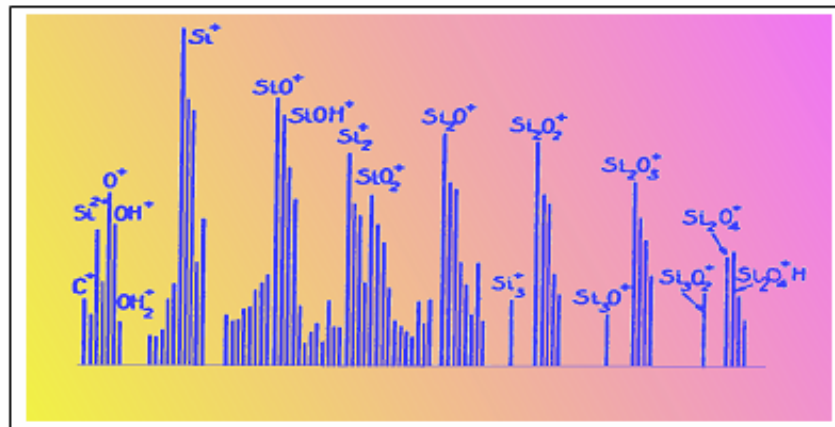
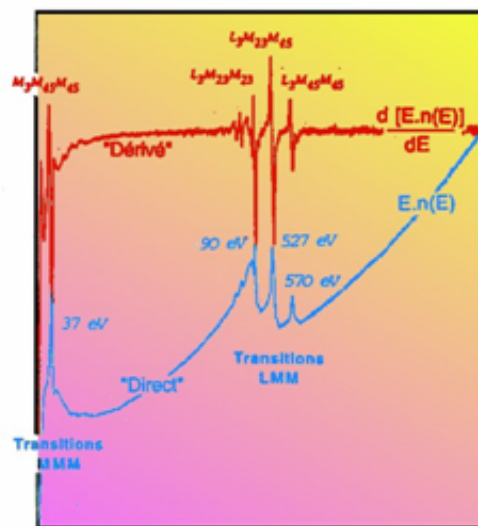


# B. MERCIER-Roscoff 2008



## INTRODUCTION A L'ANALYSE DES SURFACES@VIDE



# INTRODUCTION

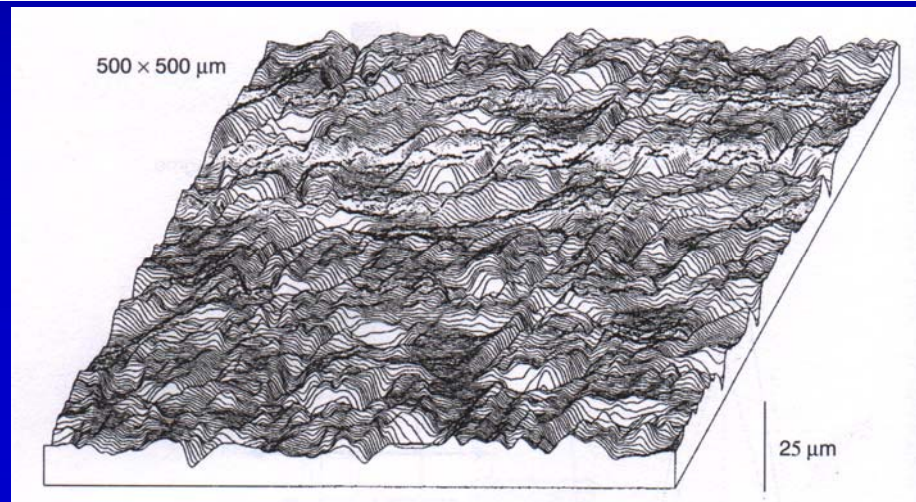
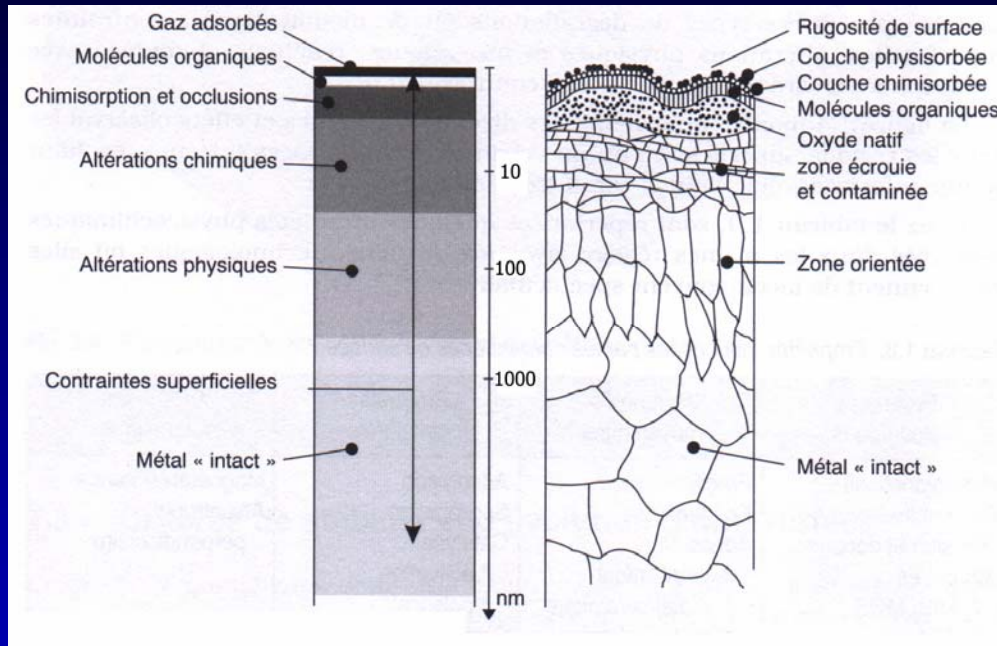
La surface est l'interface métal d'enceinte-vide. Ses interactions avec les gaz résiduel et occlus conditionnent la pression ultime.

Le spécialiste du vide est de plus en plus souvent amené à se poser 2 grandes questions:

- De quoi est fait le gaz résiduel? → **SGR**
- Qu'y-a-t'il sur la surface? → **Analyses de surface**
- Avec les sous-entendus: quels corps contaminent ou dopent? Sur quelle profondeur? En quels composés? En quelle concentration? Avec quelle évolution?

*La morphologie de surface joue un rôle secondaire et ne sera pas abordée*

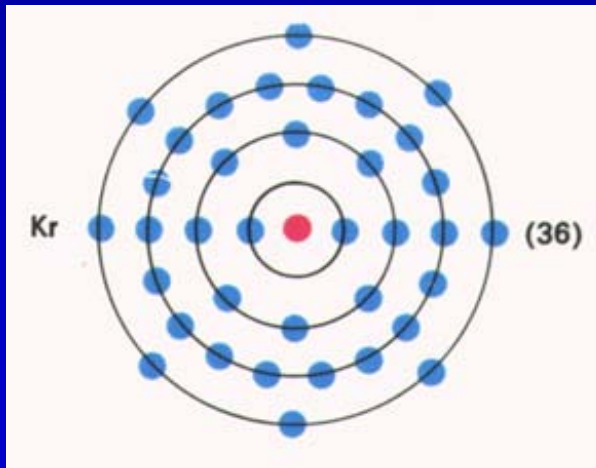
# LA SURFACE du TECH@VIDE



# L'ENQUETE!!

A la question qui est sur la surface et en quelle quantité? La réponse ne peut venir qu'en connaissant un signe distinctif indubitable du suspect.

