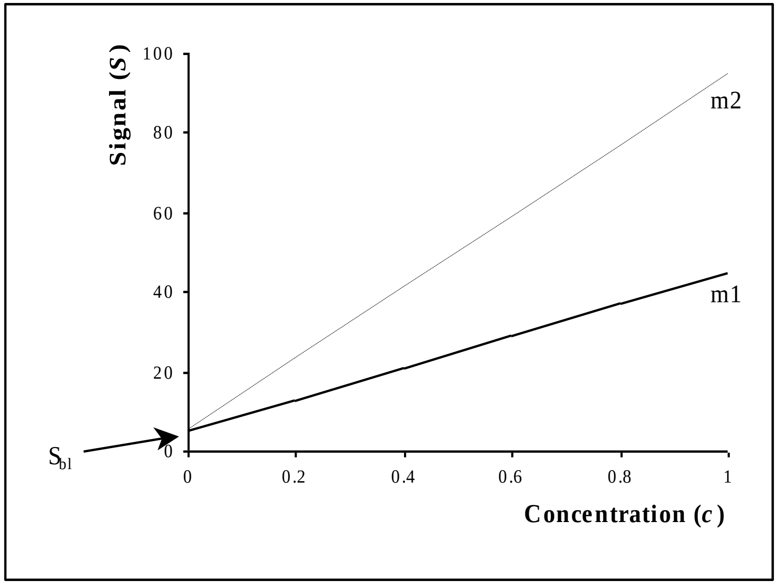
- Depending on the species that is excited, the lines are called:
  - ☐ **Line I**: emission from an atom
  - ☐ **Line II**: emission from an ion

3.1.1 ICP-AES: Emission: Principle

Intensity of the line is:

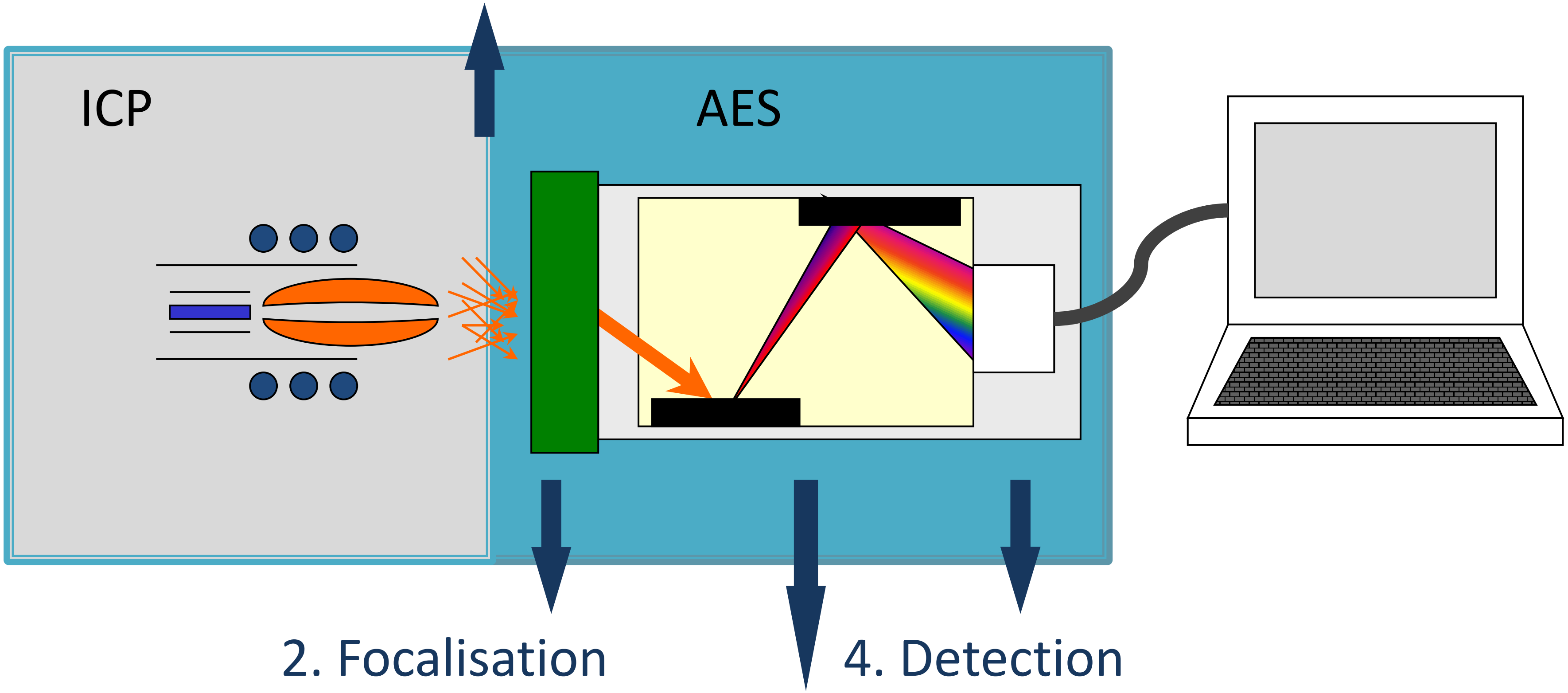
- specific to the wavelength
- proportional to the concentration of a given element





Ion lines (II) are the most used for low concentrations because they are the most sensitive ...

3.1.1 ICP-AES: Schema-principe



1. Interface ICP-AES

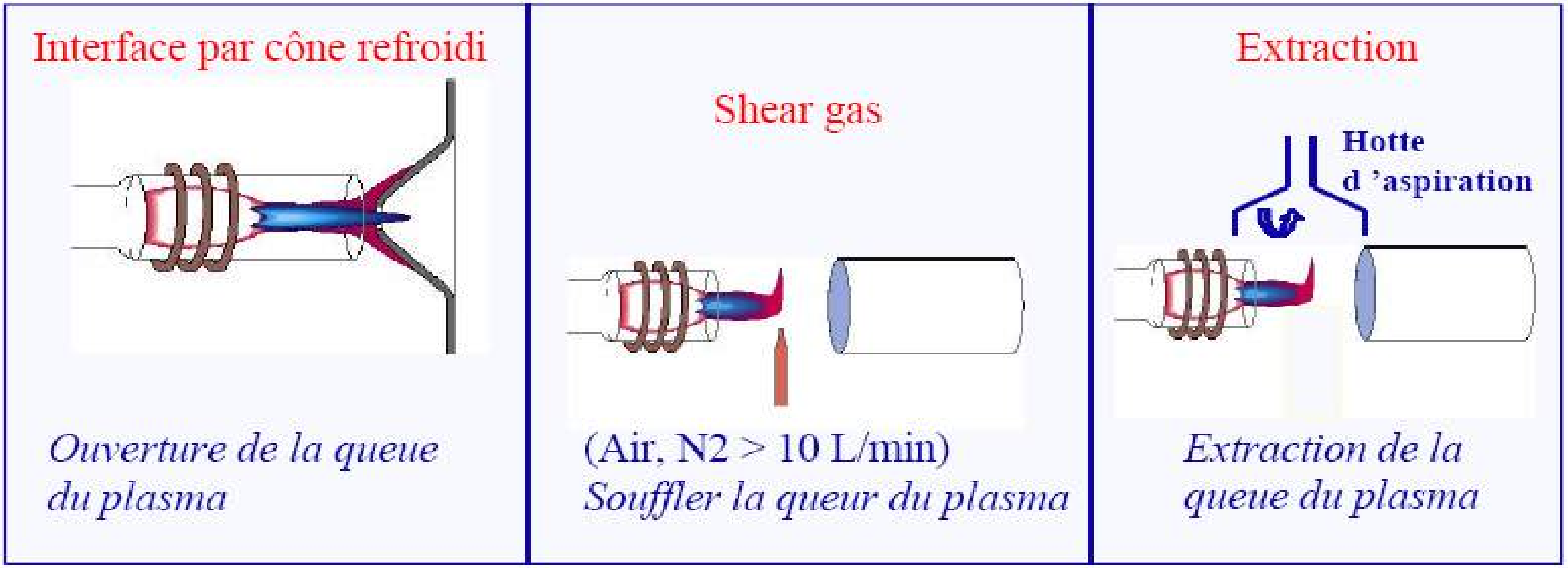
2. Focalisation

4. Detection

3. Selection by λ

3.1.1 ICP-AES: *1. Interface ICP-AES*

- 2 types of configuration: radial or axial
- Purposes:
  1. Remove the cooling zone from the plasma to limit recombinations
  2. Orient the photons as far as possible towards the spectro



Interface par cône refroidi

Ouverture de la queue du plasma

Shear gas

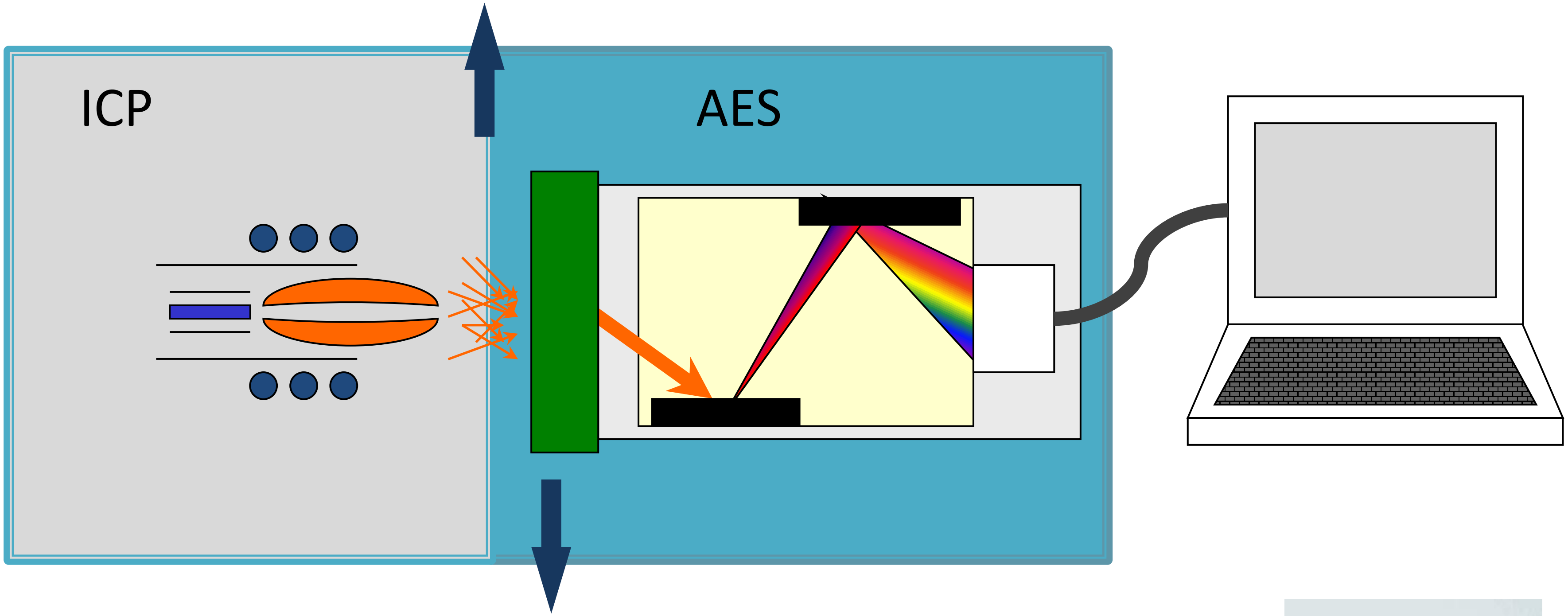
(Air, N2 > 10 L/min)
Souffler la queur du plasma

Extraction

Extraction de la queue du plasma

3.1.1 ICP-AES: Schema-principe

1. Interface ICP-AES

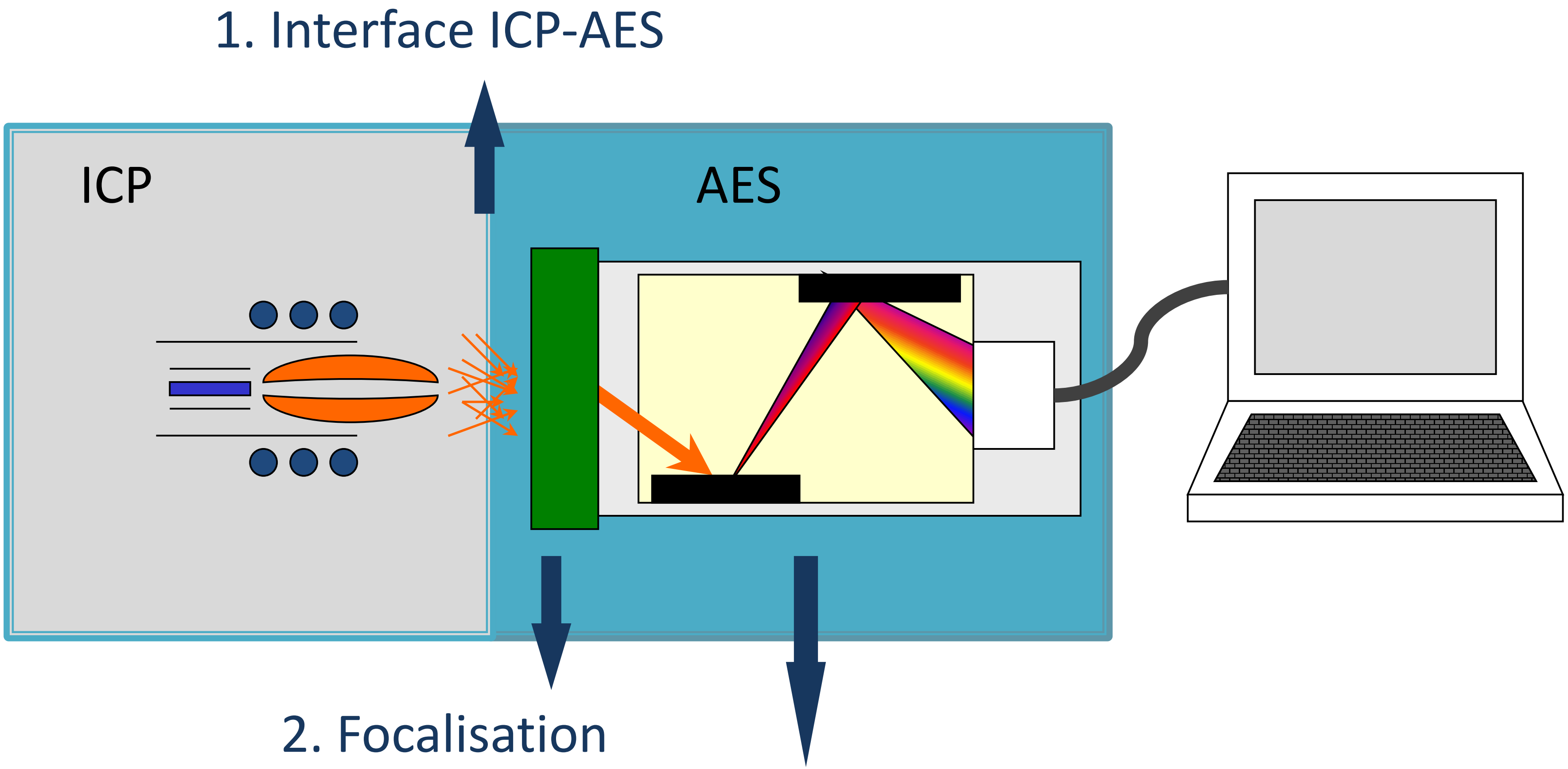


2. Focalisation

Collimation lens

(Lentille Collimation)

3.1.1 ICP-AES: Schema-principe



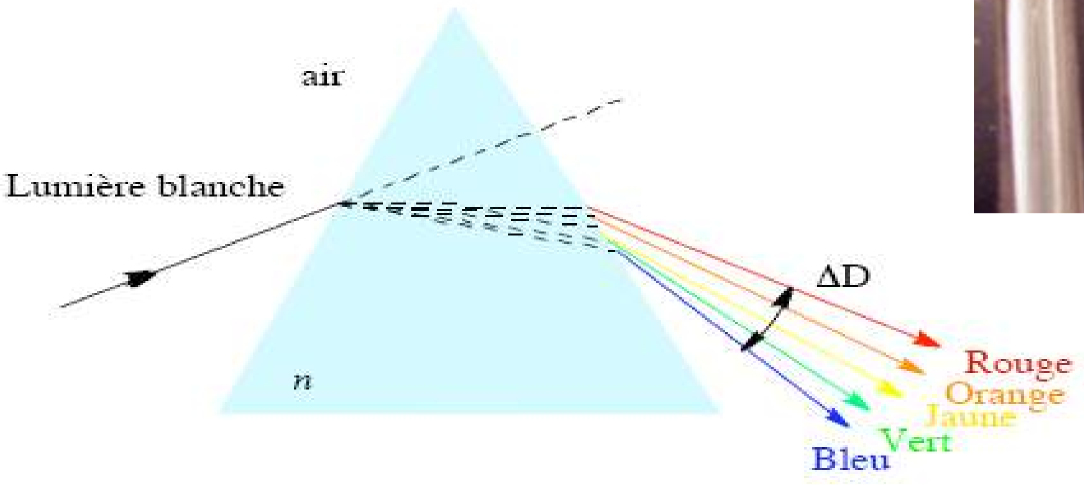
1. Interface ICP-AES

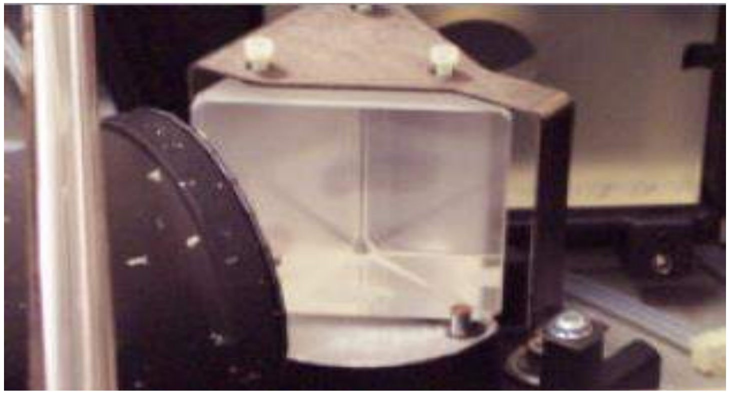
2. Focalisation

3. Selection by λ

3.1.1 ICP-AES: *3. Selection by λ = Dispersive systems*

- Purpose: Separate the analyte-emited photons as a function of their wavelengths
- 2 types of dispersive systems:
  - the prism