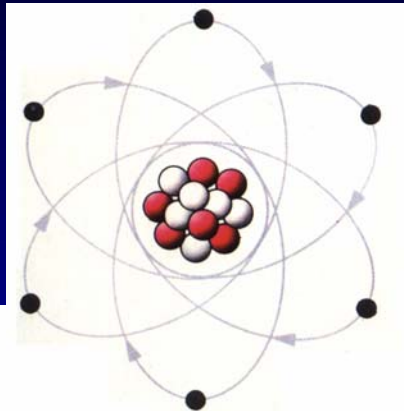
L'analyse de surface utilise des sondes pour décrypter ce signe. Il est caché obligatoirement dans la structure de l'atome.



L'analyse ne doit pas détruire la surface!

Mais elle peut prélever des échantillons révélateurs.

# L'ATOME de RUTHERFORD



Déterminer Z ou A par SM classique est trop invasif!  
Deux méthodes de micro-analyse permettent néanmoins de

déterminer A: SIMS et RBS

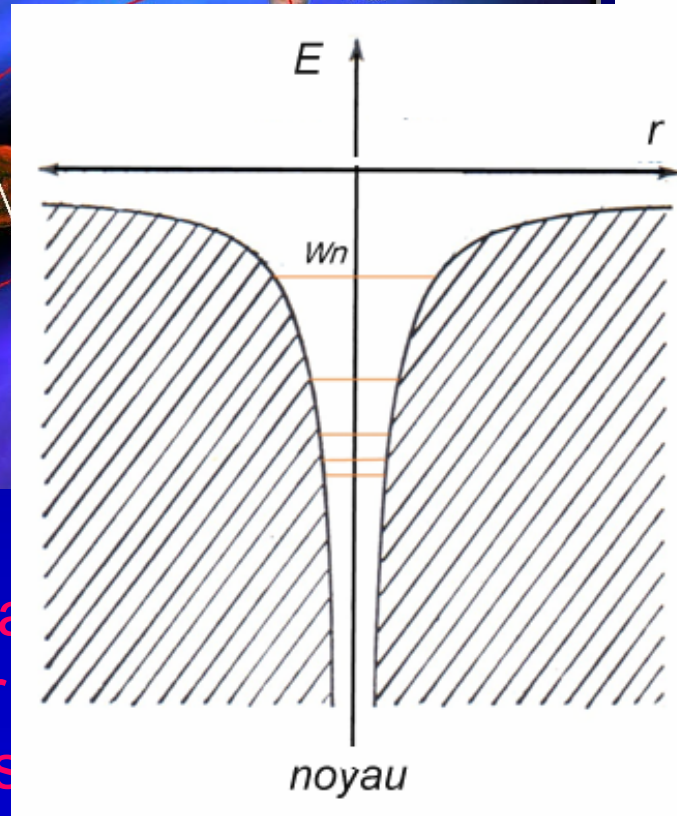
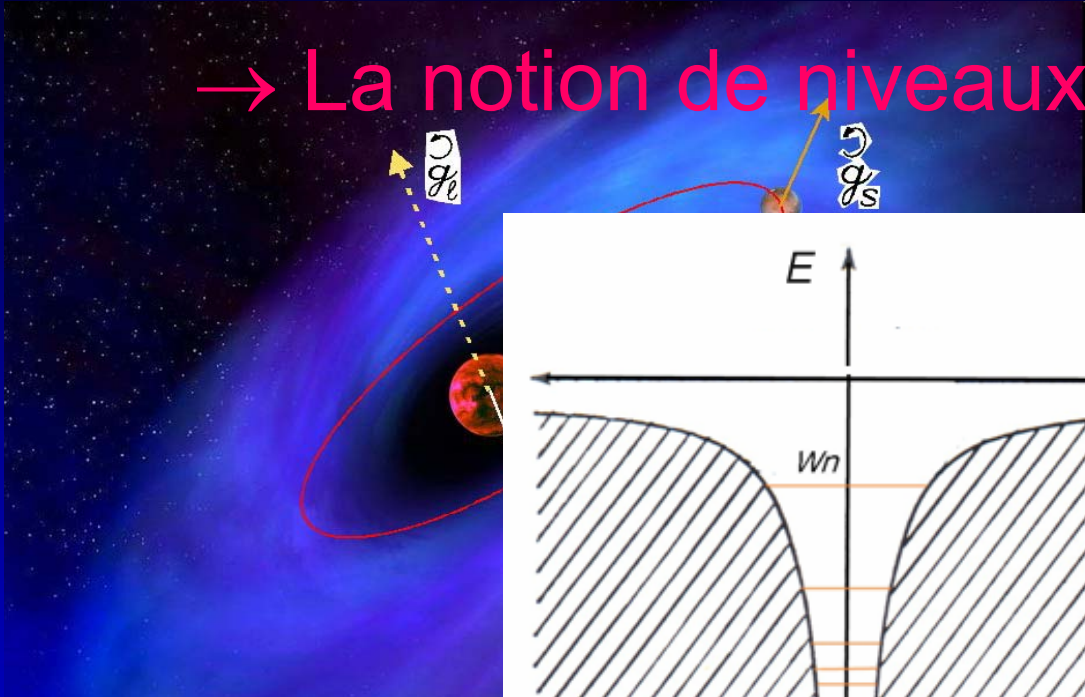
104, 105, 106, 107,  
108, 109, 110, 111...

# L'ATOME de BOHR

→ La notion de niveaux d'énergie

$$g_l = mrv \quad M_l = iA$$

$$E = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r} + f(g_l, M_l)$$

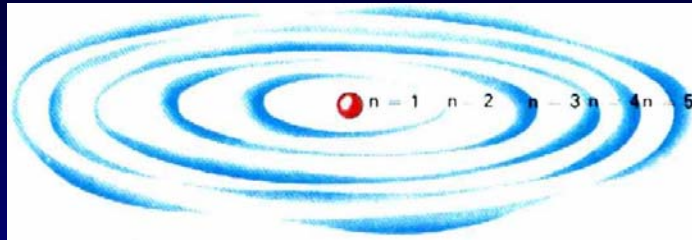


Un électron de l'atome a une énergie dépendant de  $n$ ,  $g_l$ ,  $M_l$

La nature ondulatoire impose des valeurs discrètes pour les nombres quantiques

de  $h/2\pi$ : les quanta.

# LES NOMBRES QUANTIQUES



**$n$**  entier  $> 0$       **Nombre quantique principal**  
 M.M. Détermine le rayon  
 Couches :  $n = 1 \rightarrow K$ ,  $n = 2 \rightarrow L$ ,  $n = 3 \rightarrow M$ , ...

**$l$**  entier  $0 \leq l \leq n - 1$       **Nombre quantique orbital**  
 M.M. Ellipticité - Détermine la forme du volume dans lequel se meut l'électron  
 Sous-couches :  $l = 0 \rightarrow s$     $l = 1 \rightarrow p$     $l = 2 \rightarrow d$     $l = 3 \rightarrow f$  ...

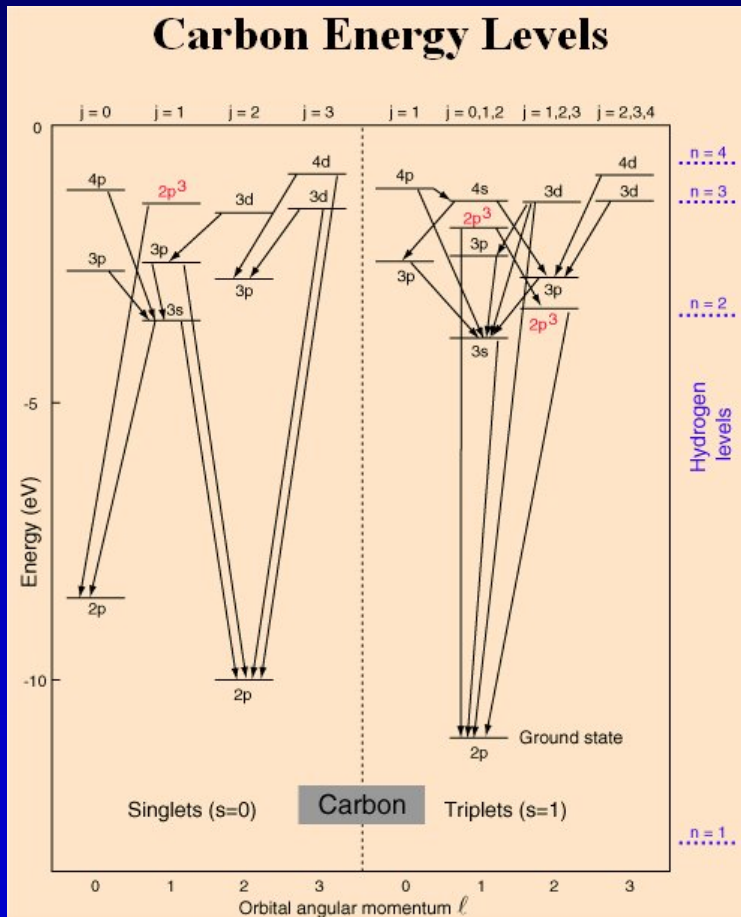
**$m_l$**      $-l \leq m_l \leq l$       **Nombre quantique magnétique**  
 M.M. Inclinaison / axe - Détermine l'orientation du volume

**$m_s = \pm 1/2$**       **"spin"**  
 M.M. Détermine le sens de rotation de l'électron

# LES NIVEAUX d'ENERGIE

Véritable code génétique de l'atome!

Deux méthodes d'analyse le décryptent: AES et XPS



Malignant transformation suppression	Cataracts	Hemochromatosis
Blues, Darker syndrome, type VI	Glaucoma, primary infantile	Neuroblastoma (neuroblastoma suppressor)
Hirschprung disease, cardiac defects	Schwarz-Jampel syndrome	Neuroblastoma, aberrant in some
Hypophosphatasia, infantile, childhood	Breast cancer, ductal	Enxozos, multiple like
Serotonin receptors	Schneider crystalline corneal dystrophy	Opoid receptor
Retinoblastoma	Retinoblastoma	Hypoparathyroidism, type II
Prostate cancer	Brain cancer	Betterer syndrome, type 3
Charcot-Marie-Tooth neuropathy	Charcot-Marie-Tooth neuropathy	Muscular dystrophy, congenital
Erythroblastosis fetalis	Deafness, autosomal dominant	Erythroblastosis fetalis
Glucose transport defect, blood-brain barrier	Deafness, autosomal dominant and recessive	Deafness, autosomal dominant and recessive
Hepatocholesterolemia, familial	Phosphatase	Glucose transport defect, blood-brain barrier
Muscle-eye-brain disease	Phosphatase	Hepatocholesterolemia, familial
Medullablastoma	Phosphatase	Neuroepithelioma, familial
Basal cell carcinoma	Phosphatase	Muscle-eye-brain disease
Cornel atrophy, glaucoma drop-like	Phosphatase	Medullablastoma
Leber congenital amaurosis	Phosphatase	Basal cell carcinoma
Retinal dystrophy	Phosphatase	Cornel atrophy, glaucoma drop-like
B-cell leukemia/lymphoma	Phosphatase	Leber congenital amaurosis
Lymphoma, MALT and follicular	Phosphatase	Retinal dystrophy
Microlithemia	Phosphatase	B-cell leukemia/lymphoma
Germ cell tumor	Phosphatase	Lymphoma, MALT and follicular
Scary syndrome	Phosphatase	Microlithemia
Colan cancer	Phosphatase	Germ cell tumor
Neuroblastoma	Phosphatase	Scary syndrome
Glycogen storage disease	Phosphatase	Colan cancer
Osteopetrosis, autosomal dominant, type II	Phosphatase	Neuroblastoma
Vanderburg syndrome, type 2B	Phosphatase	Glycogen storage disease
Vasculature reflux	Phosphatase	Osteopetrosis, autosomal dominant, type II
Chromothromatosis, episodic (paroxysmal)	Phosphatase	Vanderburg syndrome, type 2B
Hemochromatosis, type 2	Phosphatase	Vasculature reflux
Leukemia, acute	Phosphatase	Chromothromatosis, episodic (paroxysmal)
Gaucher disease	Phosphatase	Hemochromatosis, type 2
Medullary cystic kidney disease, autosomal dominant	Phosphatase	Leukemia, acute
Renal cell carcinoma, papillary	Phosphatase	Gaucher disease
transferrinopathy, congenital, with arthrosis	Phosphatase	Medullary cystic kidney disease, autosomal dominant
Medullary thyroid carcinoma	Phosphatase	Renal cell carcinoma, papillary
Hyperlipidemia, familial combined	Phosphatase	transferrinopathy, congenital, with arthrosis
Hyperparathyroidism	Phosphatase	Medullary thyroid carcinoma
Lymphoma, progression of	Phosphatase	Hyperlipidemia, familial combined
Pharyngeal webbing	Phosphatase	Hyperparathyroidism
Hemorrhagic diathesis	Phosphatase	Lymphoma, progression of
Thrombocytopenia susceptibility	Phosphatase	Pharyngeal webbing
Systemic lupus erythematosus, susceptibility	Phosphatase	Hemorrhagic diathesis
Fish-color syndrome	Phosphatase	Thrombocytopenia susceptibility
Prostate cancer, hereditary	Phosphatase	Systemic lupus erythematosus, susceptibility
Chronic granulomatous disease	Phosphatase	Fish-color syndrome
Muscular degeneration, age-related	Phosphatase	Prostate cancer, hereditary
Epidermolysis bullosa	Phosphatase	Chronic granulomatous disease
Chromosomal deficiency	Phosphatase	Muscular degeneration, age-related
Pseudohypoparathyroidism, type II	Phosphatase	Epidermolysis bullosa
Hypokalemia, periodic, paralytic	Phosphatase	Chromosomal deficiency
Milk-prim hyperthermia susceptibility	Phosphatase	Pseudohypoparathyroidism, type II
Glaucosuria with fluorescein deposits	Phosphatase	Hypokalemia, periodic, paralytic
Metastasis suppressor	Phosphatase	Milk-prim hyperthermia susceptibility
Melanin, susceptibility to	Phosphatase	Glaucosuria with fluorescein deposits
van der Woude syndrome (lip pit syndrome)	Phosphatase	Metastasis suppressor
Rippling muscle disease	Phosphatase	Melanin, susceptibility to
Hypoparathyroidism-osteoarthritis syndrome	Phosphatase	van der Woude syndrome (lip pit syndrome)
Vertical keratoconus, stress-induced polymorphic	Phosphatase	Rippling muscle disease
Furunculosis	Phosphatase	Hypoparathyroidism-osteoarthritis syndrome
Chediak-Higashi syndrome	Phosphatase	Vertical keratoconus, stress-induced polymorphic
Muckle-Wells syndrome	Phosphatase	Furunculosis
Zellweger syndrome	Phosphatase	Chediak-Higashi syndrome
Adrenoleukodystrophy, neonatal	Phosphatase	Muckle-Wells syndrome
Endometrial bleeding-associated factor	Phosphatase	Zellweger syndrome
left-right axis malformation	Phosphatase	Adrenoleukodystrophy, neonatal
Prostate cancer, hereditary	Phosphatase	Endometrial bleeding-associated factor
Chondrodysplasia punctata, rhizomelic, type 2	Phosphatase	left-right axis malformation
	Phosphatase	Prostate cancer, hereditary
	Phosphatase	Chondrodysplasia punctata, rhizomelic, type 2