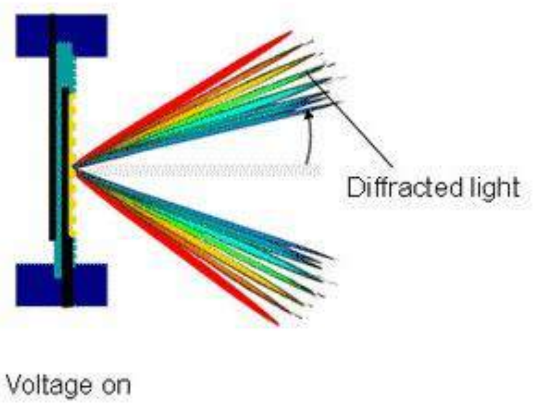


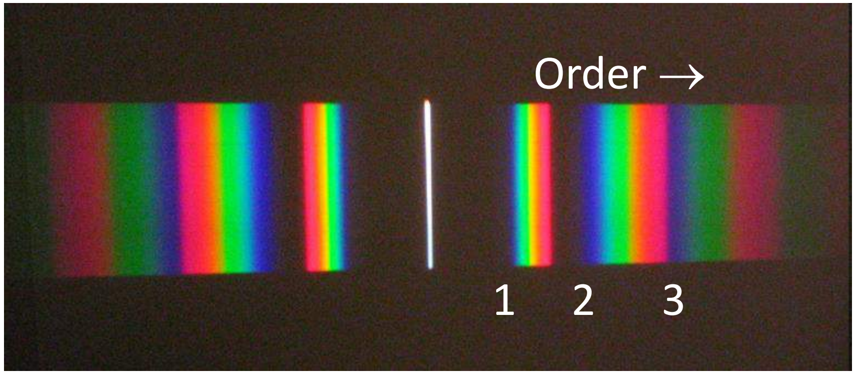


Refraction index of glass / quartz varies with wavelength

3.1.1 ICP-AES: *3. Selection by λ = Dispersive systems*

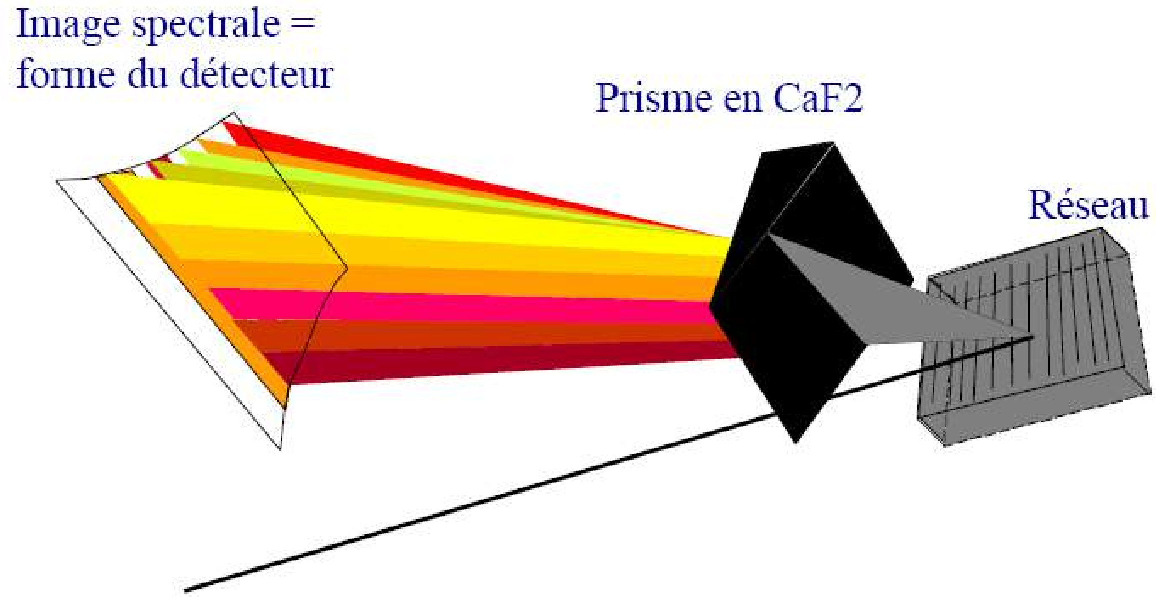
- Purpose: Separate the analyte-emiited photons as a function of their wavelengths
- 2 types of dispersive systems:
  - the prism
  - The grating system (*réseau de diffraction*): = optical surface allowing the dispersion of light via a serie of engraved lines

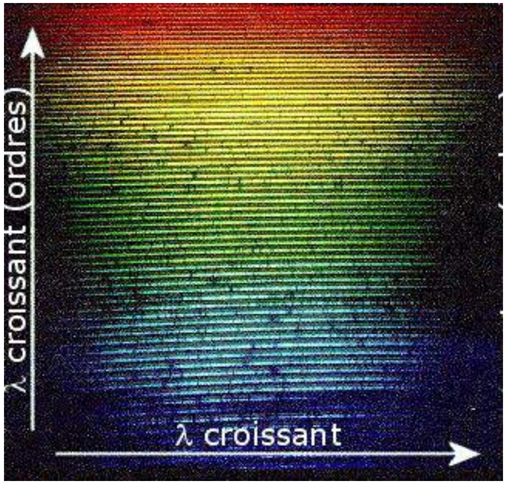




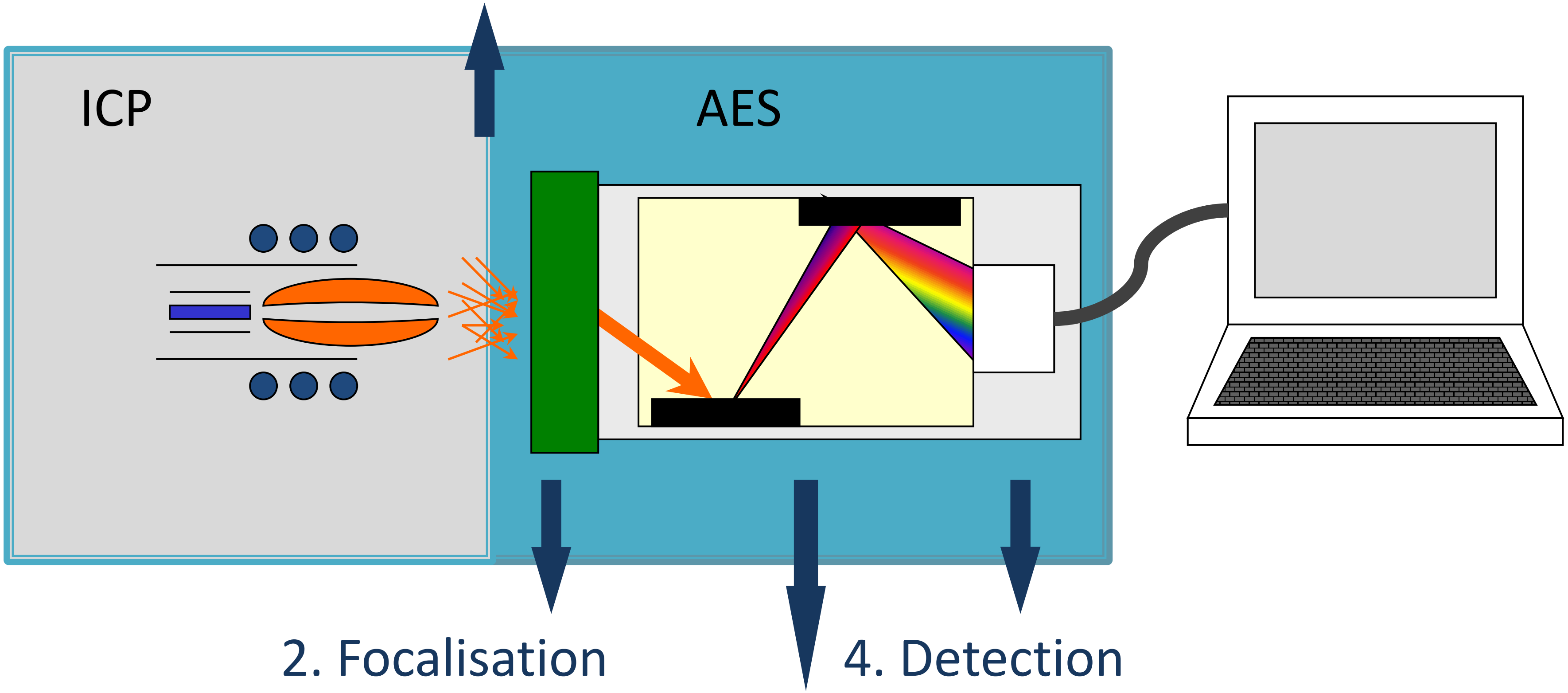
3.1.1 ICP-AES: *3. Selection by λ = Dispersive systems*

- Combined system





3.1.1 ICP-AES: Schema-principe



1. Interface ICP-AES

2. Focalisation

4. Detection

3. Selection by λ

3.1.1 ICP-AES: *4. Detection:*

- Purpose: Conversion of photons into electric current
  - Solid detector

CCD: Charge Coupled Device

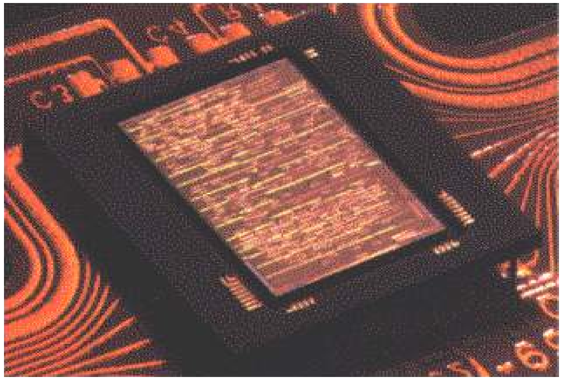
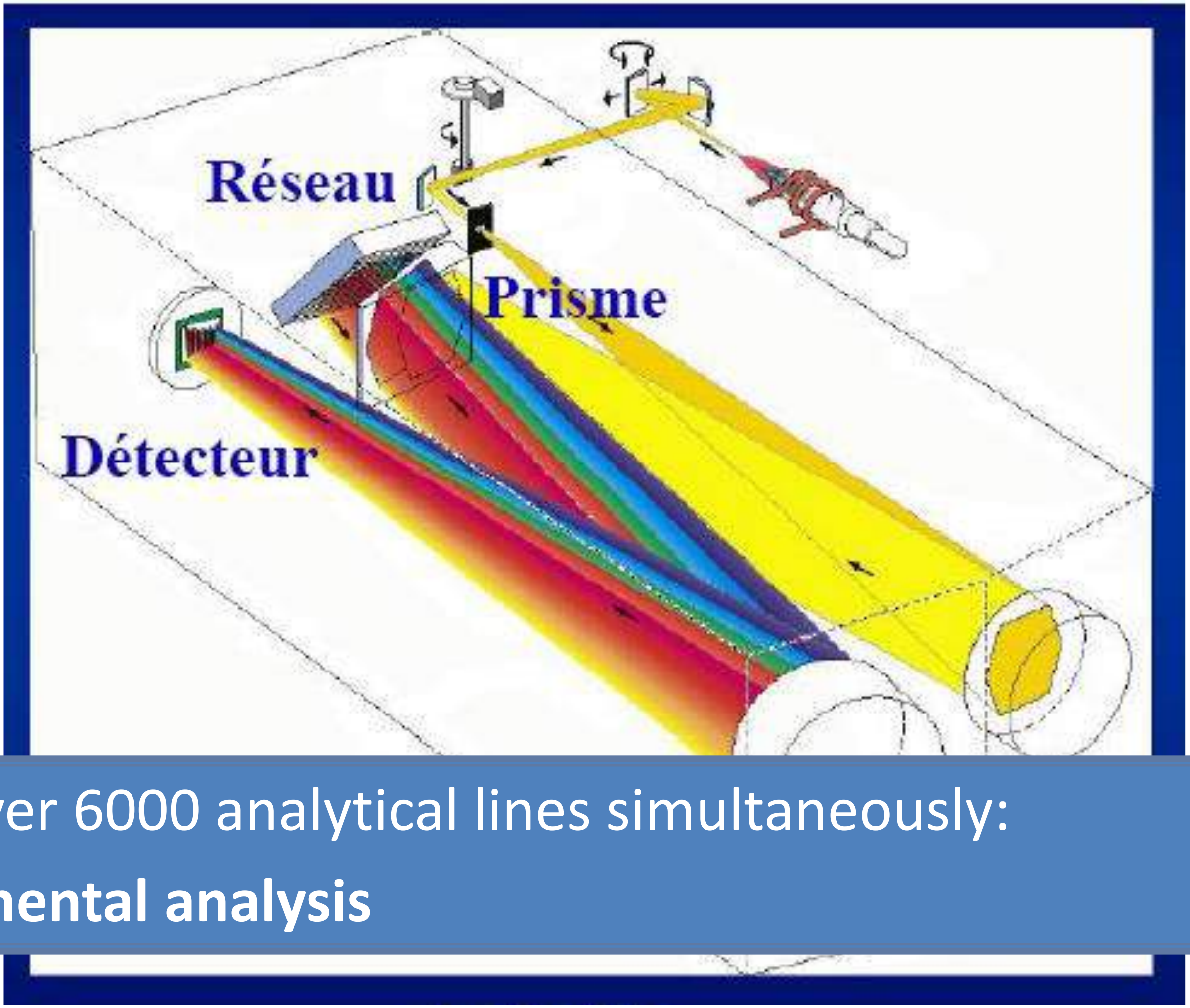


Plate comprising photosensitive silicon pixels of a size ranging from 10 to 30 µm, arranged in a matrix or bar, which convert the incident photons into electrons

3.1.1 ICP-AES:

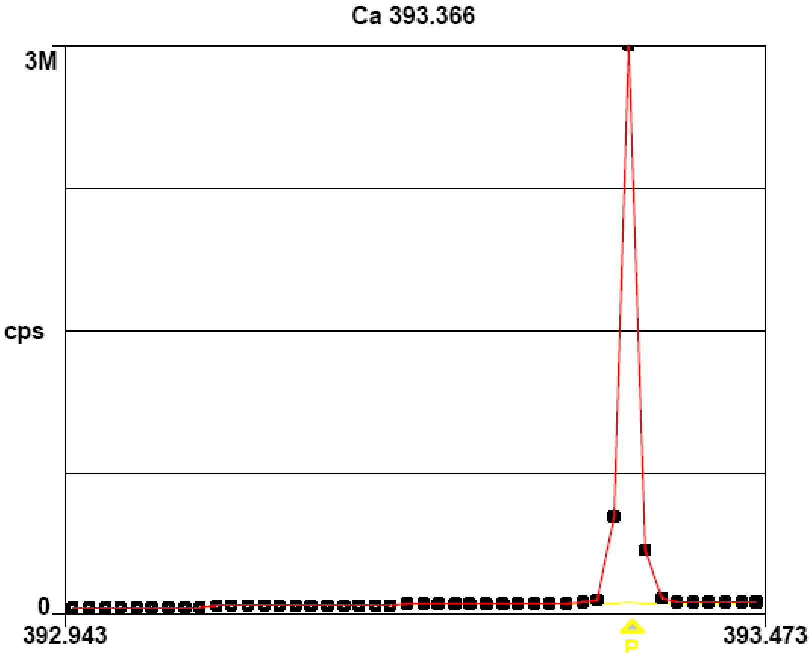


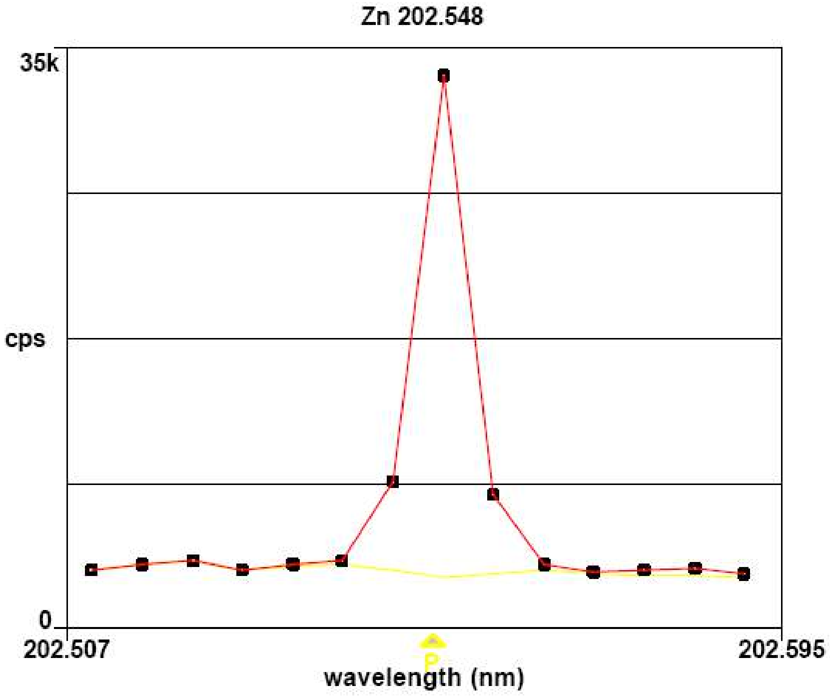
Reading over 6000 analytical lines simultaneously:

Multi-elemental analysis

3.1.1 ICP-AES: Signal measurements

Emission spectrum:

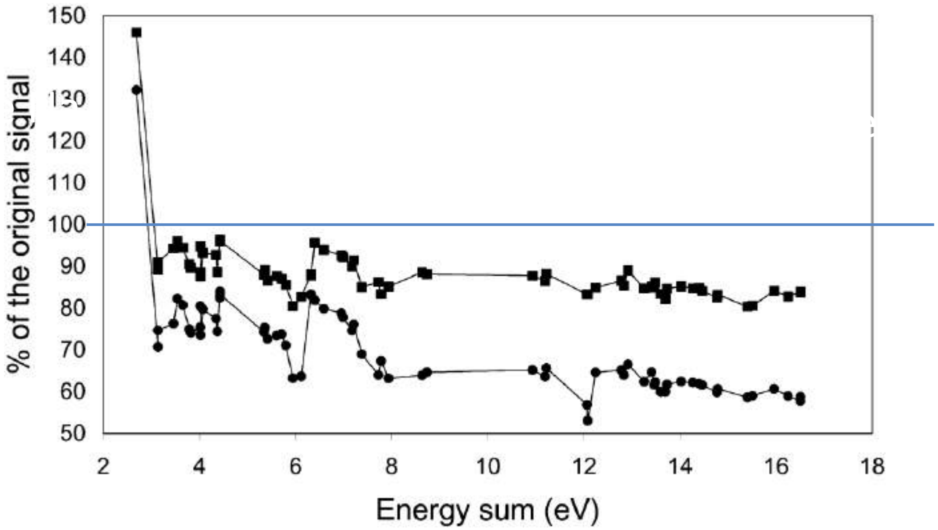

Ca 393.366


Zn 202.548

Signal measurement = peak area (surface de pic)

3.1.1 ICP-AES: Interferences

- Physico-chemical:
  - Interferences due to transport : difference of viscosity sample/standard
    - ☐ Difference of nebulisation efficiency
  - Matric effects: Presence of major elements (e.g. salts)
    - ☐ Difference of signal response between standard and samples



Romero et al., 1997

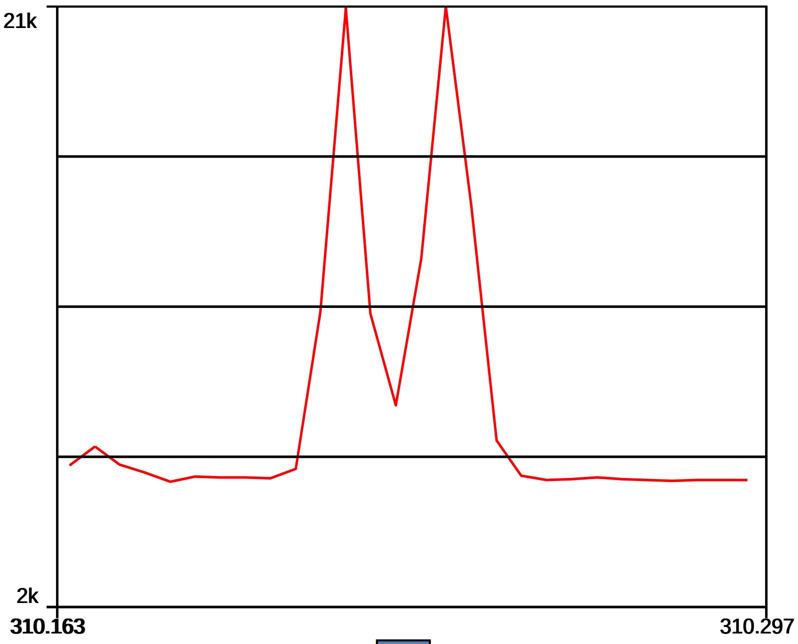
Recovery between signal without or with Na as interferent for the concentrations: 1 (■) et 10 g/L (●)

3.1.1 ICP-AES: Interferences

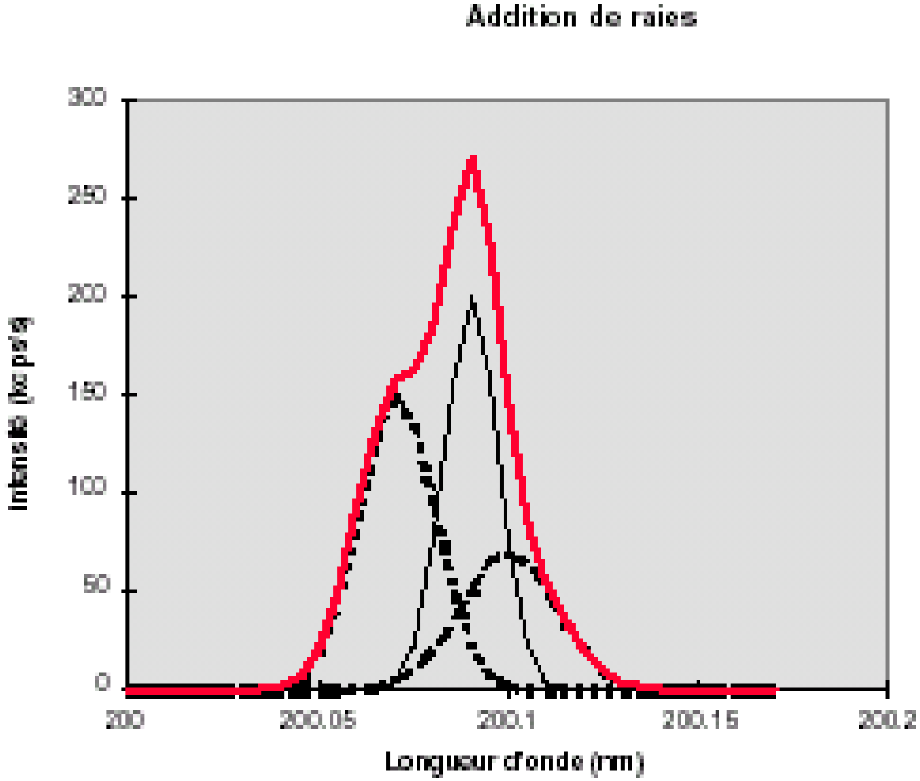
- Physico-chemical:
  - Interferences due to transport : difference of viscosity sample/standard
    - ☐ Difference of nebulisation efficiency
  - Matric effects: Presence of major elements (e.g. salts)
    - ☐ Difference of signal response between standard and samples