# LES SONDES

SONDE	PRODUITS		
	Rayons X	Électrons	Ions
<b>Photons X</b>	Fluorescence X (XRF) Réflexion X (XRR, GISAXS) Diffraction X (XRD) Absorption X (EXAFS) Réflexion X (SEXAFS et ReflEXAFS)	Spectroscopie de photoélectrons (XPS, ESCA et AES) (EXAFS, SEXAFS et ReflEXAFS)	
<b>Électrons</b>	Microsonde électronique (SEM)	Microscopie électronique (TEM et STEM) Diffraction électronique (LEED et RHEED)	
<b>Ions</b>	Impact ionique (IIX et PIXE) Microsonde ionique		Diffraction Rutherford (RBS) Réactions nucléaires (NRA) Spectroscopie d'ions secondaires (ISS) ou diffusés (SIMS)

AES: Auger Electron Spectroscopy

ESCA: Electron Spectroscopy for Chemical Analysis

EXAFS: Extended X-Ray Absorption Fine Structure

IIX: Ion-Induced X-Rays

ISS: Ion Scattering Spectroscopy

GISAXS: Grazing Incidence Small - Angle X-Ray Scattering

LEED: Low Electron Energy Diffraction

NRA: Nuclear Reaction Analysis

PIXE: Particle Induced X-Ray Emission

RBS: Rutherford Back Scattering

RHEED: Reflection High Energy Electron Diffraction