- Spectral:
  - Potentially the most important: overestimates
    - ☐ Signal superposition

3.1.1 ICP-AES: Spectral Interference

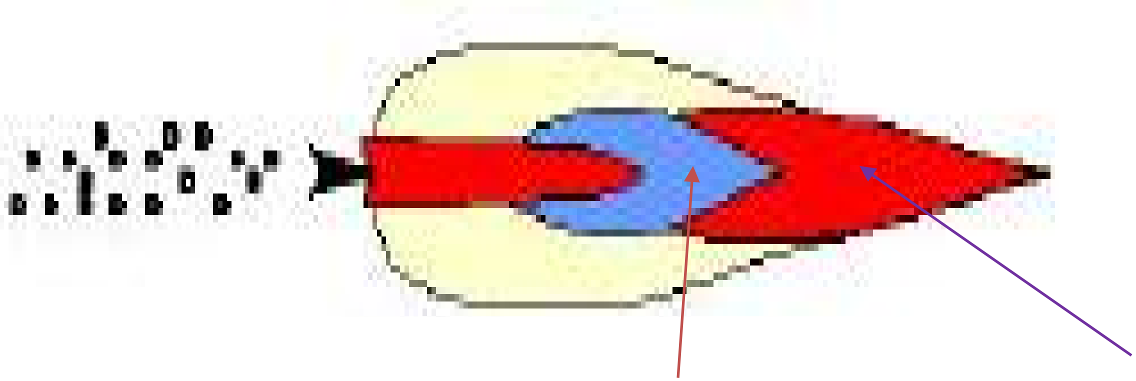


Use height of peaks



Use another wavelength

3.1. Application in Analytical Chemistry



Excitation/Ionisation

Charge transfer

Excited atoms and ions

Ions

AES

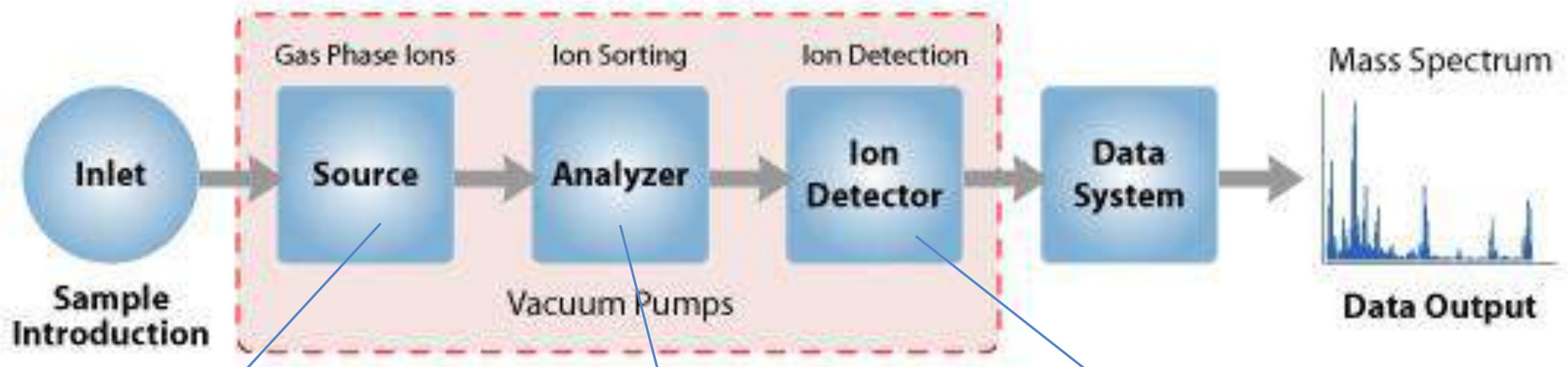
MS

B. ICP-MS

Inductively Coupled Plasma – Mass Spectrometry

Mass Spectrometry : Ions Separations

- The instrument consists of three major components:

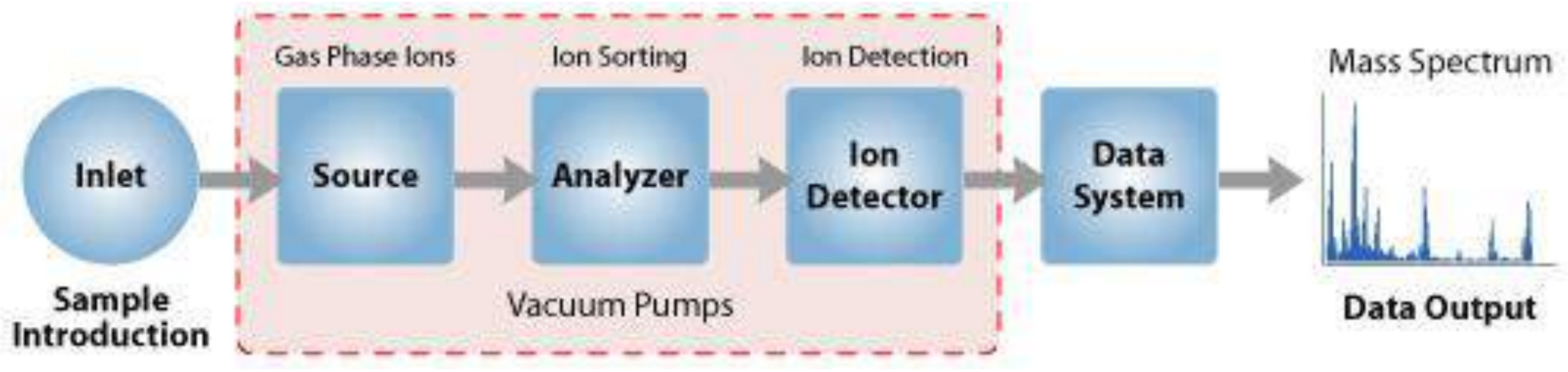


For producing gaseous ions from the matrix

For separating the ions according to their mass-to-charge ratio.

For detecting and counting the ions

3.1.2. ICP-MS:



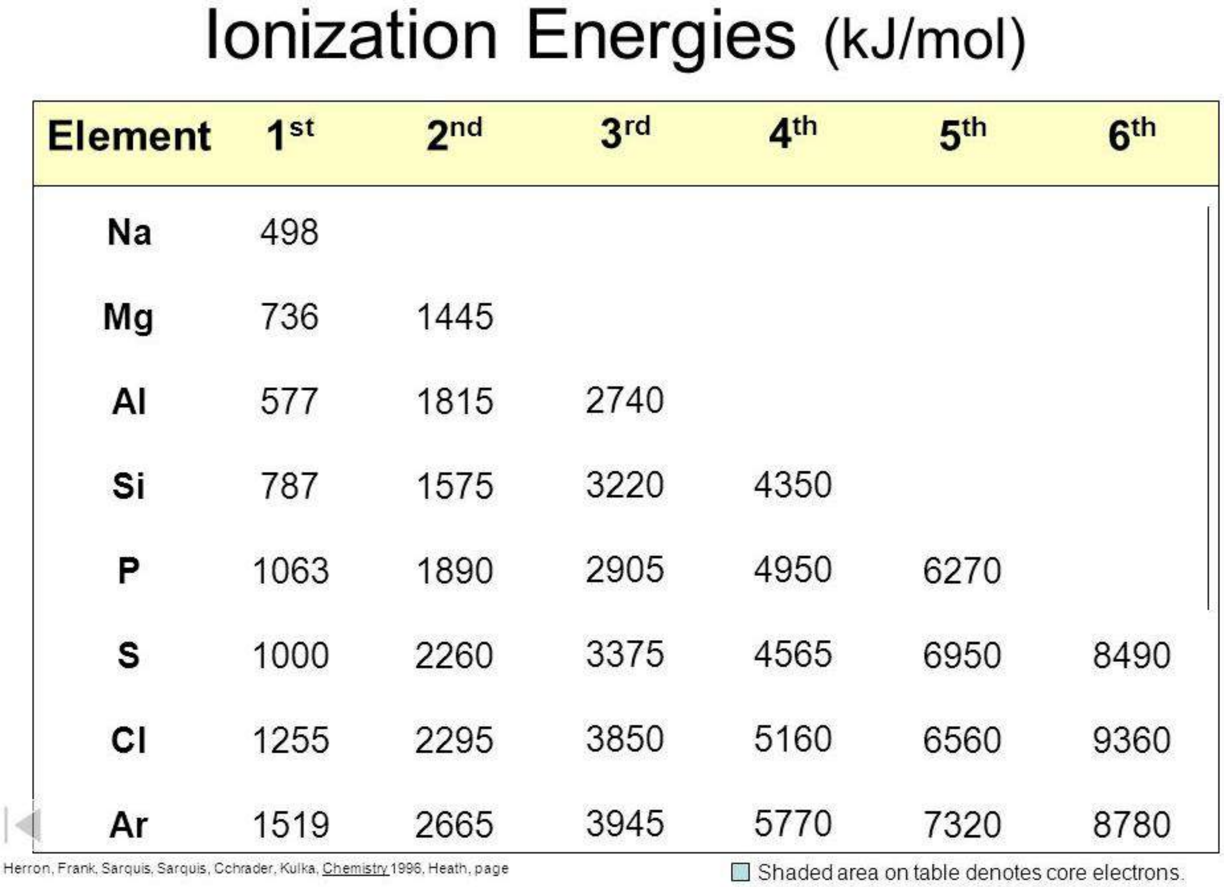
- ICP = Ion source
- MS = Analyzer + detector

NB: Plasma produces both positive and negative ions, but since the separation and transport system of cations and anions are different, we can not analyze both at the same time in ICP-MS

Unlike ICP-AES, here direct recovery of the ions to be analyzed!

3.1.2. ICP-MS: Ionisation

- Ion formation
  - Different ion charges



Ionization Energies (kJ/mol)

Element	1st	2nd	3rd	4th	5th	6th
Na	498					
Mg	736	1445				
Al	577	1815	2740			
Si	787	1575	3220	4350		
P	1063	1890	2905	4950	6270	
S	1000	2260	3375	4565	6950	8490
Cl	1255	2295	3850	5160	6560	9360
Ar	1519	2665	3945	5770	7320	8780

Herron, Frank, Sarquis, Sarquis, Cchrader, Kulka, Chemistry 1996, Heath, page

🟦 Shaded area on table denotes core electrons.

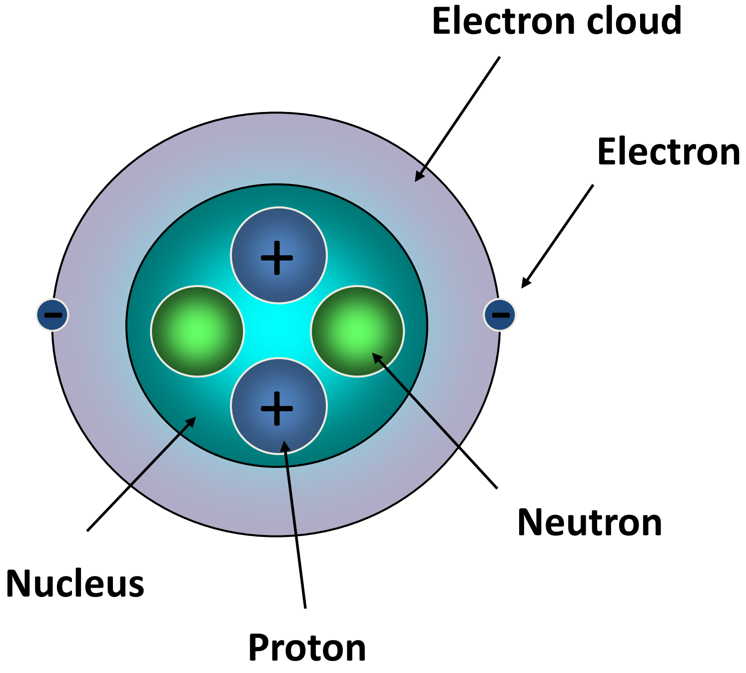
3.1.2. ICP-MS: Ionisation

- Ion formation
  - Different ion charges
  - Different ion mass → Isotopes

3.1.2. ICP-MS: Isotopes

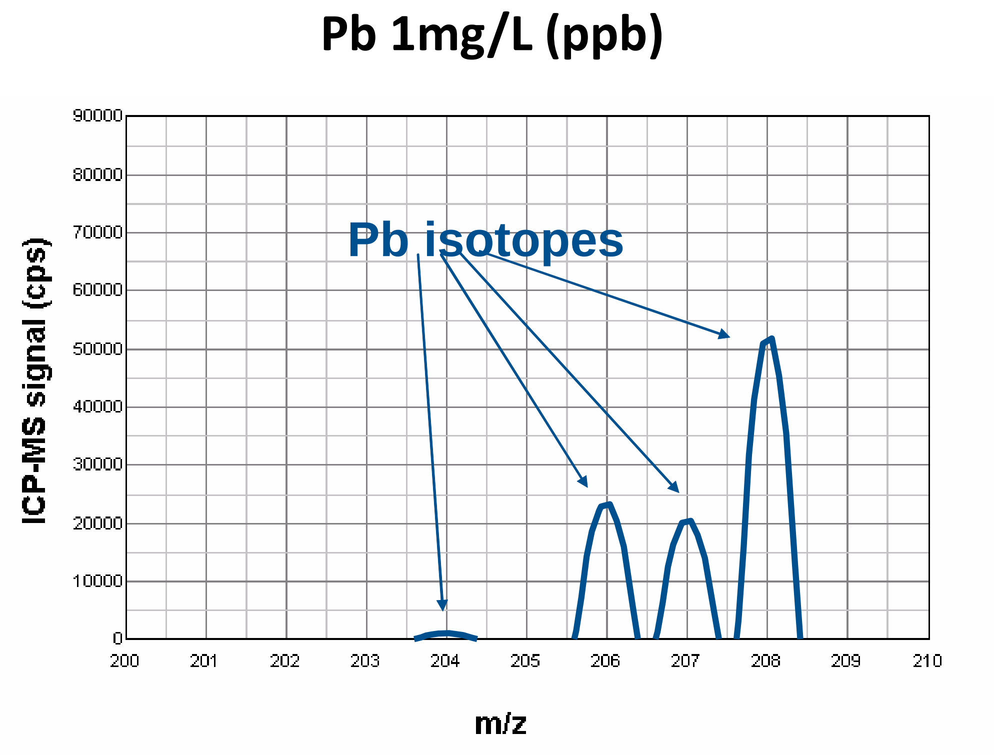
Pb **Atomic number = 82**

Atomic weight = 207.2 g



Isotopes	Abundance(%)	Protons	Neutrons	M
^{204}Pb	1.4	82	122	204
^{206}Pb	24.1	82	124	206
^{207}Pb	22.1	82	125	207
^{208}Pb	52.4	82	126	208

3.1.2. ICP-MS: Ionisation

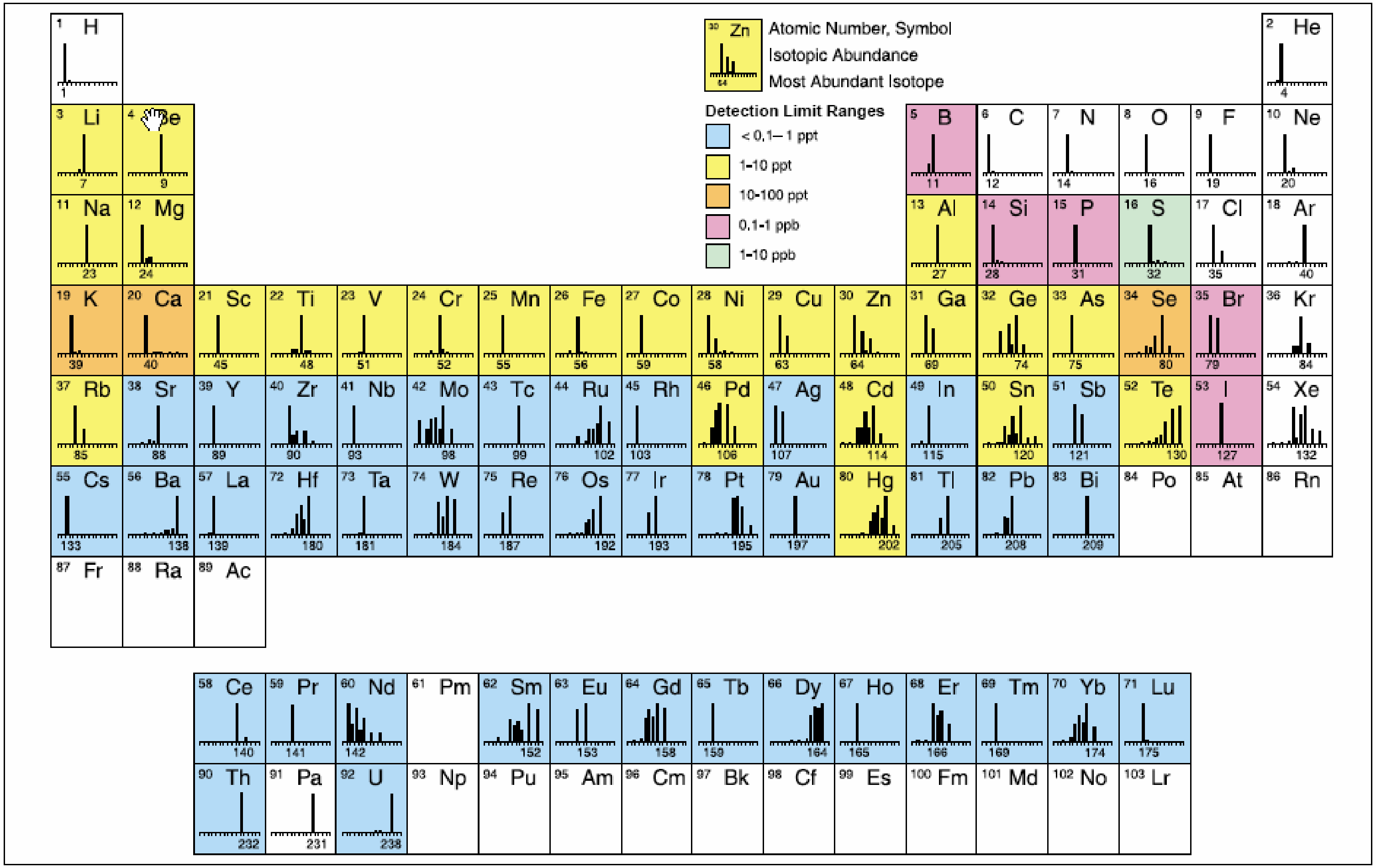


The line spectrum is specific to a given element.

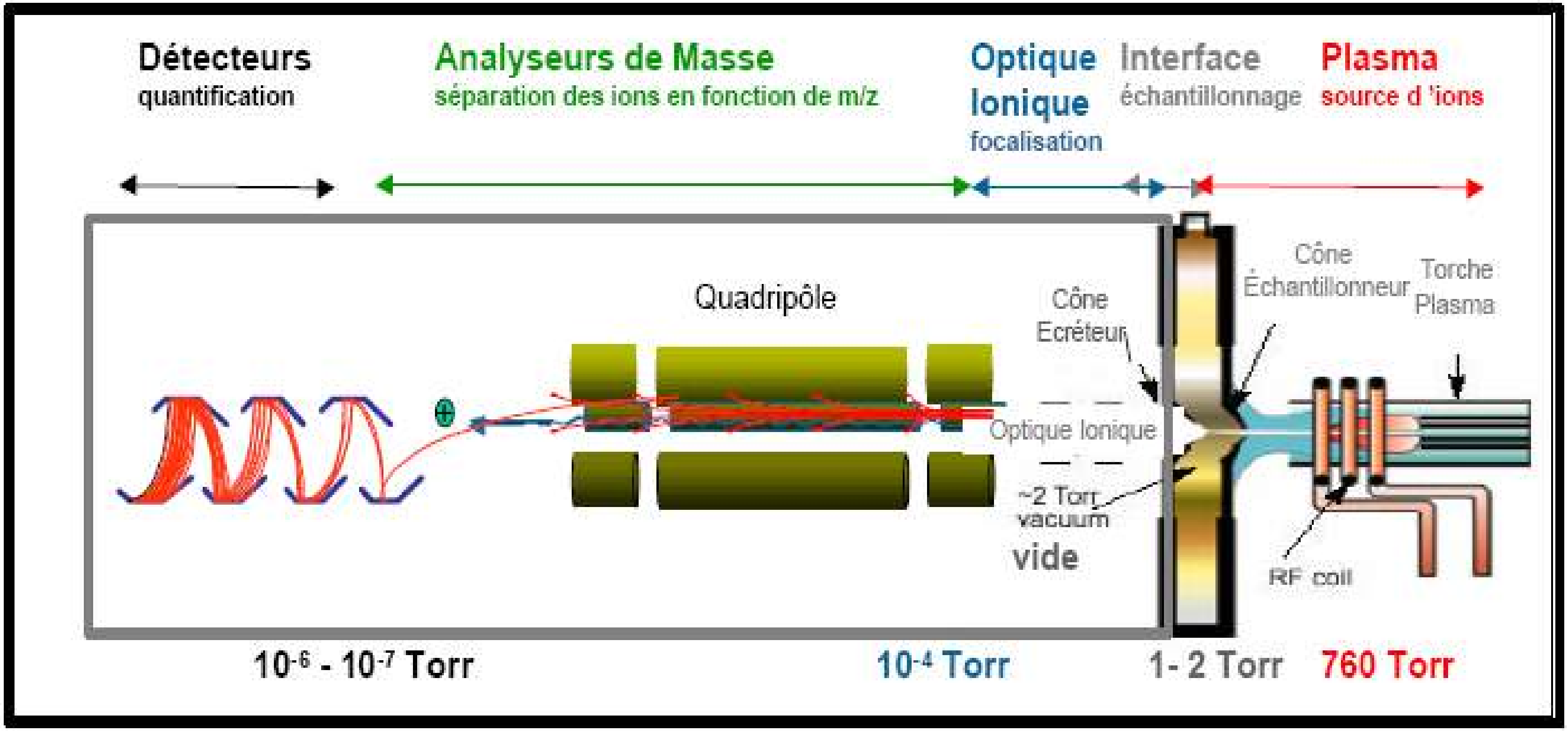
Depending on the element, it may be more or less rich in line: Pb / 4 lines; Ni / 5 lines; Hg / 8 lines ....

Identification of elemental composition + isotopic information

3.1.2. ICP-MS: Isotopic abundance



3.1.2. ICP-MS: Schema principle

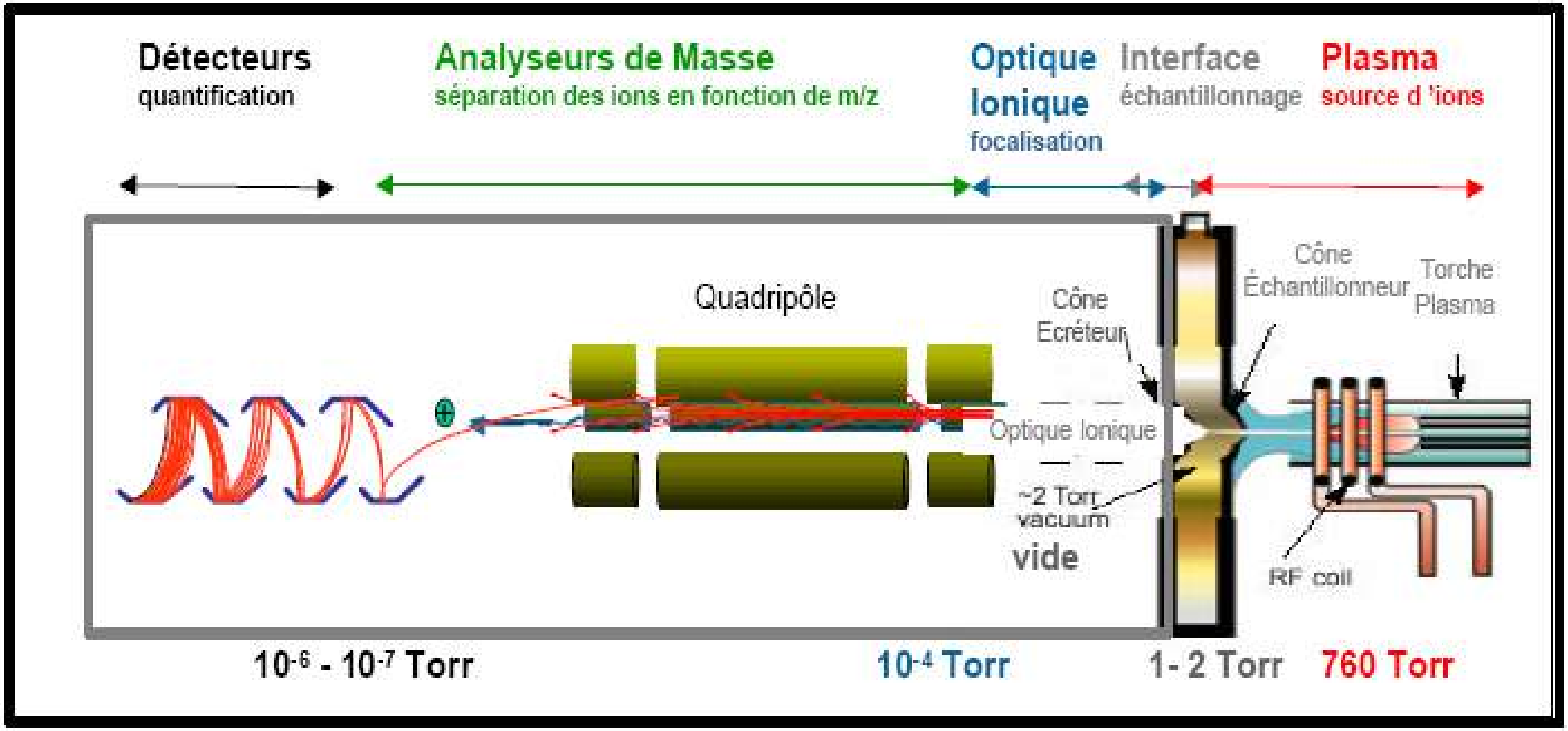


3.1.2. ICP-MS: *1. Interface*

- Aims:
  - Take the ions where they are formed, that is to say in the cold zone of the plasma (ionization + charge transfer).
  - Move from atmospheric pressure to a vacuum compatible with the mass spectrometer.
  - Decrease the temperature from 6000 K to room temperature.

- 2 cones: sampler cone (*échantillonneur*) and skimmer cone (*écremeur /écorceur*)
  - Very resistant for high tempretaures (Ni or Pt)

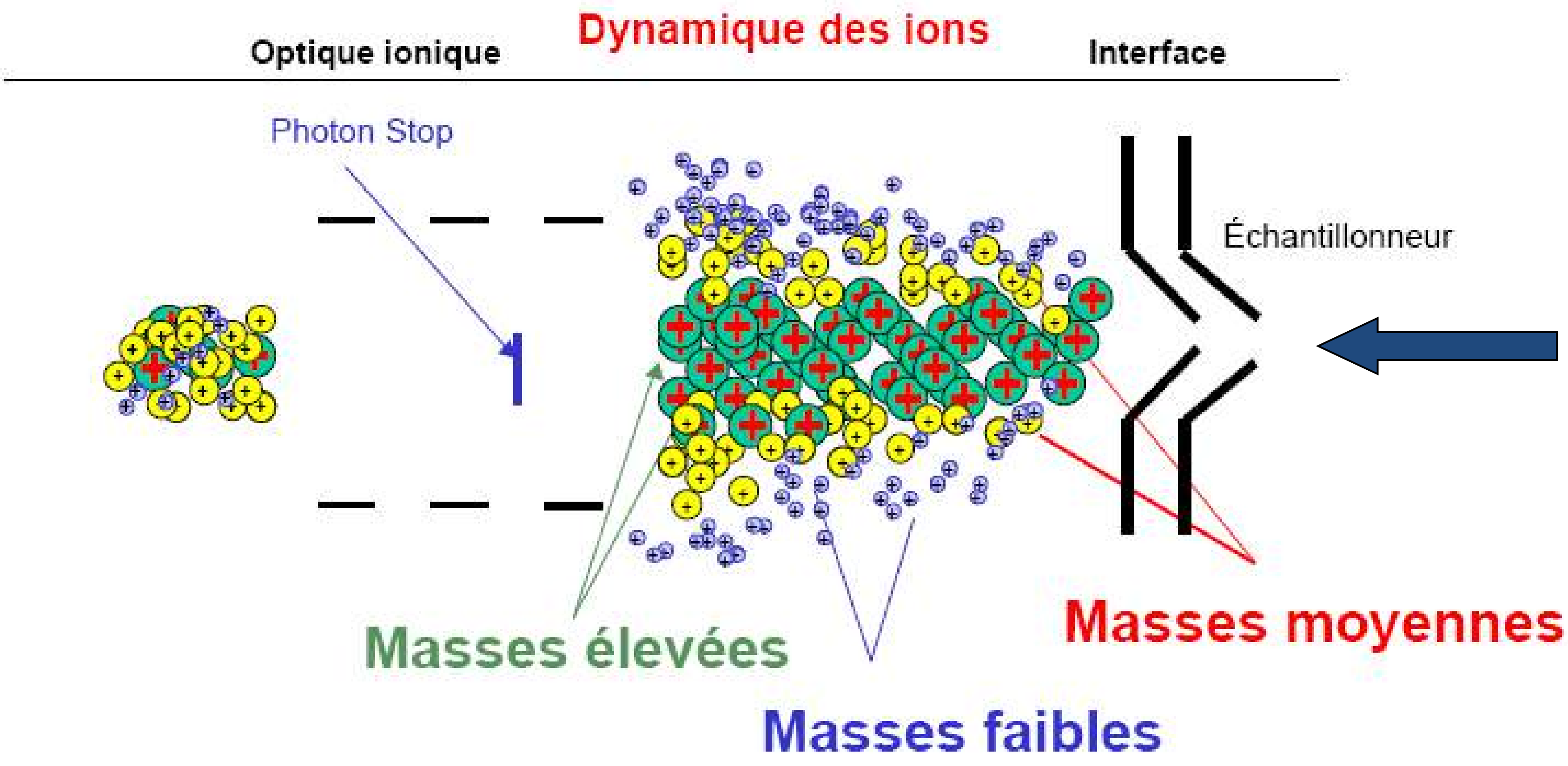
3.1.2. ICP-MS: Schema principle



3.1.2. ICP-MS: *2. Ion lens (Optique ionique)*

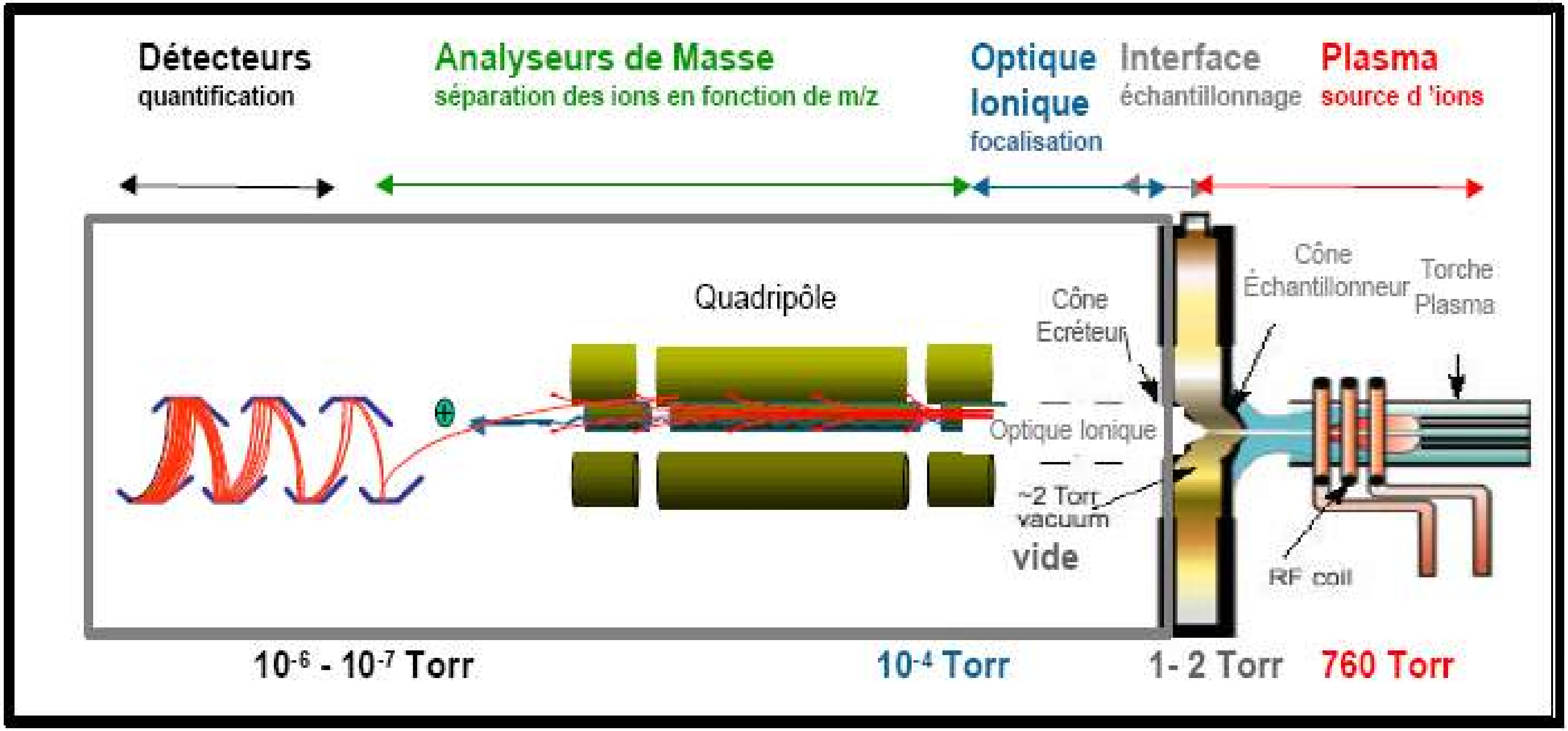
- Aims:
  - Optimize the trajectory of the ions for a better focus in the mass analyzer
  - Stop the photons so that they do not reach the detector.
- Ion lenses including photon stop

3.1.2. ICP-MS: *2. Ion lens*



Ion lenses (electrostatical lenses)

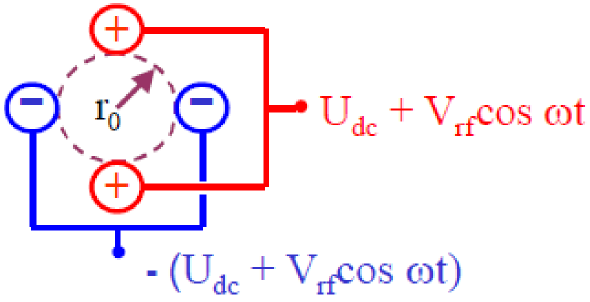
3.1.2. ICP-MS: Schema principle

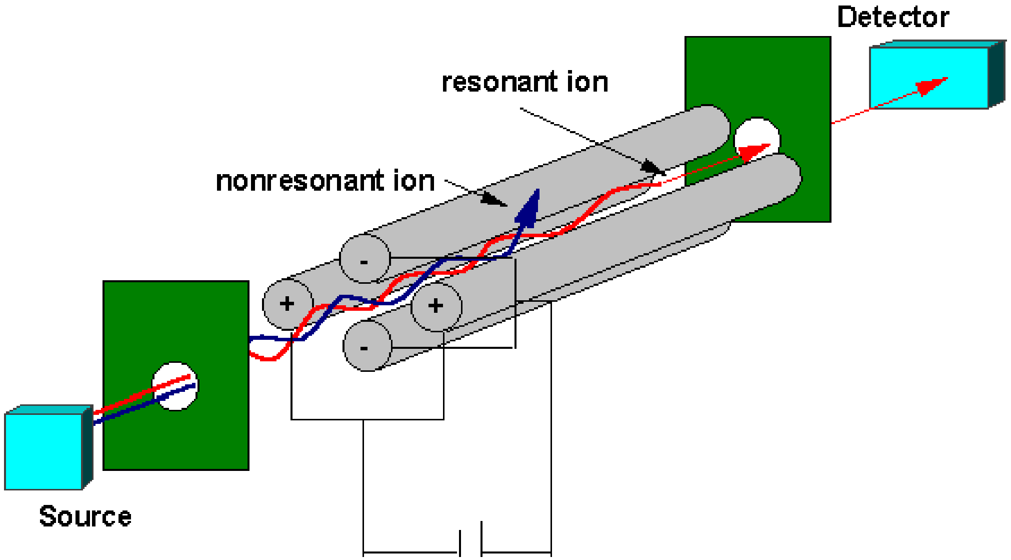


3.1.2. ICP-MS: *3. Mass analyzers*

- **Main types:**
  - **Mass filtering device:**
    - Quadrupole (*quadripôle*)
    - Ion traps (*Trappe à ions*)
  - **Ion transport device:**
    - time-of-flight (TOF) (*Temps de vol*)
  - **Selection in space:**
    - Magnetic sector fileld (*Secteur à champs magnétique*)

3.1.2. ICP-MS: Quadrupole





Equations différentielles dites équations de Matthieu dont la solution permet d'estimer la trajectoire d'un ion en fonction de m, U et V

Pour une distance $2r_0$ séparant deux barres diamétralement opposées :

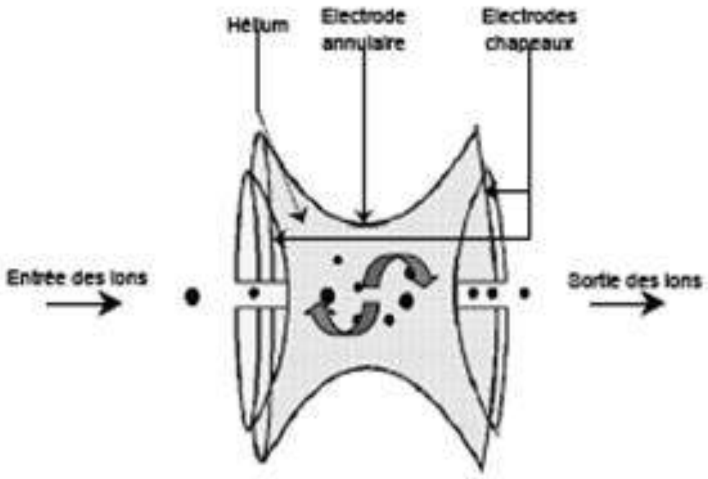
$$\frac{\partial^2 x}{\partial\left(\omega t/2\right)^2} + \left[a + 2q\cos\left(2\left(\omega t/2\right)\right)x\right] = 0$$

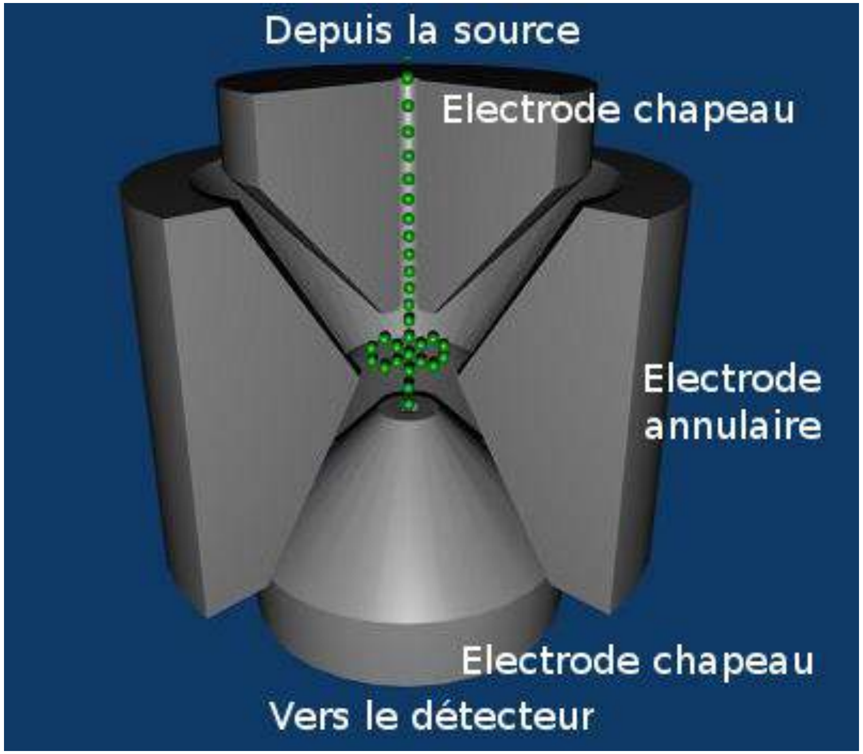
$$\frac{\partial^2 y}{\partial\left(\omega t/2\right)^2} - \left[a + 2q\cos\left(2\left(\omega t/2\right)\right)y\right] = 0$$

où $a = \frac{8zeU}{mr_0^2\omega^2}$ et $q = \frac{4zeV}{mr_0^2\omega^2}$; soit $\frac{a}{q} = \frac{2U}{V}$