ReflEXAFS: Reflection Extended X-Ray Absorption Fine Structure

SEM: Scanning electron Microscopy

SEXAFS: Surface Extended X-Ray Absorption Fine Structure

SIMS: Secondary Ion Mass Spectrometry

STEM: Scanning Transmission Electron Microscopy

TEM: Transmission Electron Microscopy

UPS: Ultraviolet Photoelectron Spectroscopy

XPS: X-Ray Photoelectron Spectroscopy

XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence Analysis

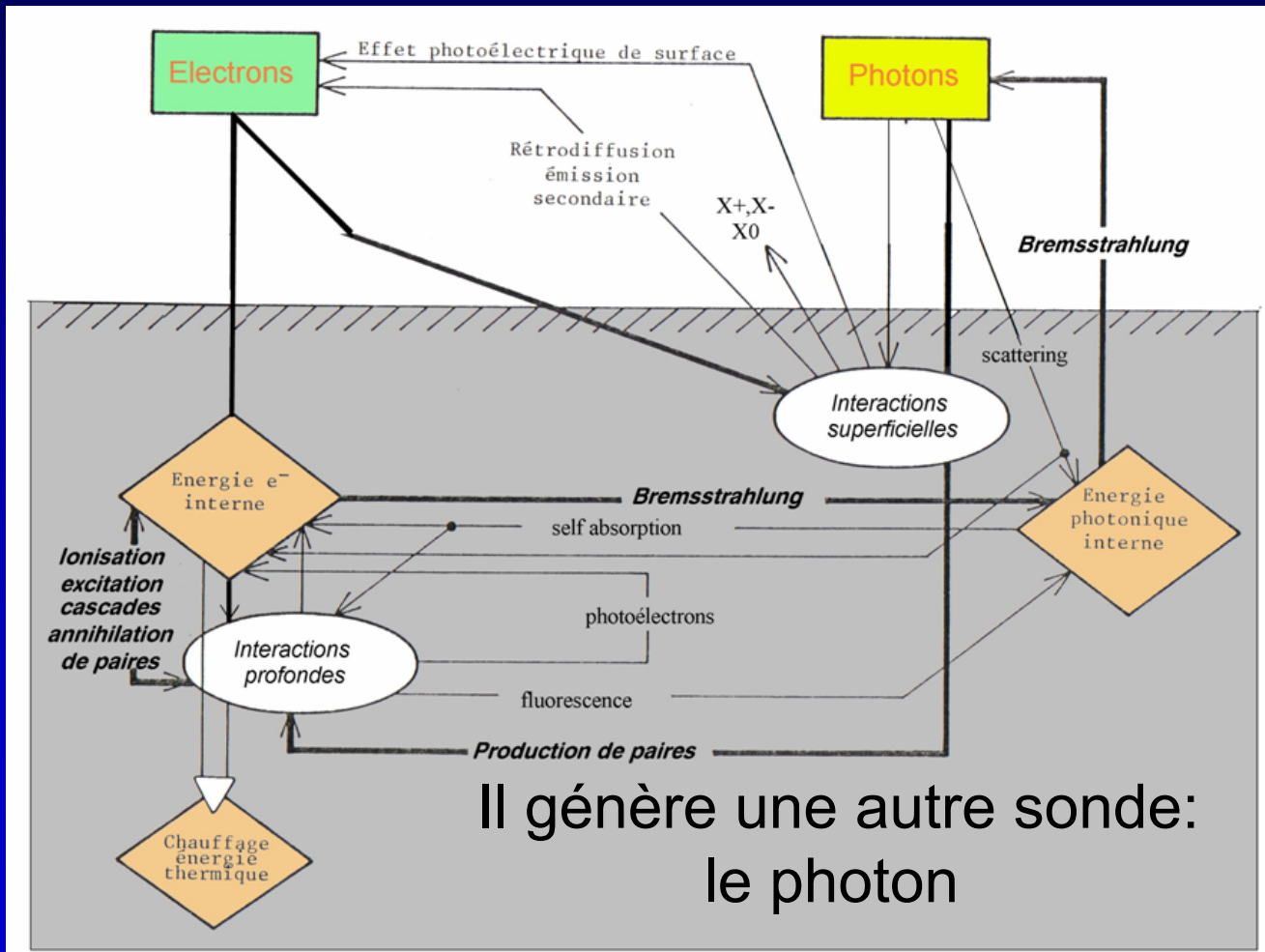
XRR: X-Ray Reflection

# L'EXPLOITATION

Renseignement	Méthode	Vide requis
Analytique	AES XRF RBS LAMMA SIMS XPS – ESCA	Ultravide Vide conventionnel Vide conventionnel Vide conventionnel Ultravide + gaz Ultravide
Morphologique	MEB AFM STM	Vide conventionnel Non Ultravide/Atmosphère
Structural longue distance	XRD LEED	Non Ultravide
courte distance	STM	Ultravide

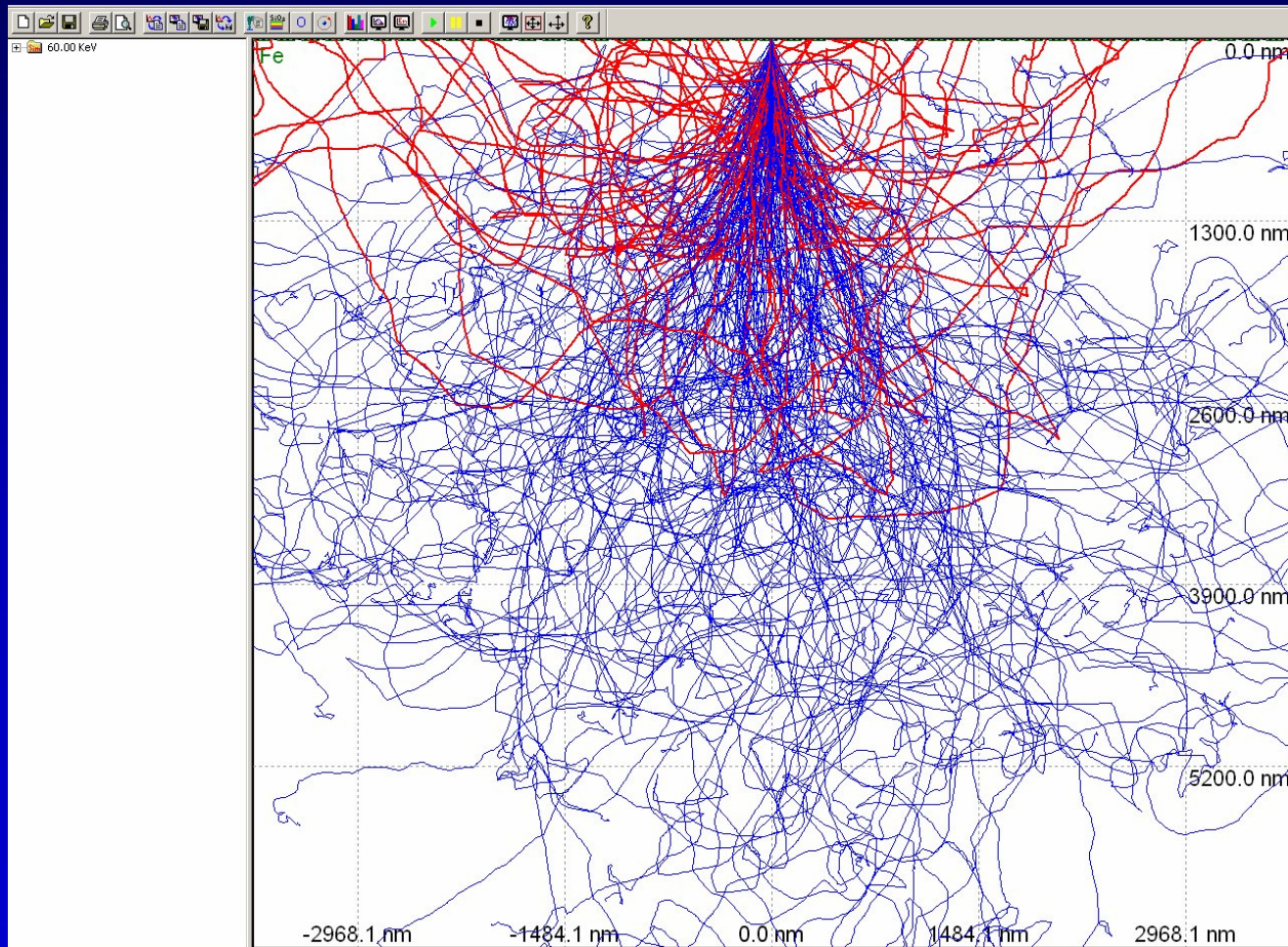
# LA SONDE ELECTRONIQUE

L'électron, facile à produire, a de nombreuses interactions avec la matière.



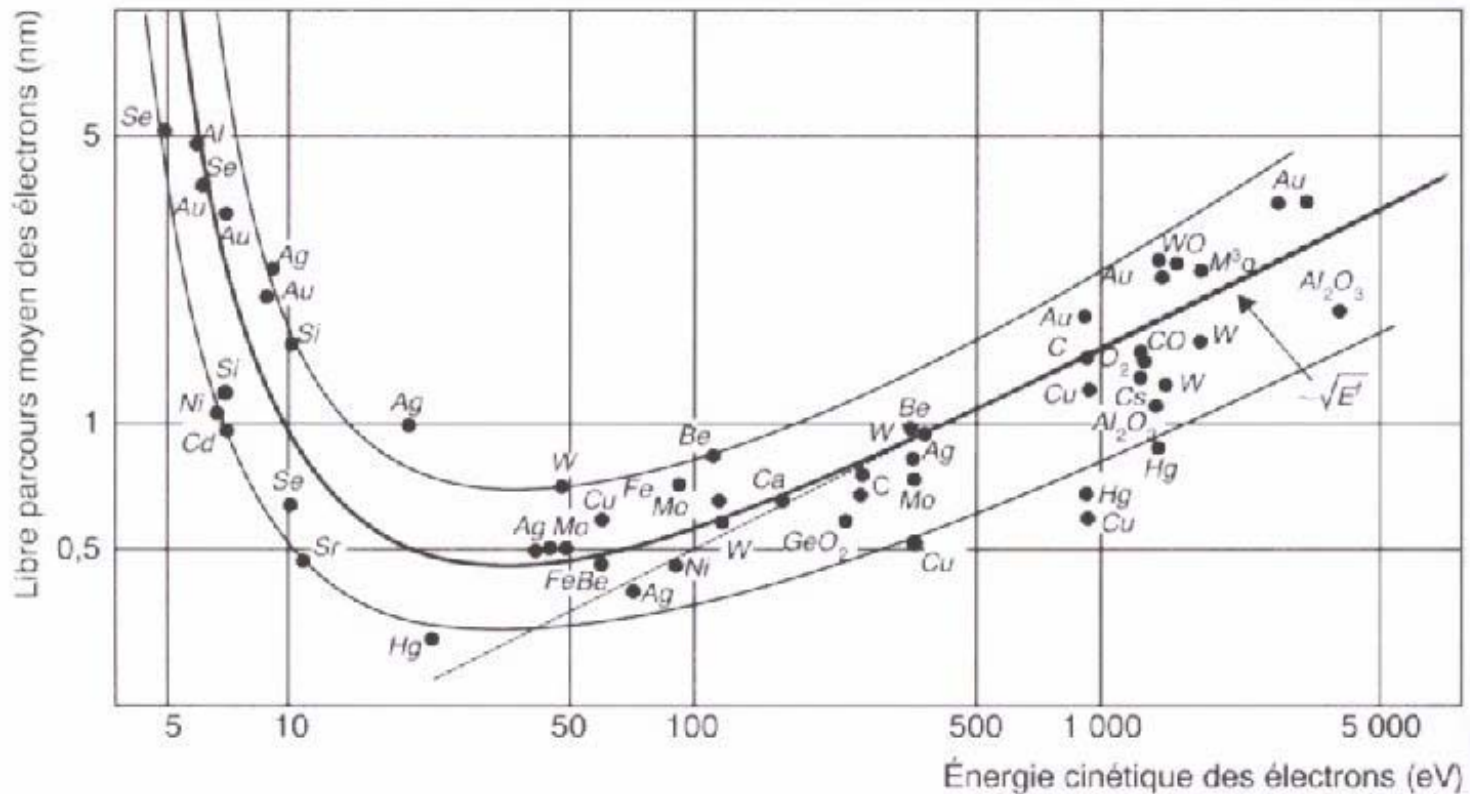
# SONDE FRAGILE?