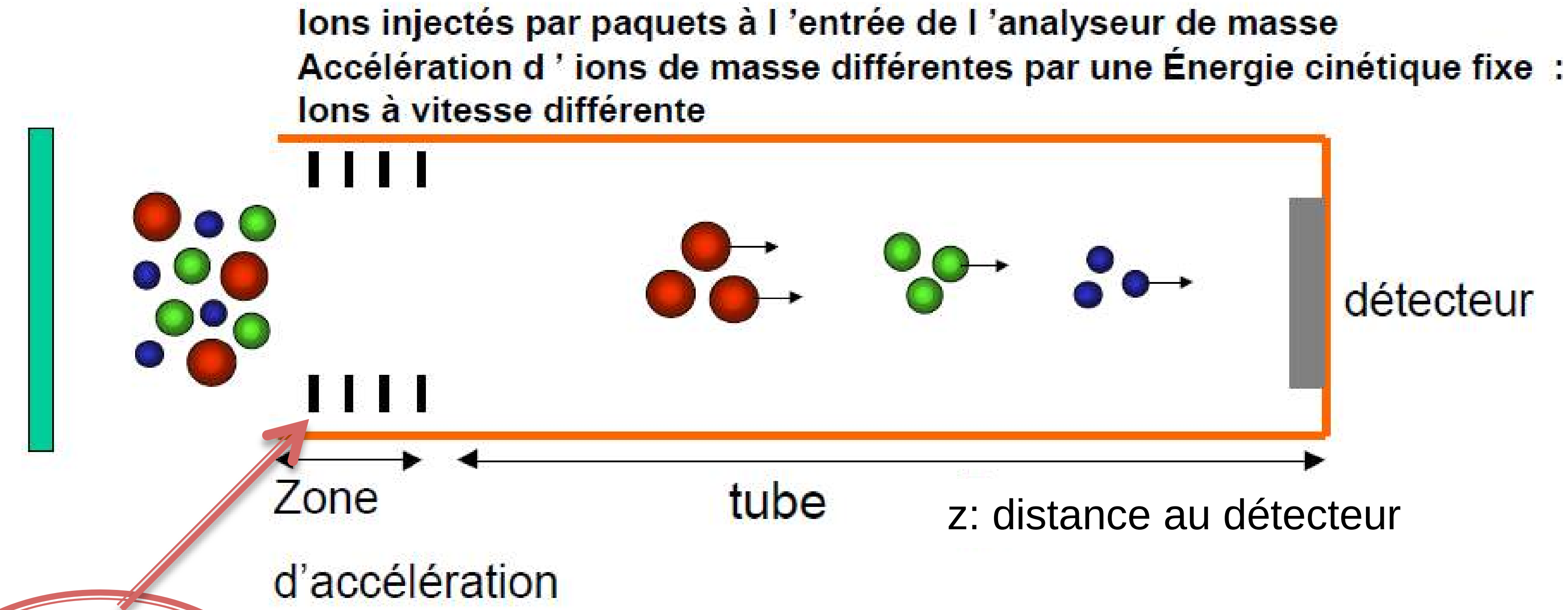
3.1.2. ICP-MS: Ion trap

- Trappe à ions ou piège à ions = quadrupole mass analyzer, using two hyperbolic metal electrodes (end caps) facing each other, and a ring electrode placed halfway between the end cap electrodes





3.1.3. ICP-MS: Time-of-Filght



Ions injectés par paquets à l 'entrée de l 'analyseur de masse

Accélération d ' ions de masse différentes par une Énergie cinétique fixe :

Ions à vitesse différente

z: distance au détecteur

Champ électrique (tension U)

$$Ec = 1/2mv^2 = z.U$$

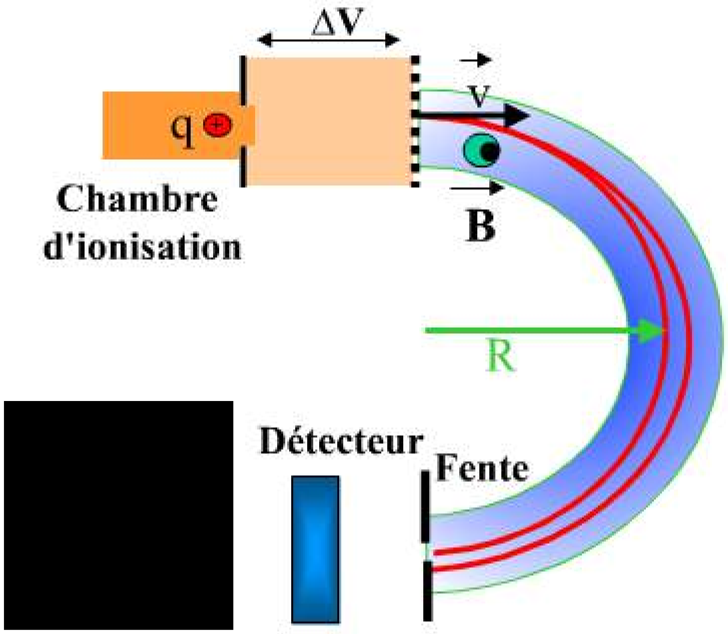
3.1.3. ICP-MS: Magnetic Sector: Principle

Action of magnetic field

Pour un mouvement circulaire uniforme, ona F= force centripète

$$F = z.v.B = mv^2/R$$

Rayon de courbure $R = m.v / z.B$



La vitesse à l'entrée est telle que

$\frac{1}{2} mv^2 = z\Delta V$ (tension d'accélération)

$$m/z = B^2.R^2/2\ \Delta V$$

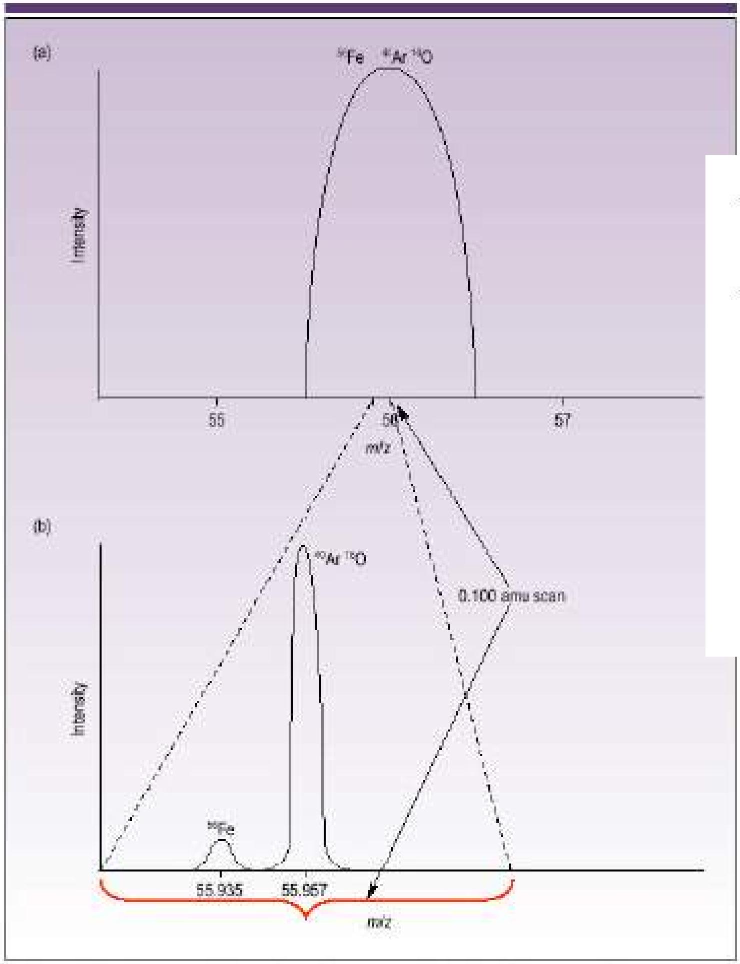
Si on fait varier B et delta V, on peut faire passer tous les ions par la fente…

3.1.3. ICP-MS: *3. Mass analyzers*

Résolution : ^{56}Fe - $^{40}Ar^{16}O$

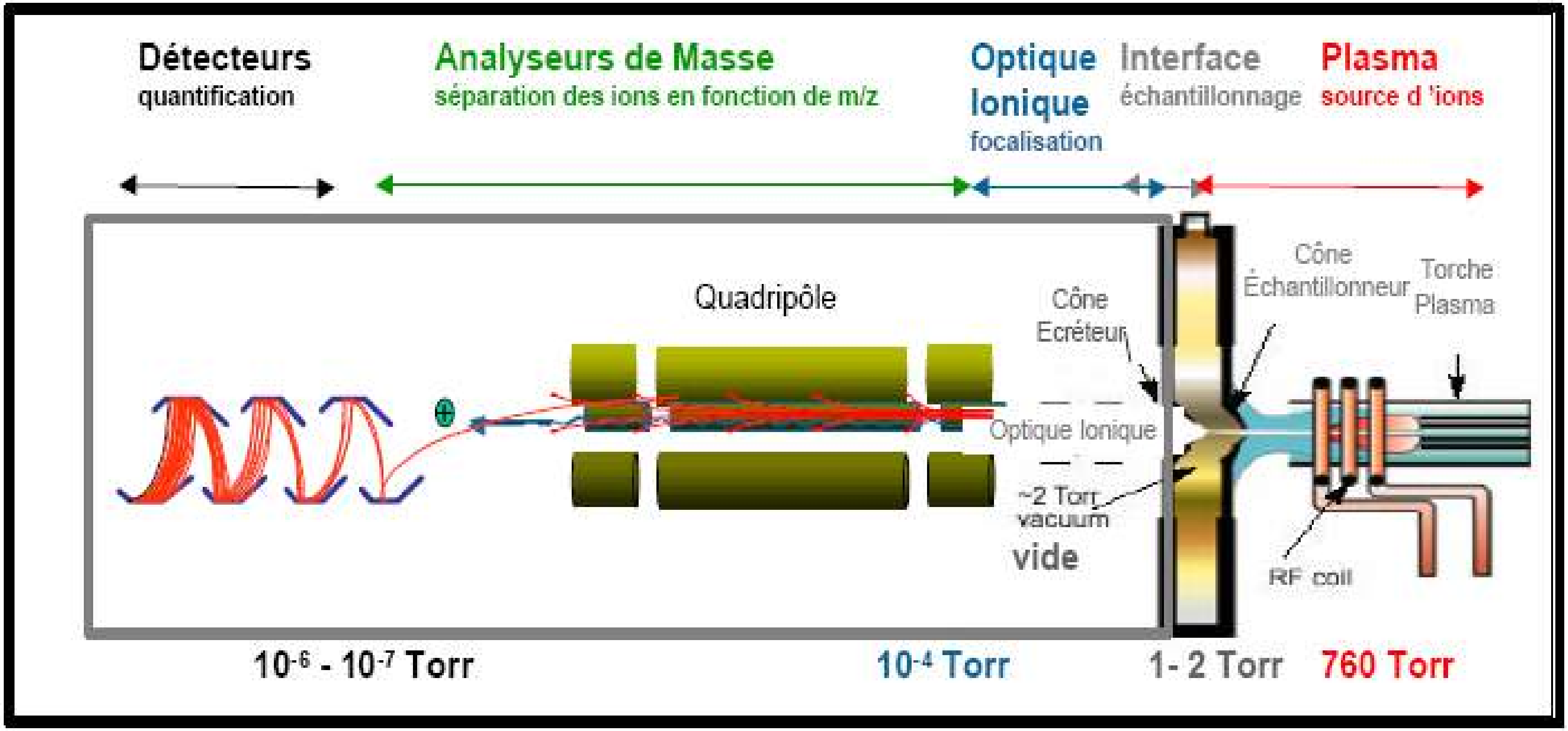
QUAD

Secteur Magnétique



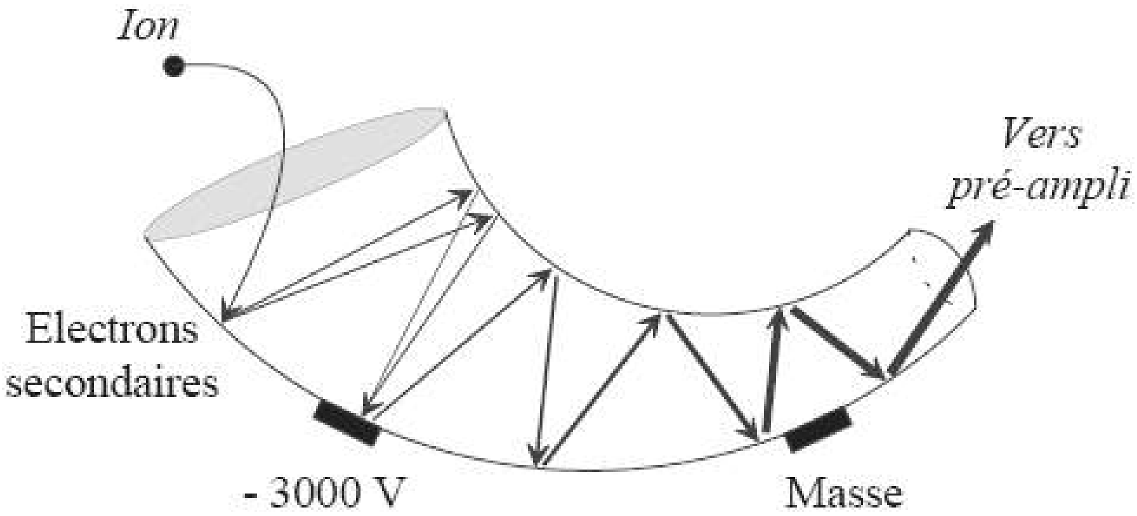
Systèmes	ΔM
Quadripôle	0.8
Trappe à ions	0.18
Temps de vol	0.12 - 0.5
Secteur magnétique	0.01 - 0.02

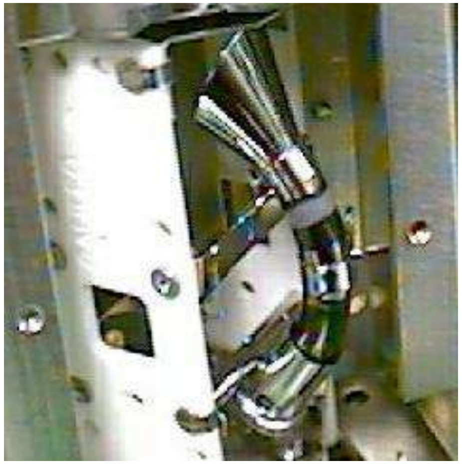
3.1.2. ICP-MS: Schema principle



3.1.B. ICP-MS: *4. Detection*

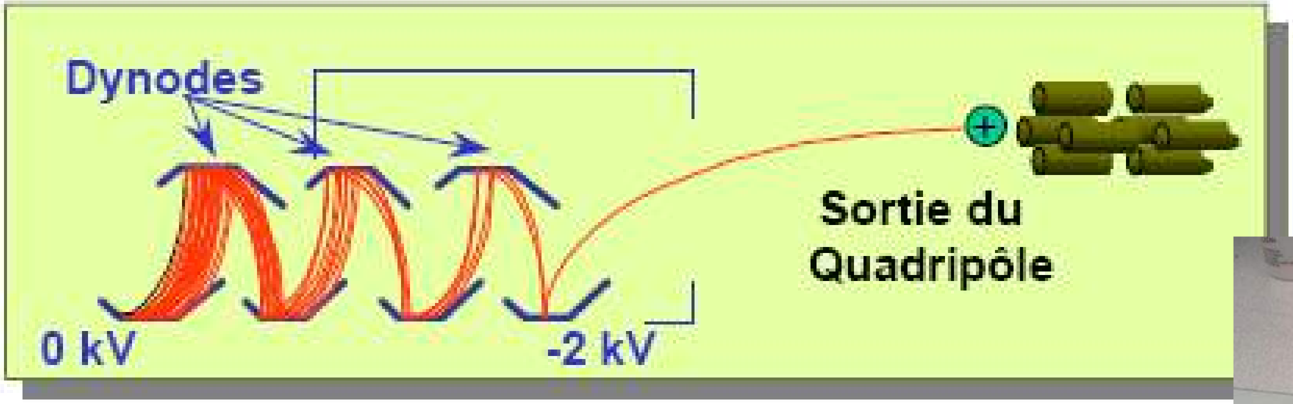
- Conversion of ions into a quantifiable electrical signal proportional to the number of ions
  - **Channeltron**

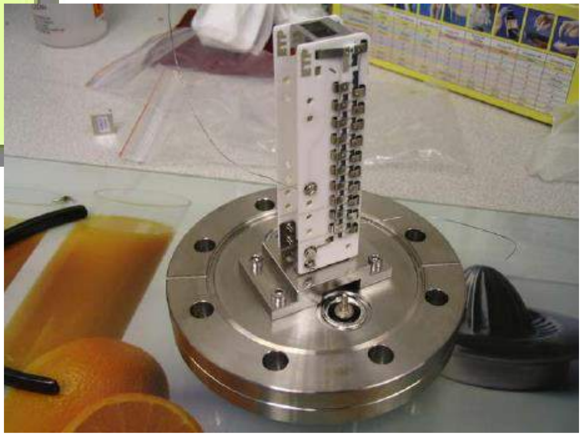




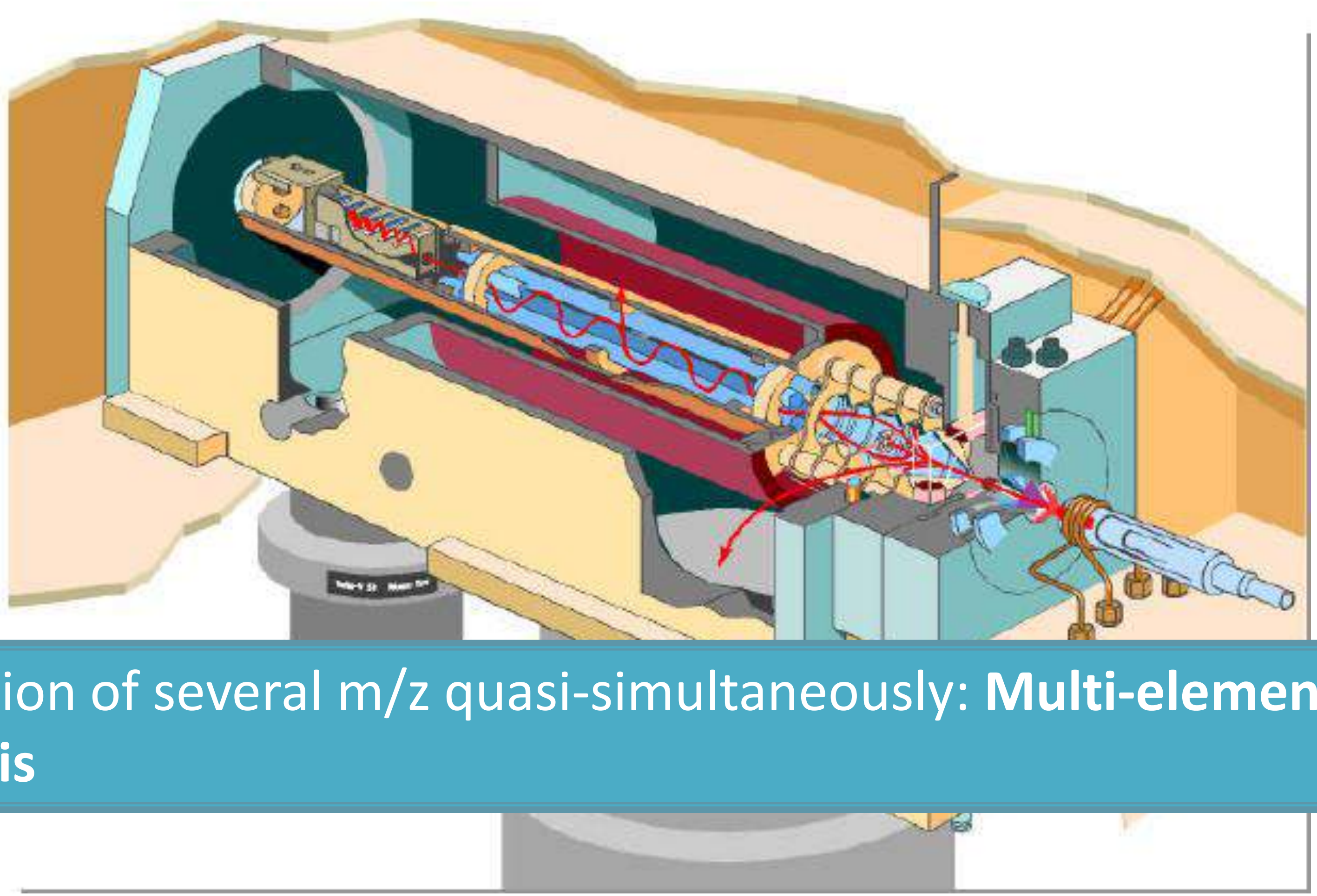
3.1.B. ICP-MS: *4. Detection*

- Conversion of ions into a quantifiable electrical signal proportional to the number of ions
  - **Channeltron**
  - **Discrete Dynode Electron Multiplier : DDEM**