Sa charge lui fait perdre rapidement de l'énergie



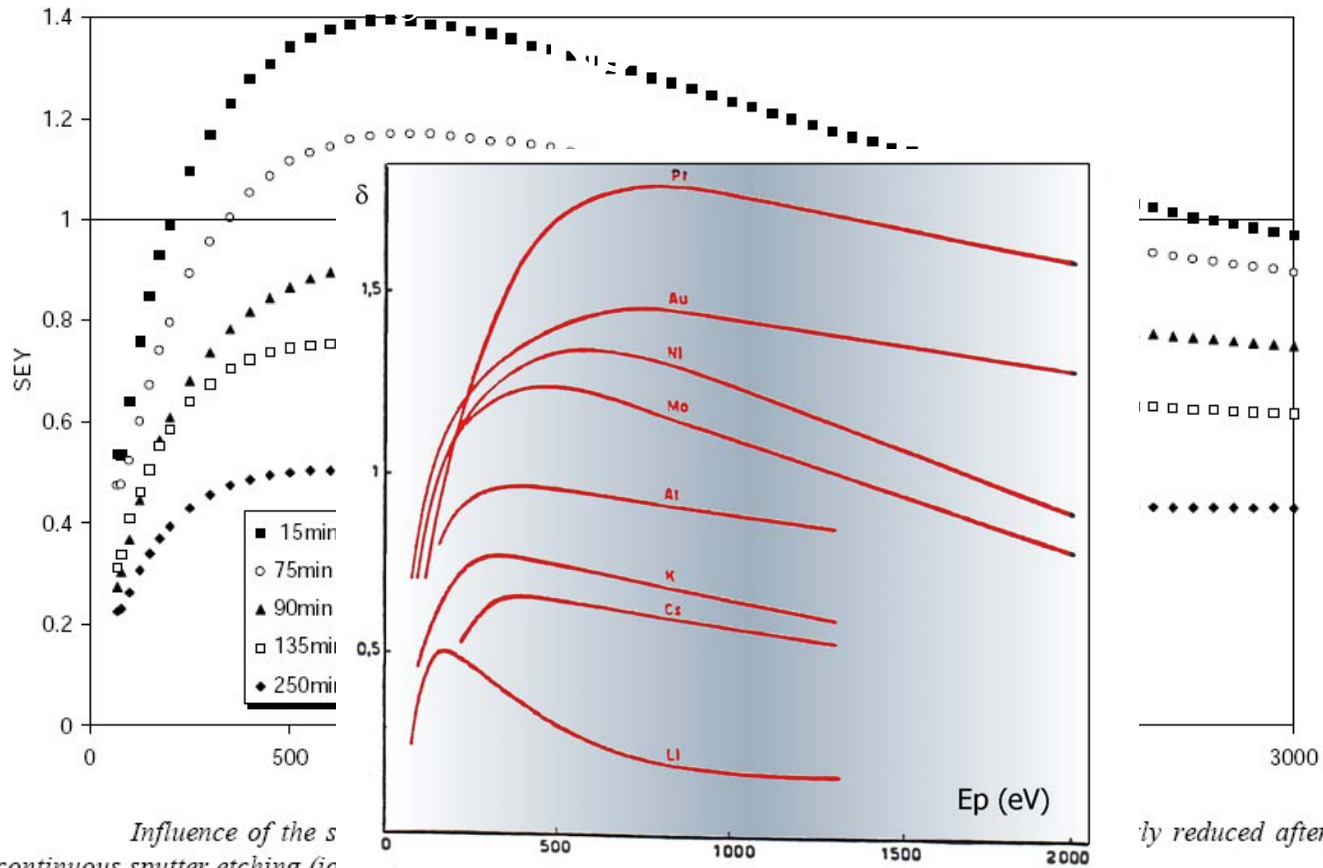
# SONDE FRAGILE?

Sa charge lui fait perdre rapidement de l'énergie

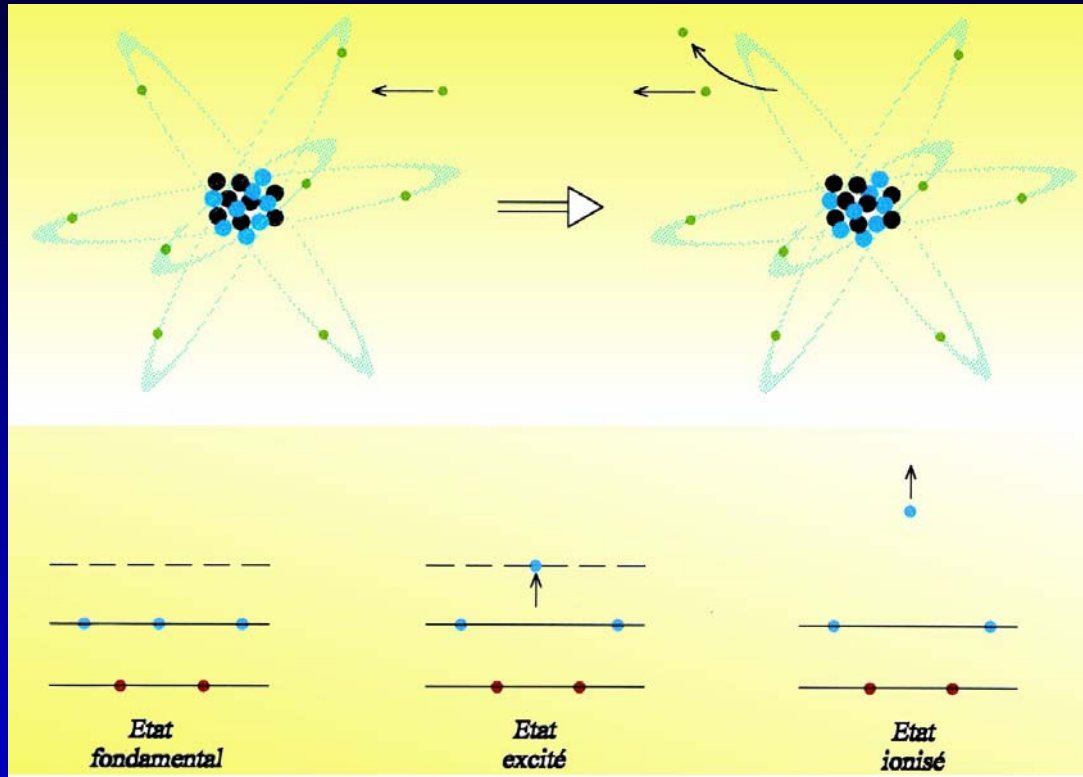


Libre parcours moyen des électrons en fonction de leur énergie.

# L'EMISSION SECONDAIRE



# L'IONISATION

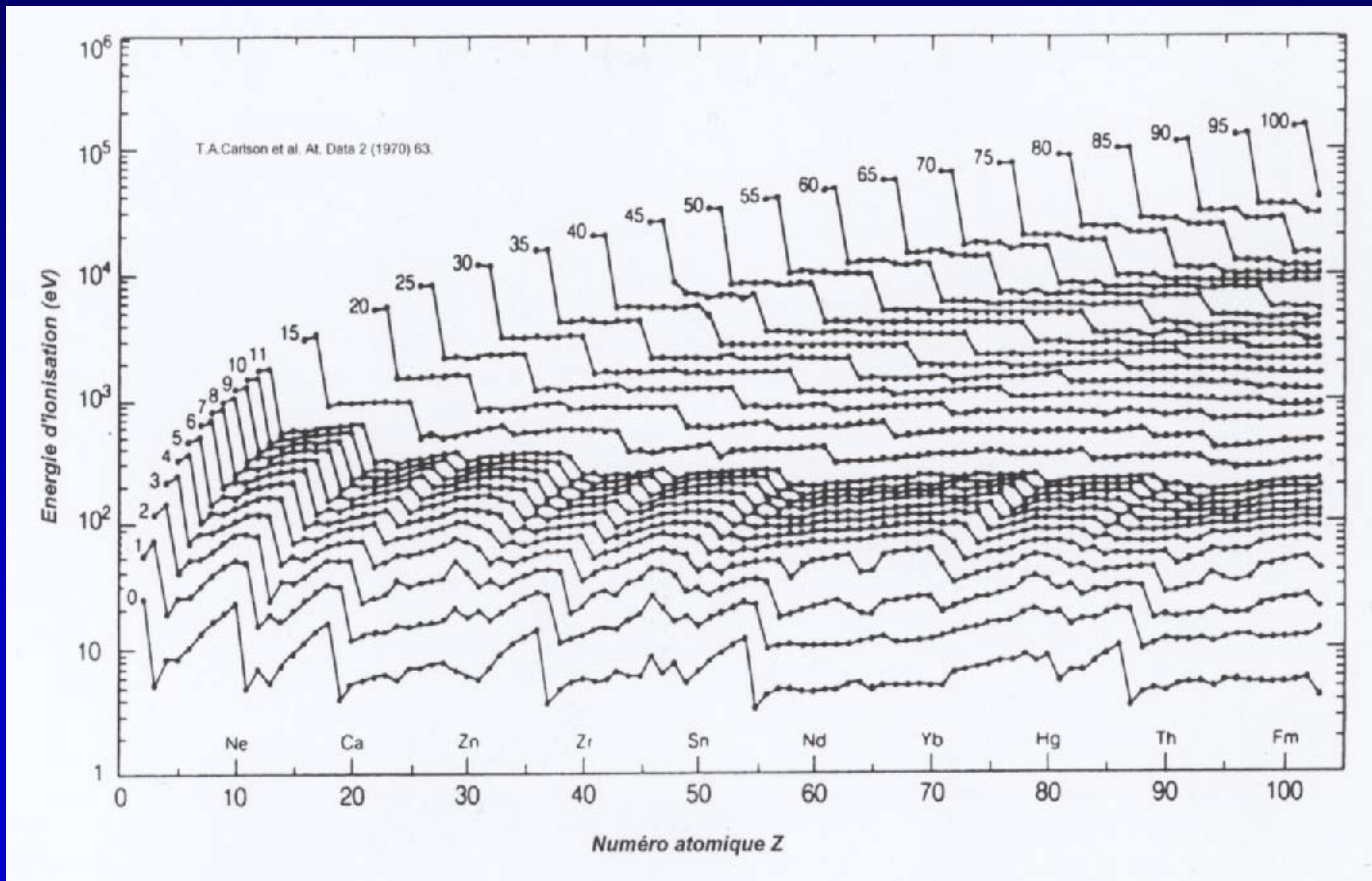


Un niveau ne peut rester dépeuplé (sauf!).

Le trou est comblé par l'habitant (désexcitation) ou par un électron moins lié du même atome (effet Auger).