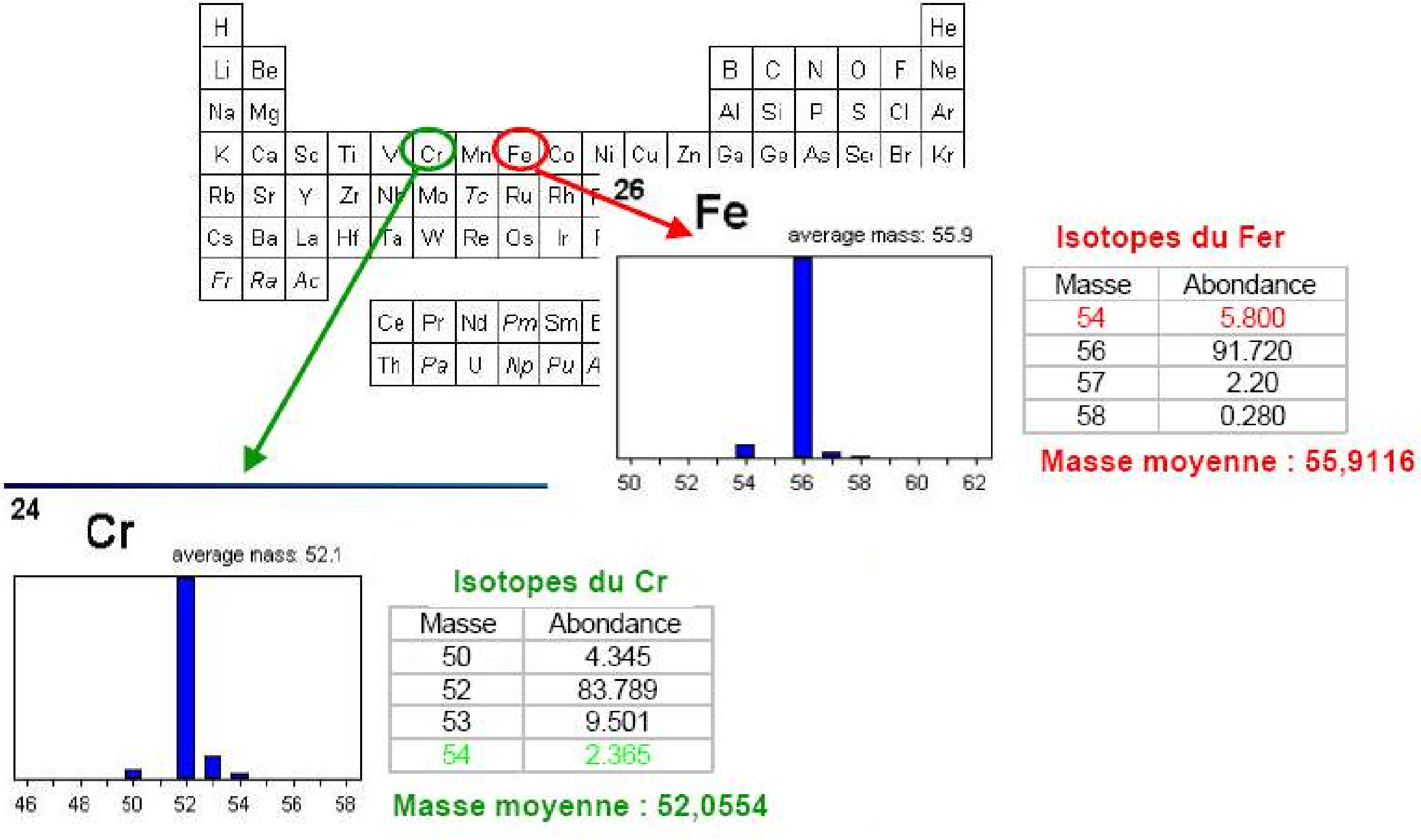
3.1.B. ICP-MS: General system



Detection of several m/z quasi-simultaneously: **Multi-elemental analysis**

3.1.B. ICP-MS: Signal measurement

Mass/charge spectra:



Isotopes du Fer

Masse	Abondance
54	5.800
56	91.720
57	2.20
58	0.280

Masse moyenne : 55,9116

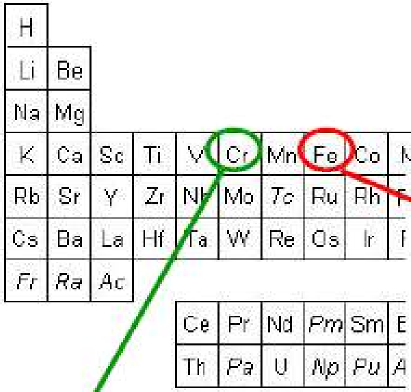
Isotopes du Cr

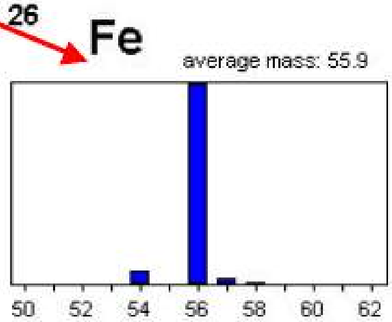
Masse	Abondance
50	4.345
52	83.789
53	9.501
54	2.365

Masse moyenne : 52,0554

3.1.B. ICP-MS: Interferences

Isobaric interferences:

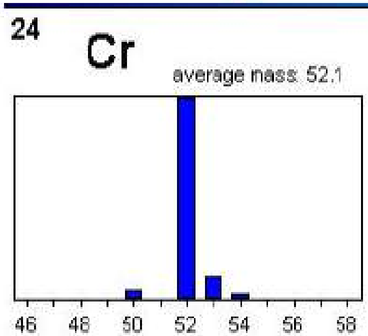




Isotopes du Fer

Masse	Abondance
54	5.800
56	91.720
57	2.20
58	0.280

Masse moyenne : 55,9116



Isotopes du Cr

Masse	Abondance
50	4.345
52	83.789
53	9.501
54	2.365

Masse moyenne : 52,0554

Interférences Isobariques

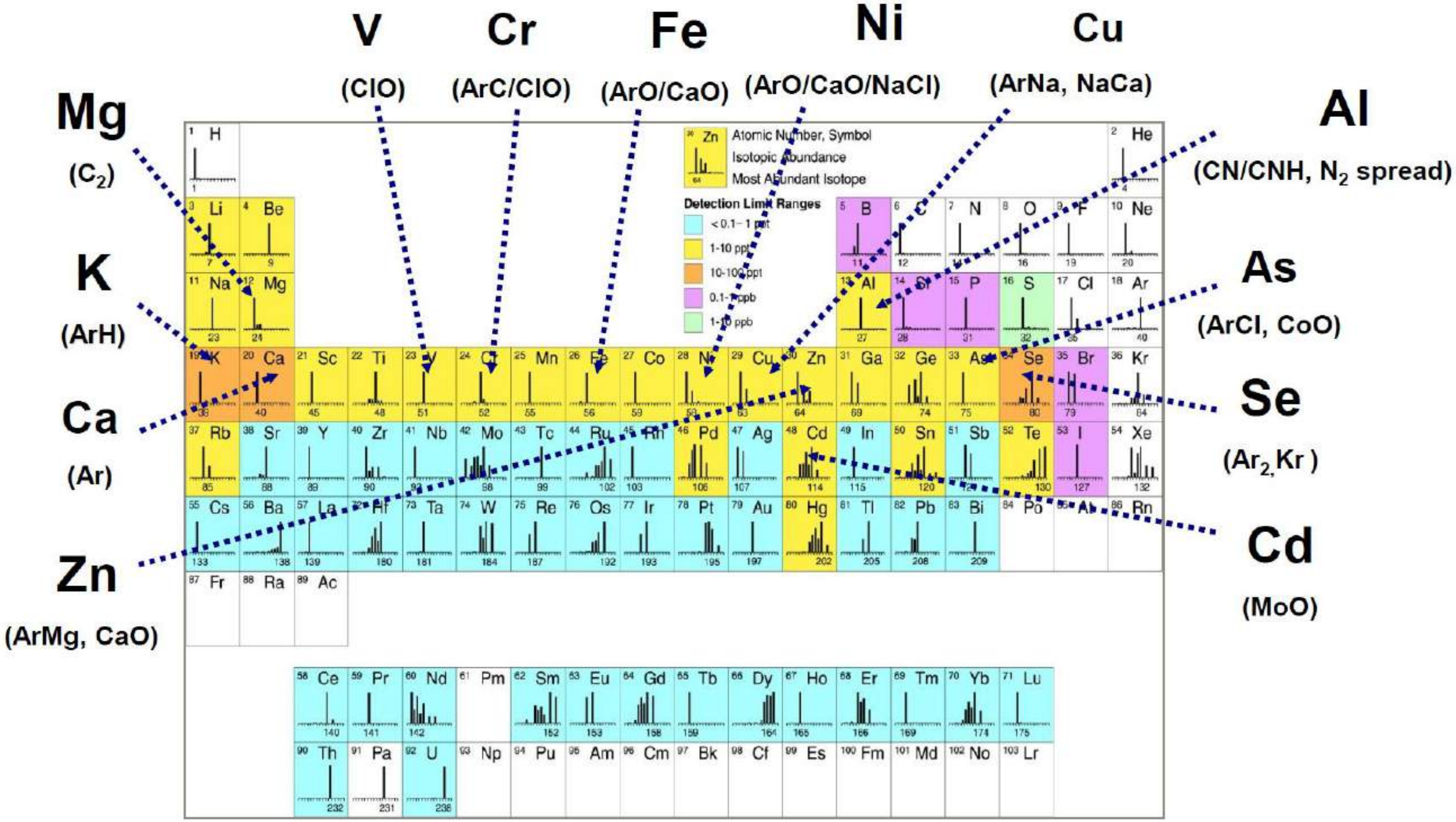
Masse 54

Isotope du Fe
Isotope du Cr

3.1.B. ICP-MS: Interferences

- Spectral interferences:
  - Isobaric interferences: elements with a same m/z ratio:
    - Isotopes with the same m/z (Ex: $^{54}Fe^+$ and $^{54}Cr^+$)
    - Doubly charged ions à M/2
      - ☐Ex: $^{136}Ba^{2+}$ and $^{68}Zn^+$
  - Polyatomic Interference, formed with Ar and major elements of the matrix (O, H, N)

3.1.B. ICP-MS: Polyatomic Interferences



3.1.B. ICP-MS: Polyatomic interferences: how to get by?

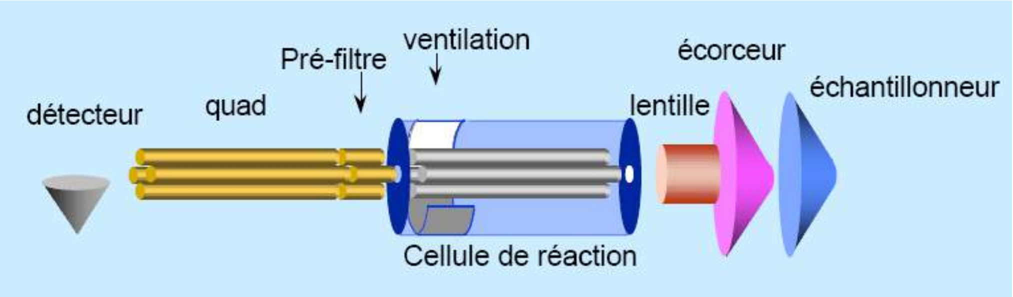
- Collision/Reaction cell:
- Based on element reactivity:
  - Reaction forming neutral species
    - Ex: $^{40}Ar^{16}O^+$ and $^{56}Fe^{+}$:

$ArO^+ + NH_3 \Leftrightarrow ArO + NH_3^+$

Rate constant 1.4×10^{-9}

$Fe^+ + NH_3 \Leftrightarrow Fe + NH_3^+$

Rate constant 9.1×10^{-12}



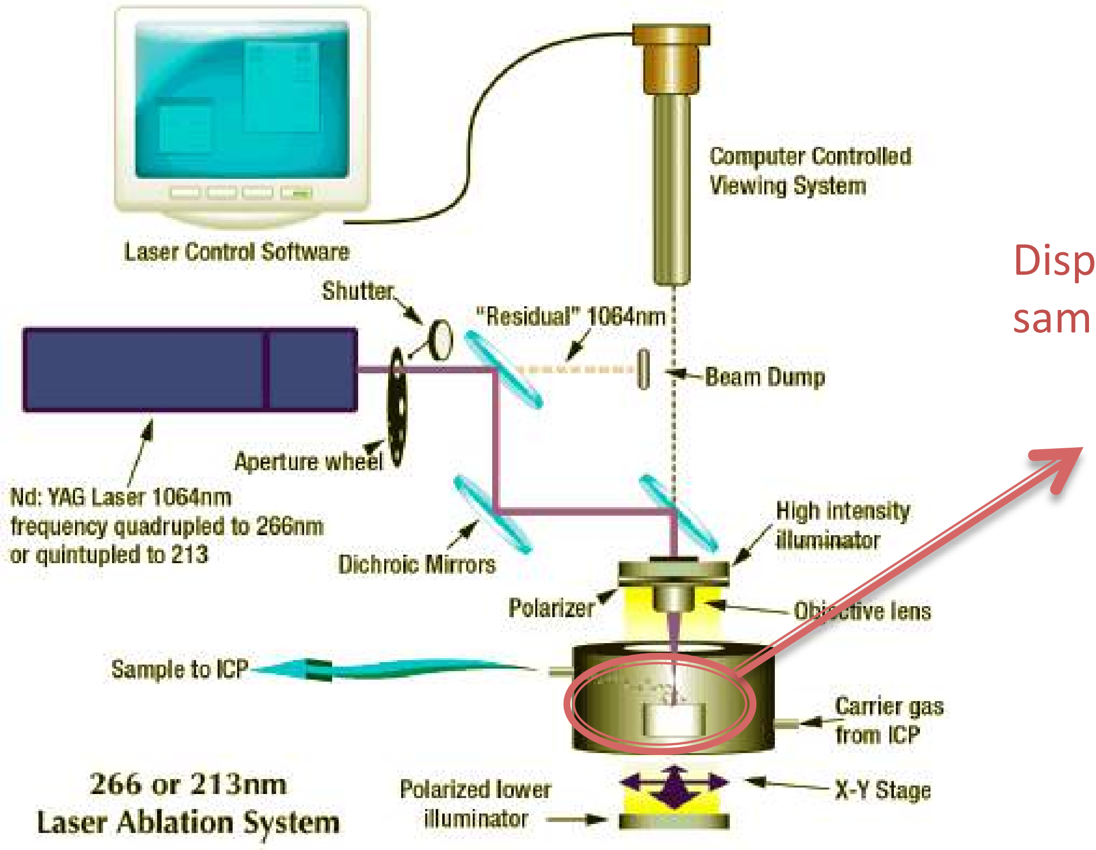
  - Réactions forming ions with different masses
    - Ex: $^{80}Ar_2^+$ and $^{80}Se^+$

$Ar_2^+ + CH_4 \Leftrightarrow Ar_2H^+ + CH_3$

- Based on buffer gas (He) or collision gas (N_2,H_2)
  - The polyatomic interferes are dissociated by collisions

3.1.B. ICP-MS and laser ablation

- For elemental measurements from solid samples without dissolution:
  - Case of layered samples (par ex.: sediment cores, tree rings…)



Dispersion of sample as aerosols

3.1.B. ICP-MS and HPLC

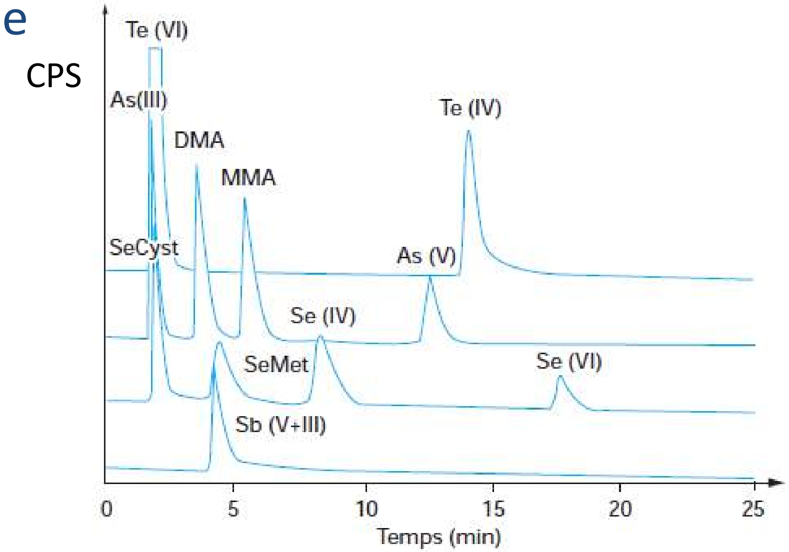
- ICP-AES et ICP-MS → No information about redox or organic/inorganic speciation
  - Possibility to associate ICP to chromatography in order to separate the different chemical forms before elemental

  → **HPLC-ICP-MS**
    - Measurements for redox speciation of metals (CrIII or CrVI)
    - Measurements for organic speciation of metals (inorganic or organic As)

3.1.B. ICP-MS and HPLC

- HPLC: Separation of studied molecules (separation from polarity or charges)
- ICP-MS: Determination of metals concentrations in each of molecules
  - Detection more sensitive than other classical techniques in HPLC → possibility to measure trace elements
  - Multi-elemental analysis → Possibility to measure several metals simultaneously in a same molecule

Ex: Simultaneaous speciation of arsenic, selenium, antomony and tellurium



3.1. Finally

ICP-AES	ICP-MS
µg. L^{-1} → ~1000 mg. L^{-1}	ng. L^{-1} → mg. L^{-1}
robust	versatile
Average cost	expensive

NF EN ISO 17294:2007
Qualité de l'eau - Application de la spectrométrie de masse avec plasma à couplage inductif (ICP-MS)

NF ISO 11885:2009 Qualité de l'eau - Dosage d'éléments choisis par spectroscopie d'émission optique avec plasma induit par haute fréquence (ICP-OES)

NF ISO 15202:2012
Air des lieux de travail - Détermination des métaux et métalloïdes dans les particules en suspension dans l'air par spectrométrie d'émission atomique avec plasma à couplage inductif

3. Metals analysis:

- **But**: heavy and trace metals analysis
- **Techniques applicable to liquid and solid phases (after dissolution):**
  - Atomic Absoprtion Spectrometry
  - Atomic Emission Spectrometry
  - Mass Spectrometry

In coupling with plasma technology:
ICP-AES et ICP-MS

- **Techniques applicable to soild phases**:
  - X-ray Spectrometry

3.2. X-ray Spectrometry

- **X-Ray?**

THÉORIE, DOMAINES DU SPECTRE ÉLECTROMAGNÉTIQUE

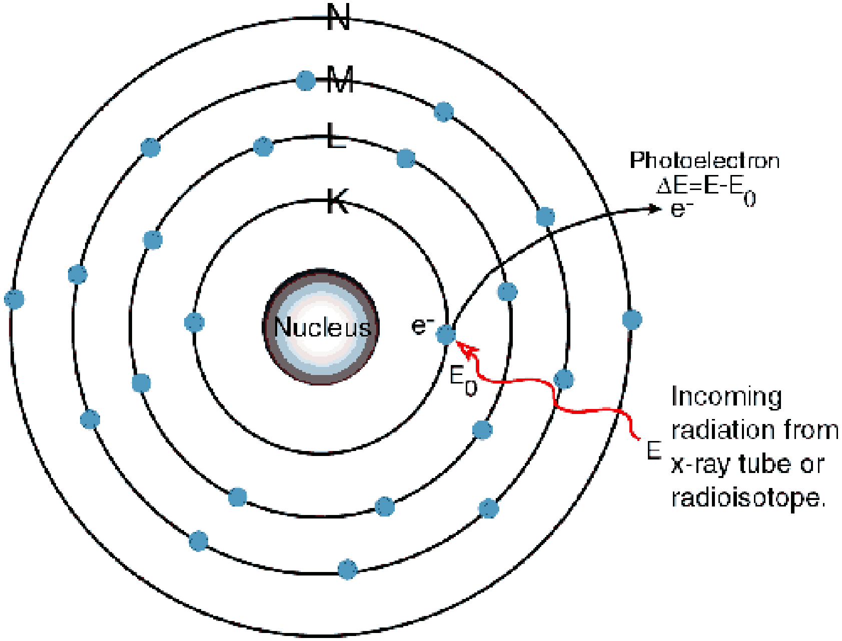
discovered on November 8, 1895 by Wilhelm Conrad RÖNTGEN (Germ.)

Publication on December 22, 1895 in an article at the Academy of sciences with as an illustration the "radiography" of the hand of his wife

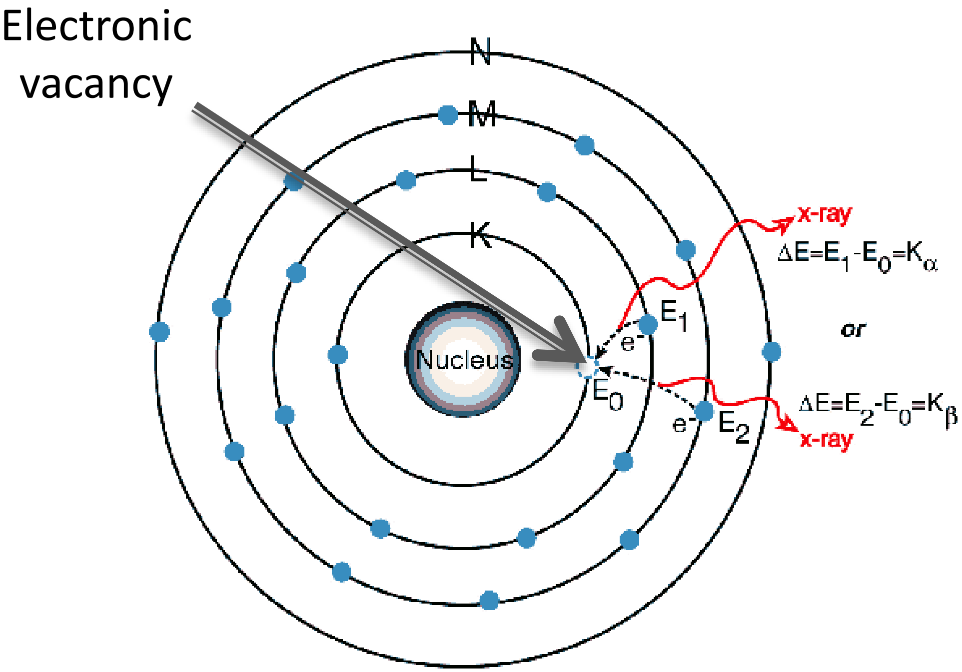

Photographie de la main de Anna Bertha Ludwig Roentgen prise le 22 décembre 1895

3.2. Spectrométrie des rayons X: Principe

- X-ray emissions, how's it possible?



1. An orbital electron is knocked out of the inner electron shell thanks to incoming X-ray from electronic bombardment

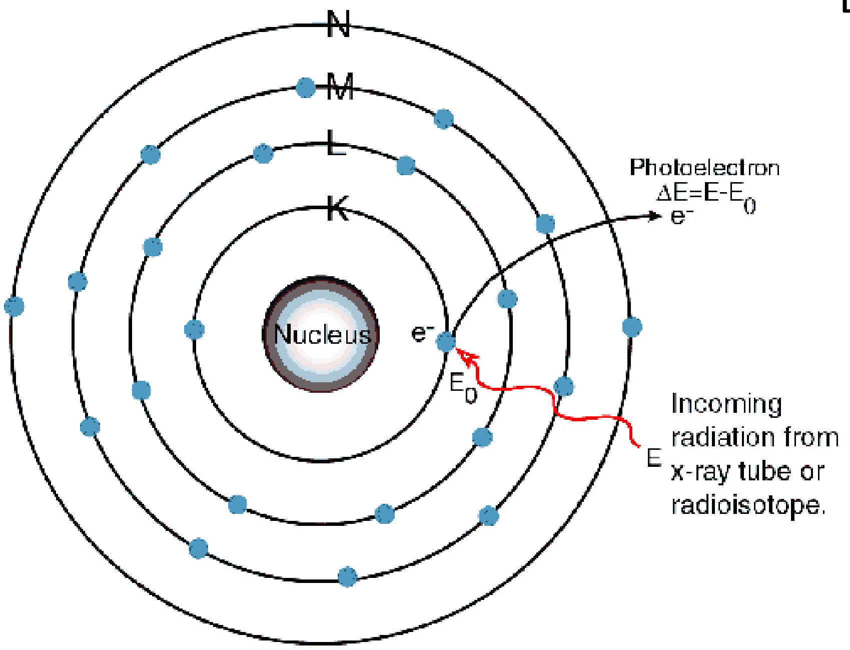

Electronic vacancy

2. As a result electrons from higher energy levels (L or M) then fill up the vacancy on K with energy loss by X-ray photons emission

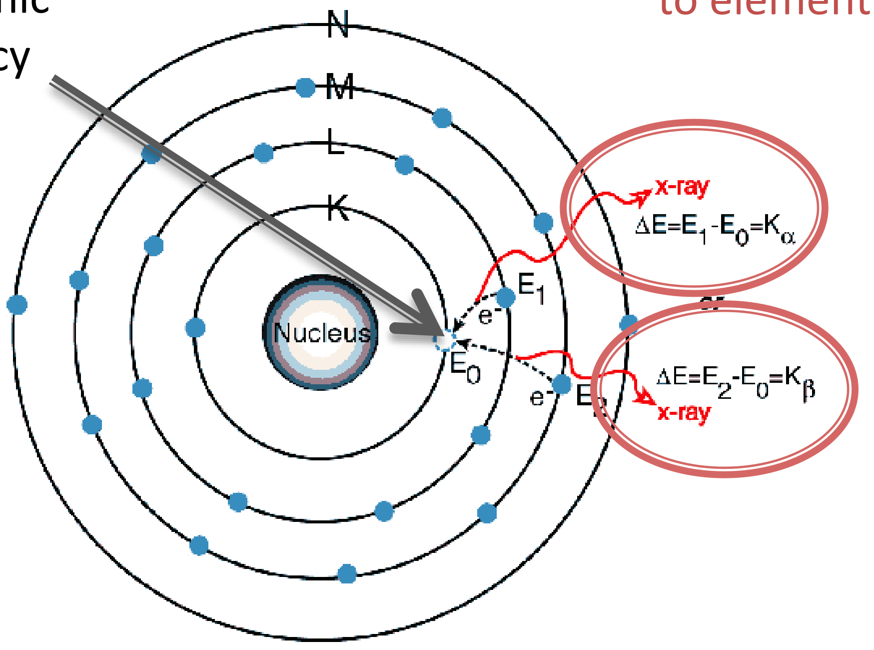
3.2. Spectrométrie des rayons X: Principe

- X-ray emissions, how's it possible?

Energy and wavelength of emitted photons are related to element



Electronic vacancy

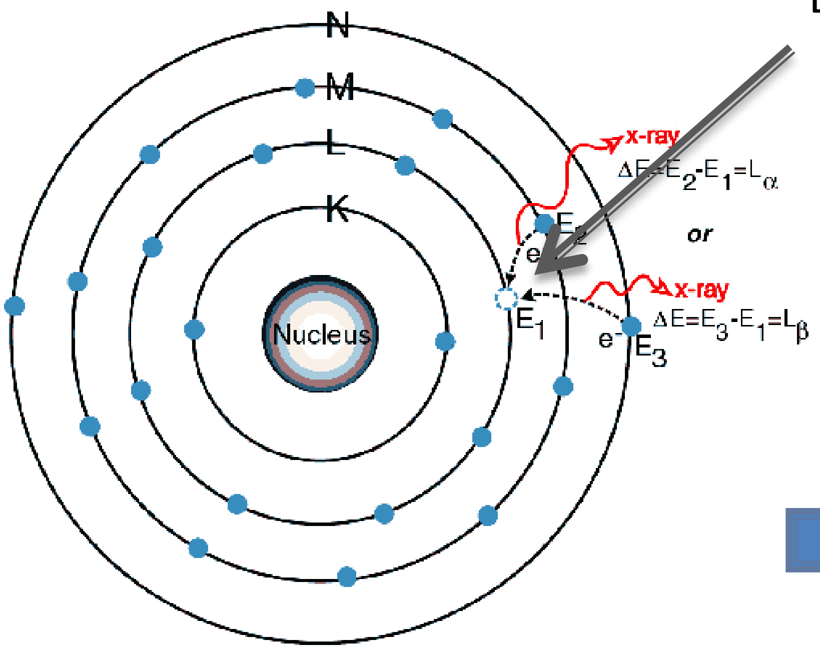


1. An orbital electron is knocked out of the inner electron shell thanks to incoming X-ray from electronic bombardment

2. As a result electrons from higher energy levels (L or M) then fill up the vacancy on K with energy loss by X-ray photons emission

3.2. Spectrométrie des rayons X: Principe

- X-ray emissions, how's it possible?



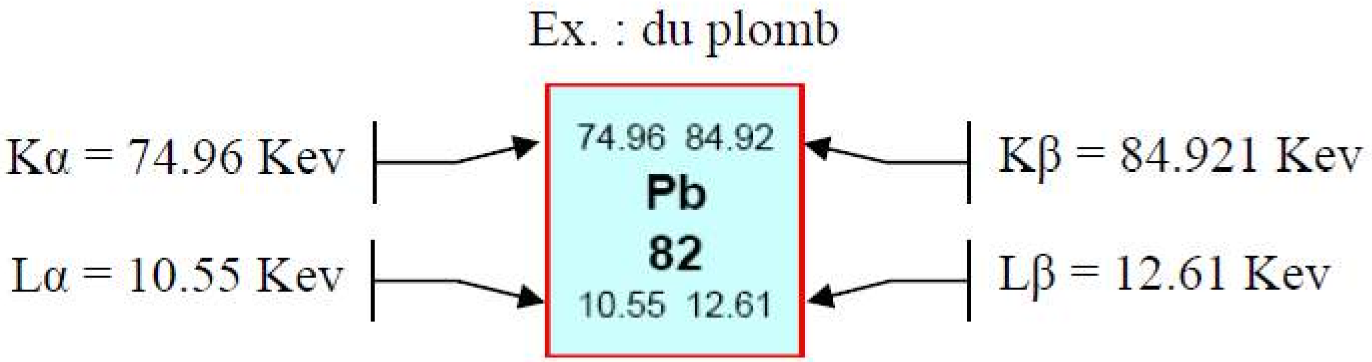
Electronic vacancy

For one knocked electron → several electronic transitions → several emitted X-ray photons

1. The new vacancy is filled by electrons transfert from higher energy levels (M or N) with other X-Ray photons emissions

3.2. X-ray Spectrometry

- Conditions to create electron vacancy
  - Electrons of the inner layer so energy> ionization energy which corresponds to electrons of the outer layers

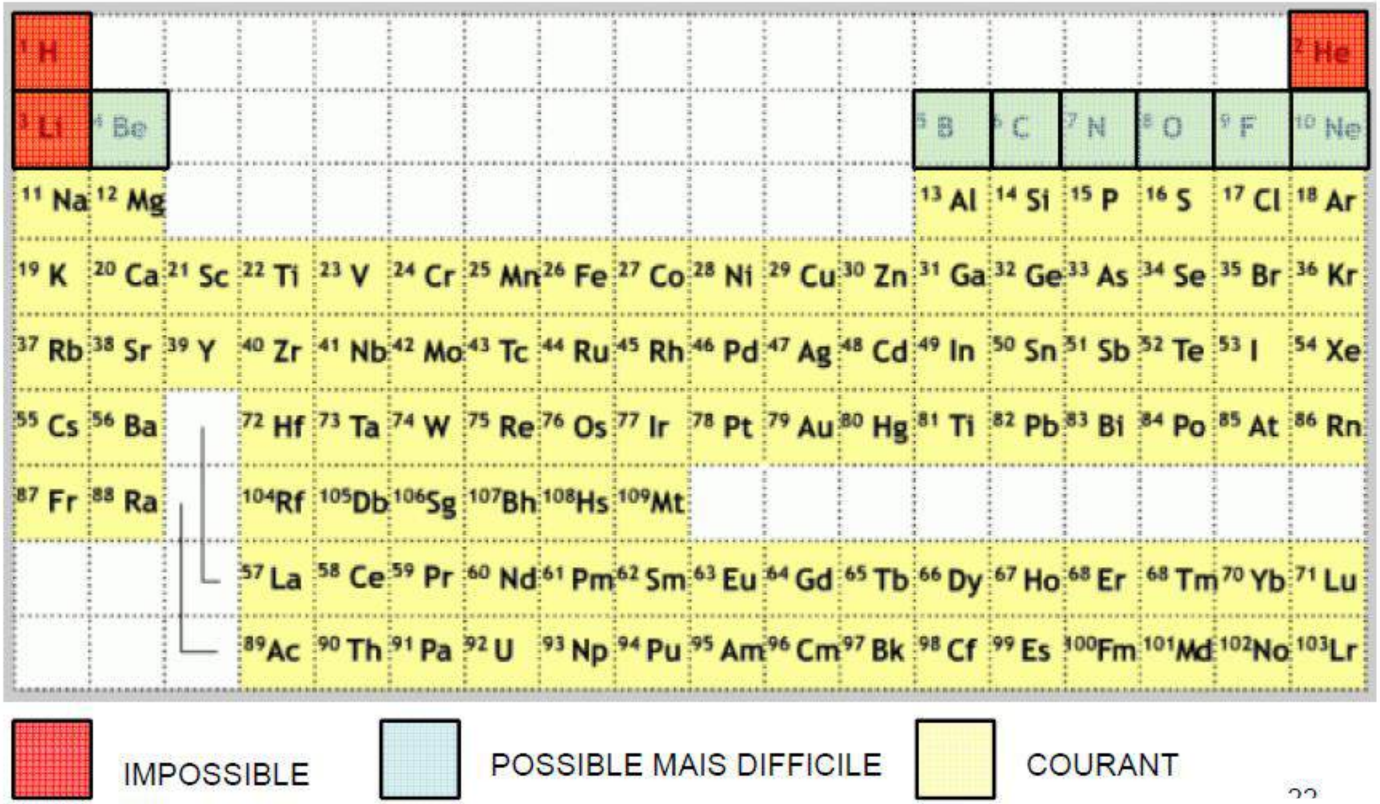


Whereas the first ionization energy of Pb is 7.4 eV

  - The X-ray photon of wavelength λ (E = h.c / λ) will be exciter only if it has enough energy to allow the ejection of the electron.

3.2. X-ray Spectrometry

- Conditions to create electron vacancy
  - There must be possibility of electronic transitions between K and L:



🟥 1 H																	🟥 2 He
🟥 3 Li	🟦 4 Be											🟦 5 B	🟦 6 C	🟦 7 N	🟦 8 O	🟦 9 F	🟦 10 Ne
🟨 11 Na	🟨 12 Mg											🟨 13 Al	🟨 14 Si	🟨 15 P	🟨 16 S	🟨 17 Cl	🟨 18 Ar
🟨 19 K	🟨 20 Ca	🟨 21 Sc	🟨 22 Ti	🟨 23 V	🟨 24 Cr	🟨 25 Mn	🟨 26 Fe	🟨 27 Co	🟨 28 Ni	🟨 29 Cu	🟨 30 Zn	🟨 31 Ga	🟨 32 Ge	🟨 33 As	🟨 34 Se	🟨 35 Br	🟨 36 Kr
🟨 37 Rb	🟨 38 Sr	🟨 39 Y	🟨 40 Zr	🟨 41 Nb	🟨 42 Mo	🟨 43 Tc	🟨 44 Ru	🟨 45 Rh	🟨 46 Pd	🟨 47 Ag	🟨 48 Cd	🟨 49 In	🟨 50 Sn	🟨 51 Sb	🟨 52 Te	🟨 53 I	🟨 54 Xe
🟨 55 Cs	🟨 56 Ba		🟨 72 Hf	🟨 73 Ta	🟨 74 W	🟨 75 Re	🟨 76 Os	🟨 77 Ir	🟨 78 Pt	🟨 79 Au	🟨 80 Hg	🟨 81 Ti	🟨 82 Pb	🟨 83 Bi	🟨 84 Po	🟨 85 At	🟨 86 Rn
🟨 87 Fr	🟨 88 Ra		🟨 104 Rf	🟨 105 Db	🟨 106 Sg	🟨 107 Bh	🟨 108 Hs	🟨 109 Mt									
			🟨 57 La	🟨 58 Ce	🟨 59 Pr	🟨 60 Nd	🟨 61 Pm	🟨 62 Sm	🟨 63 Eu	🟨 64 Gd	🟨 65 Tb	🟨 66 Dy	🟨 67 Ho	🟨 68 Er	🟨 68 Tm	🟨 70 Yb	🟨 71 Lu
			🟨 89 Ac	🟨 90 Th	🟨 91 Pa	🟨 92 U	🟨 93 Np	🟨 94 Pu	🟨 95 Am	🟨 96 Cm	🟨 97 Bk	🟨 98 Cf	🟨 99 Es	🟨 100 Fm	🟨 101 Md	🟨 102 No	🟨 103 Lr

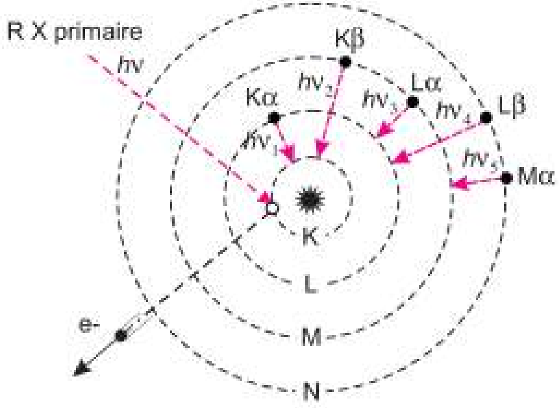
🟥 IMPOSSIBLE

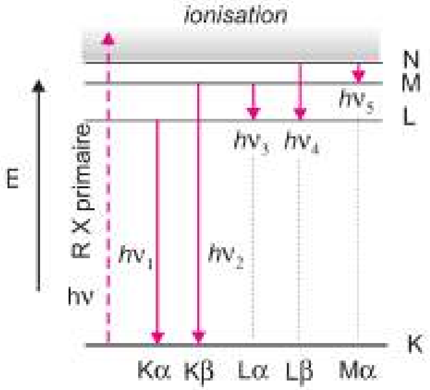
🟦 POSSIBLE MAIS DIFFICILE

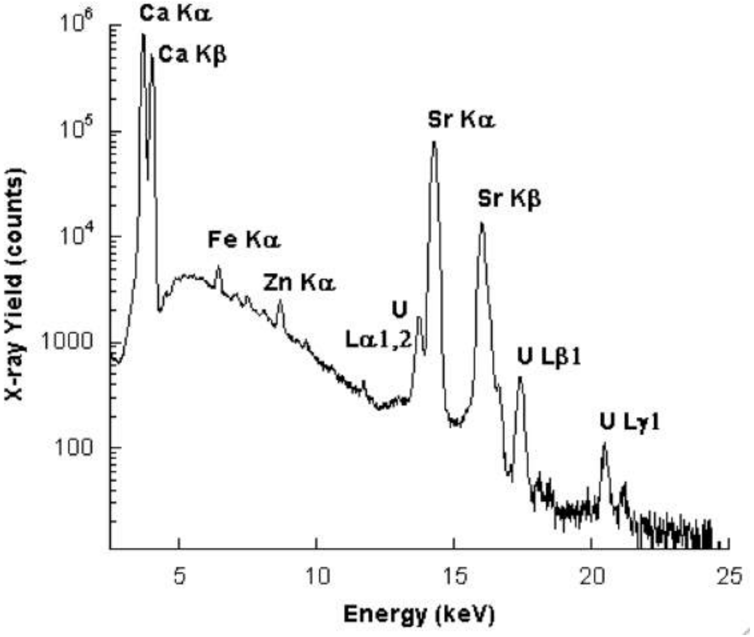
🟨 COURANT

3.2. X-ray Spectrometry and analytical chemistry

- Principle of use in analytical chemistry is based on the counting of X photons emitted after knocking electrons of the inner shells (K and L):
  - Each X-ray photon has a level of energy specific to each element
  - The quantity of emitted photons is proportional to the quantity of the element present in the sample





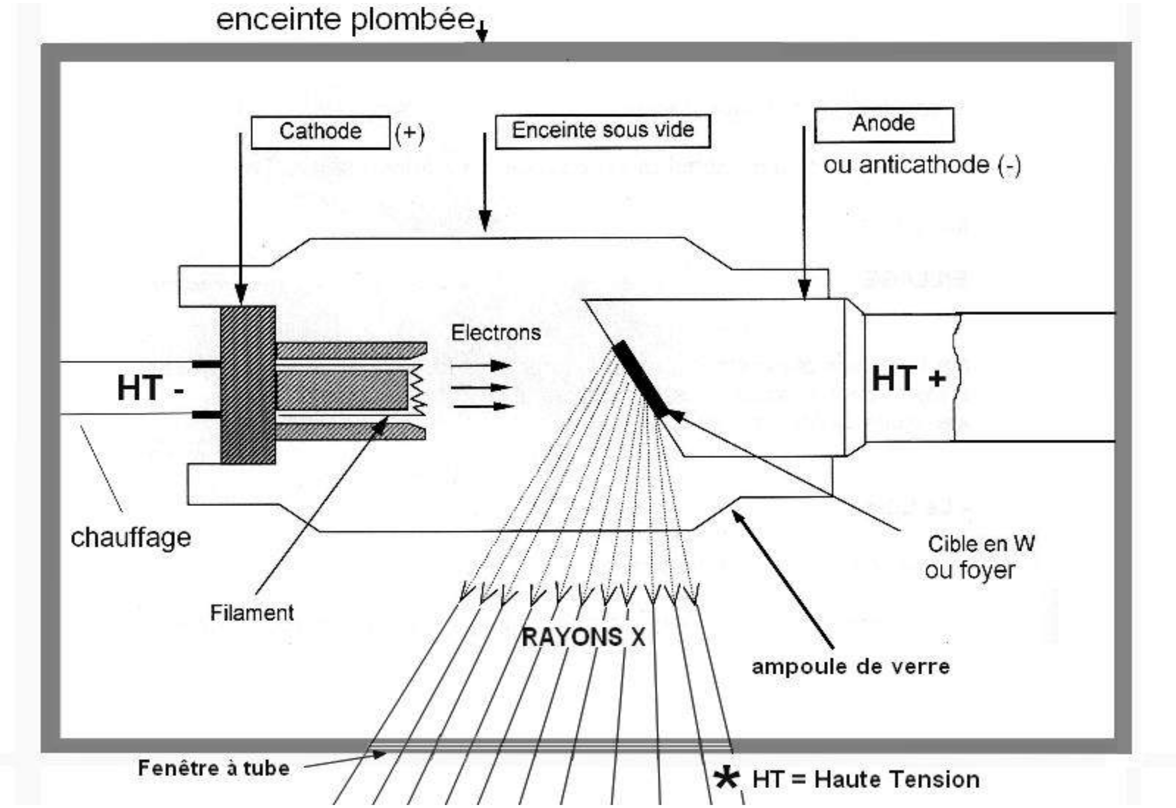


3.2. X-ray Spectrometry

- To be able to study a sample, we need:
  - To generate X-rays that can excite an atom and eject an electron
    - X-ray fluorescence (*XRF*) when emissions come from a material that has been excited by bombarding with high-energy X-rays

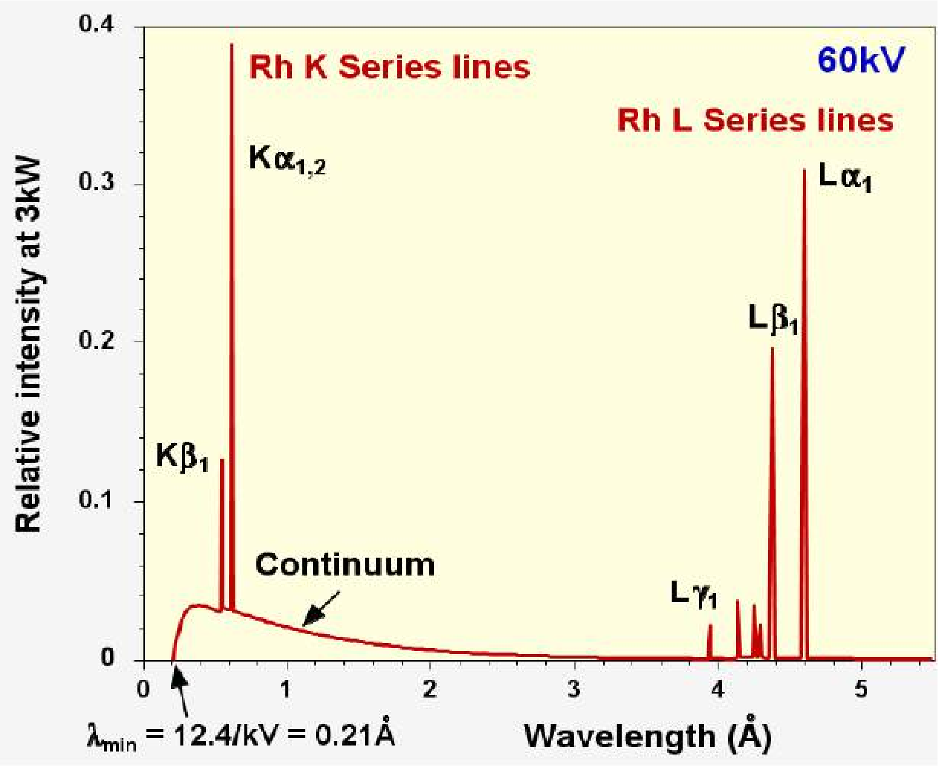
3.2. X-ray Spectrometry

- To produce primary X-ray photons (or excitators) → Use of an X-ray tube



3.2. X-ray Spectrometry

- X-ray tube: Practically
  - Target tube is generally in **Rhodium** (Rh) because
    - Exotic enough not to be analyzed
    - characteristic energies of this element are simultaneously suitable for exciting both heavy and light elements.



3.2. X-ray Spectrometry and analytical chemistry

- To be able to study a sample, we need:
  - To generate X-rays that can excite an atom and eject an electron
    - X-ray fluorescence (*XRF*) when emissions come from a material that has been excited by bombarding with **high-energy X-rays**
  - To catch, select and count the emitted photons
    - Energy dispersive system (EDXRF)
    - Wavelength dispersive system (WDXRF)

3.2. X-ray Spectrometry

- 2 types of X-ray detectors
  - Energy dispersive X-ray : uses difference of energies

$$E = h.\upsilon = \frac{1.2396}{\lambda}$$

Quanta theory

  - Wavelength dispersive X-ray fluorescence technique (WDXRF): uses diffraction effect

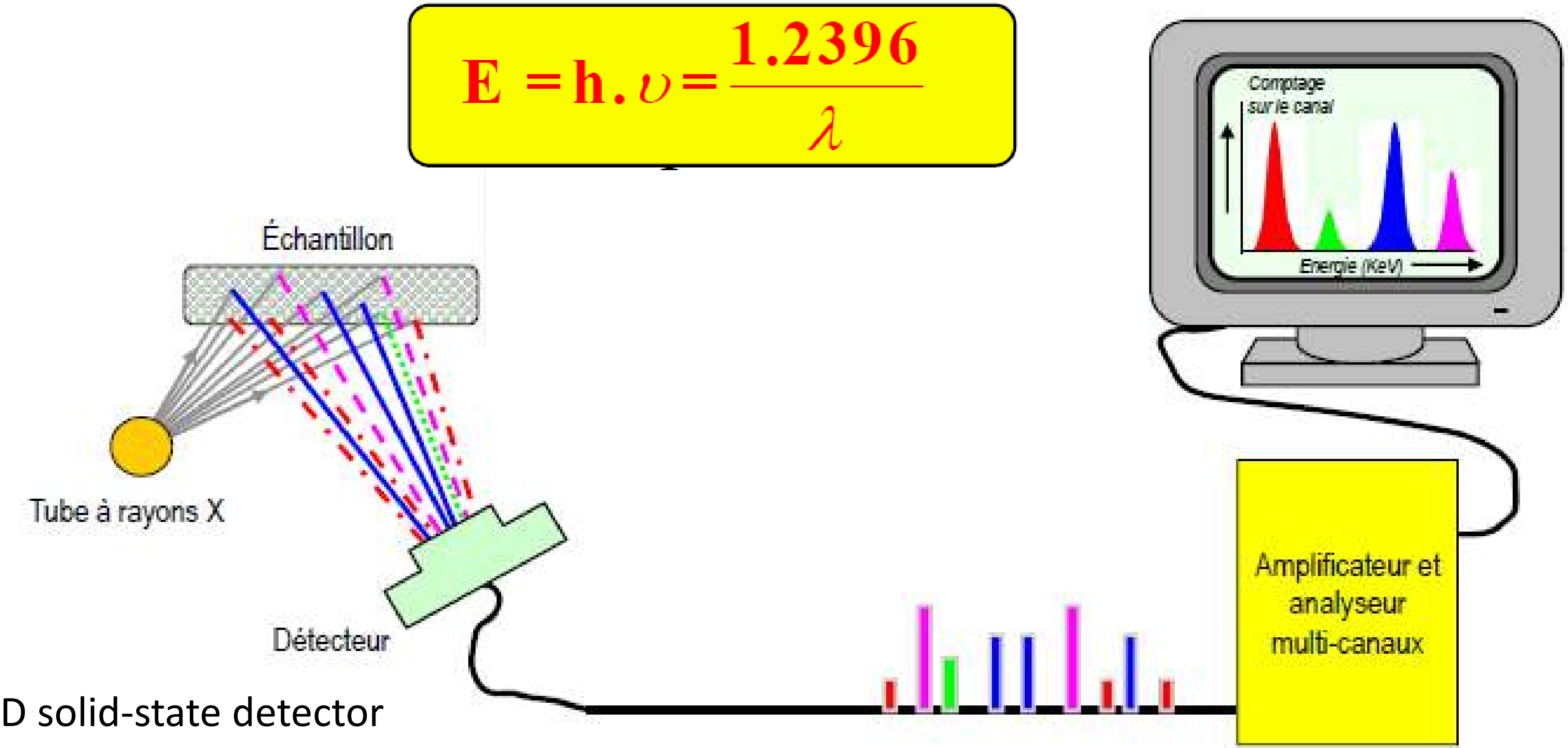
$$\lambda = \frac{2d}{n}\sin\theta$$

Bragg’s law

3.2. X-ray Spectrometry

- Energy dispersive X-ray (EDXRF)

$$E = h.\upsilon = \frac{1.2396}{\lambda}$$

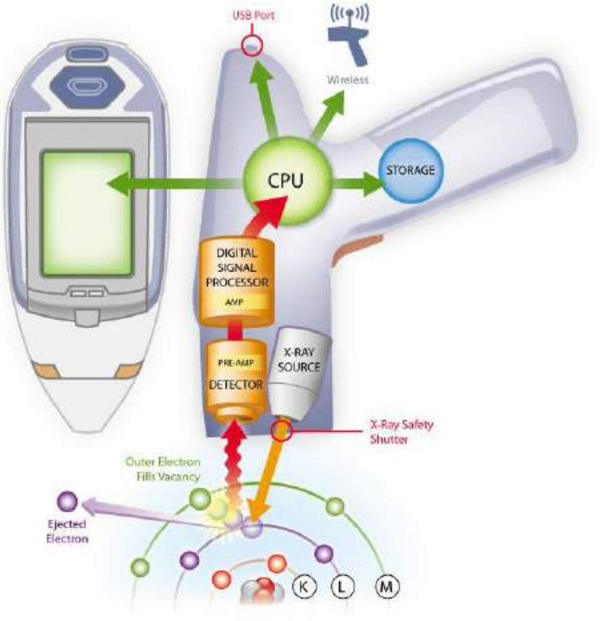


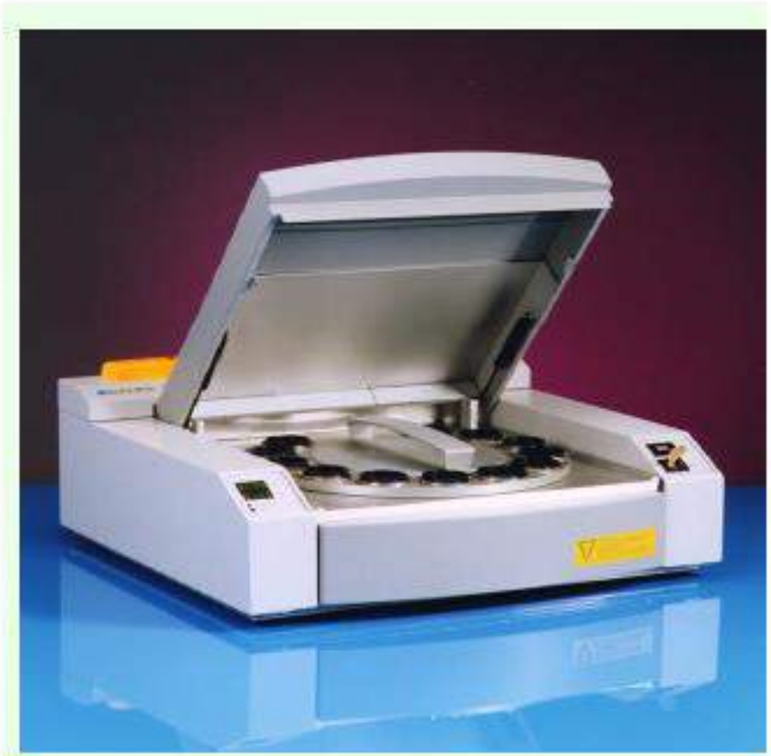
= ED solid-state detector (*détecteur solide*) ou Gas-filled detector (*proportionnel à flux gazeux*)

Simultaneous detection of all photons according to their energy

3.2. X-ray Spectrometry

- Energy dispersive X-ray (EDXRF)



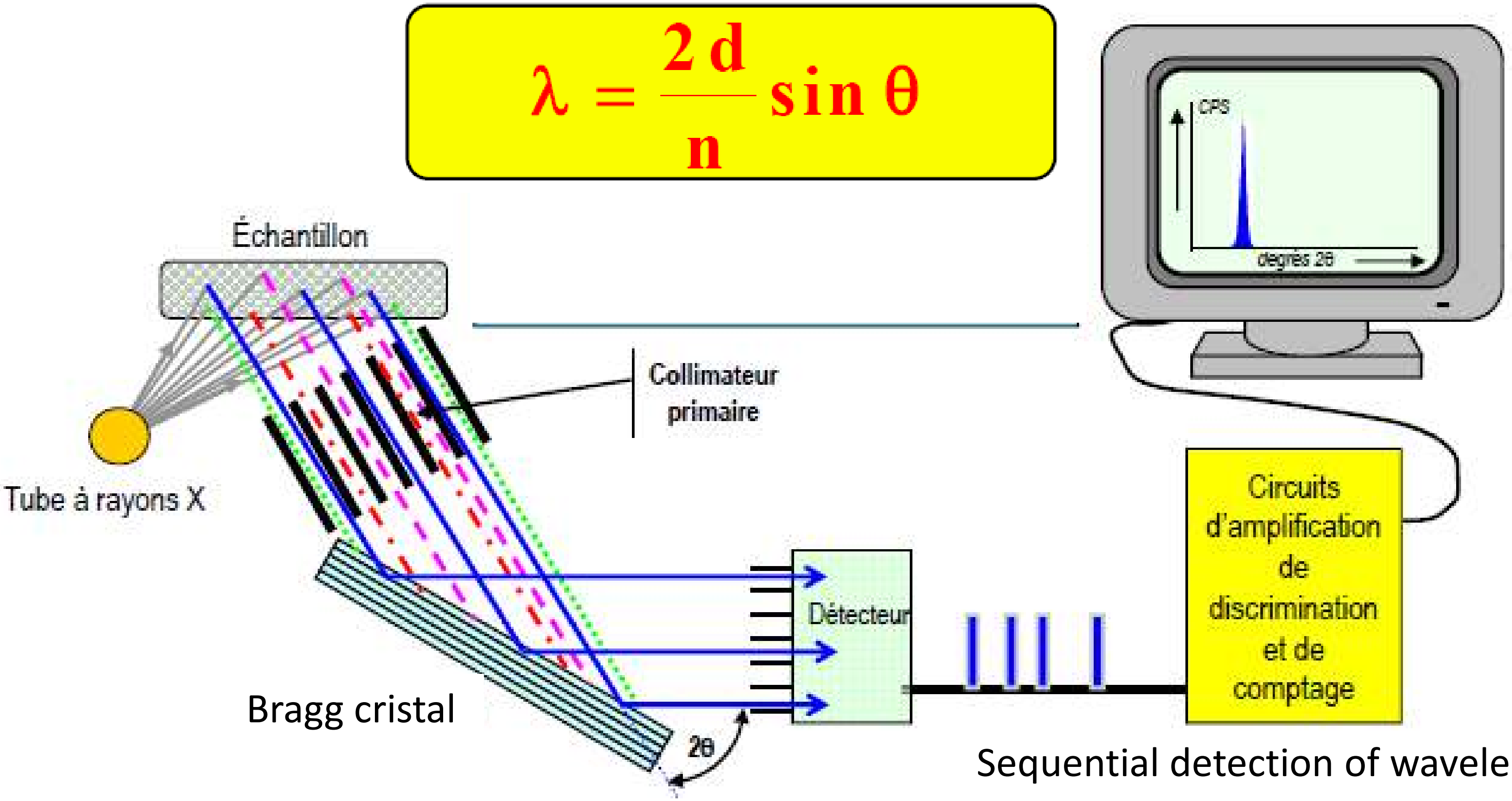


Low sensitivity and low resolution but simultaneous

3.2. X-ray Spectrometry

- Wavelength dispersive X-ray fluorescence (WDXRF):

$$\lambda = \frac{2d}{n} \sin\theta$$



Bragg cristal

Sequential detection of wavelengths

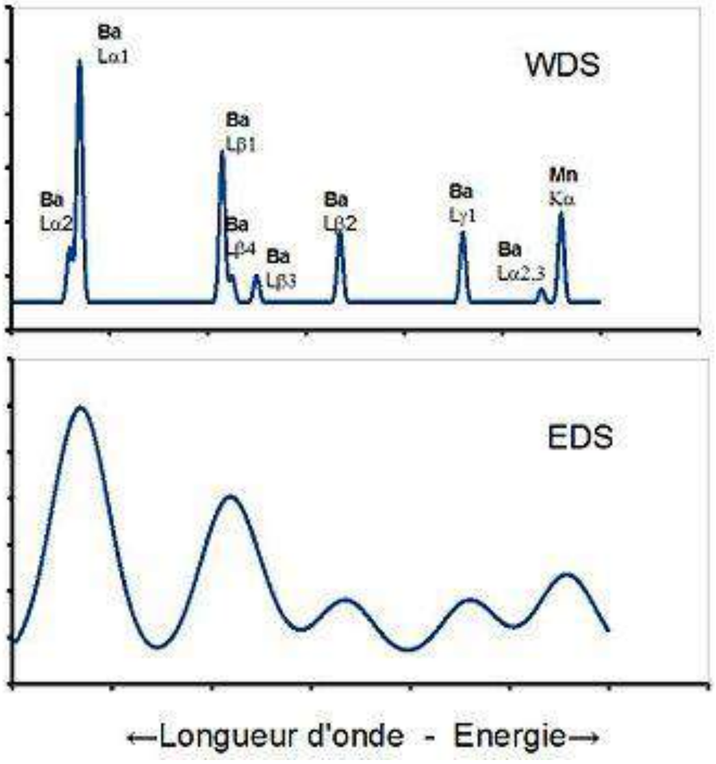
3.2. X-ray Spectrometry

- Wavelength dispersive X-ray fluorescence (WDXRF):

More sensitive but sequential

3.2. X-ray Spectrometry

- Wavelength dispersive X-ray fluorescence (WDXRF):



More sensitive but sequential

A suivre