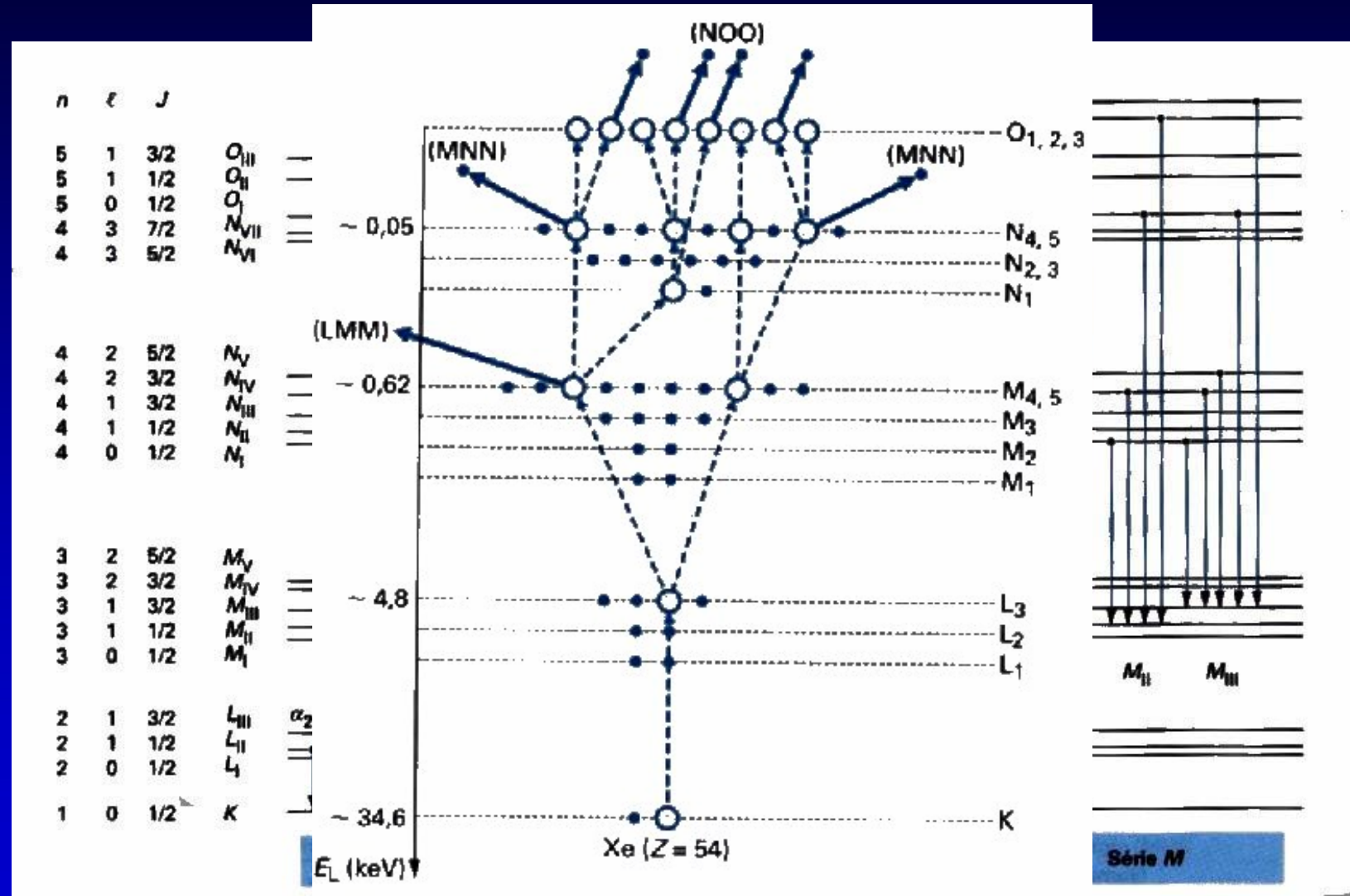
# L'IONISATION

L'exploration profonde nécessite des électrons très énergiques.



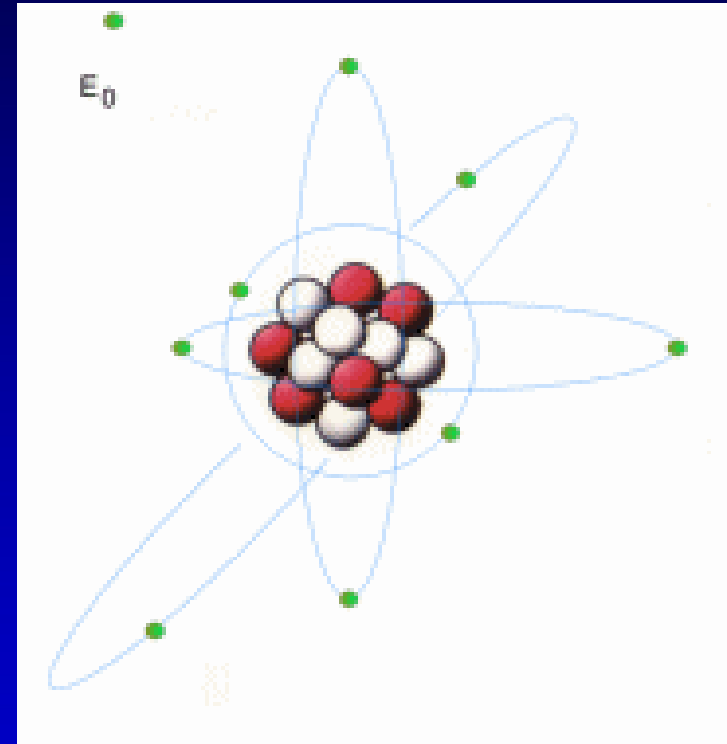
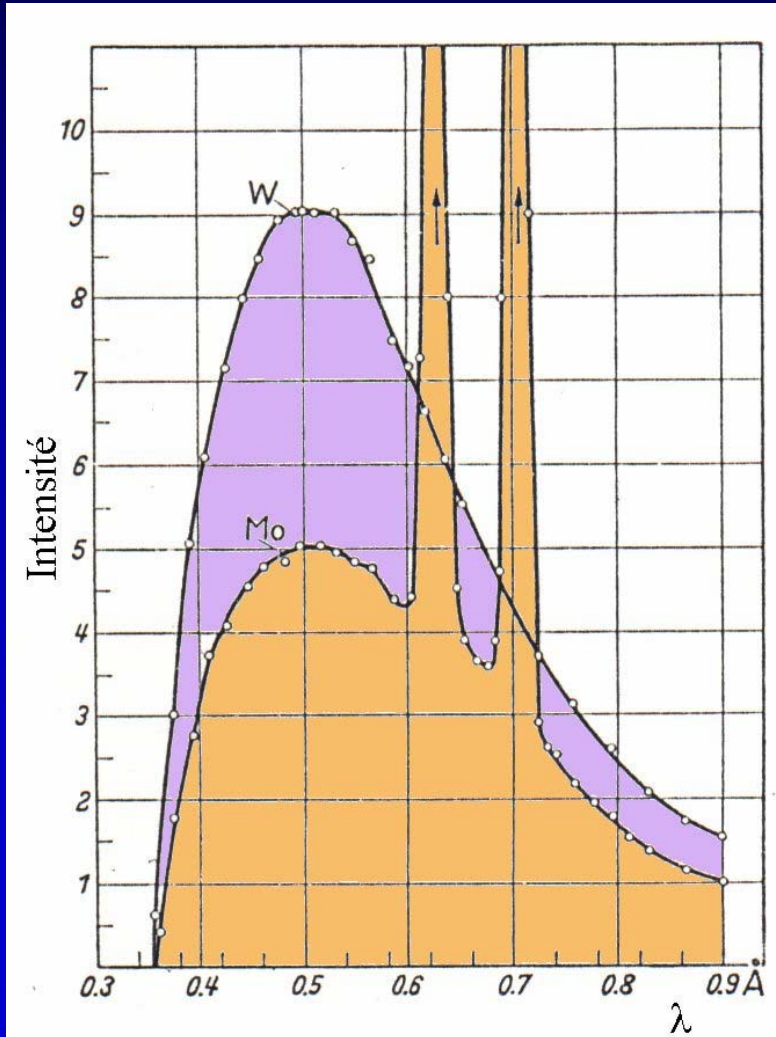


# L'EFFET & LA CASCADE AUGER



# LA PRODUCTION DE PHOTONS

Bremsstrahlung/ rayonnement de freinage



$$I = kZE^2$$

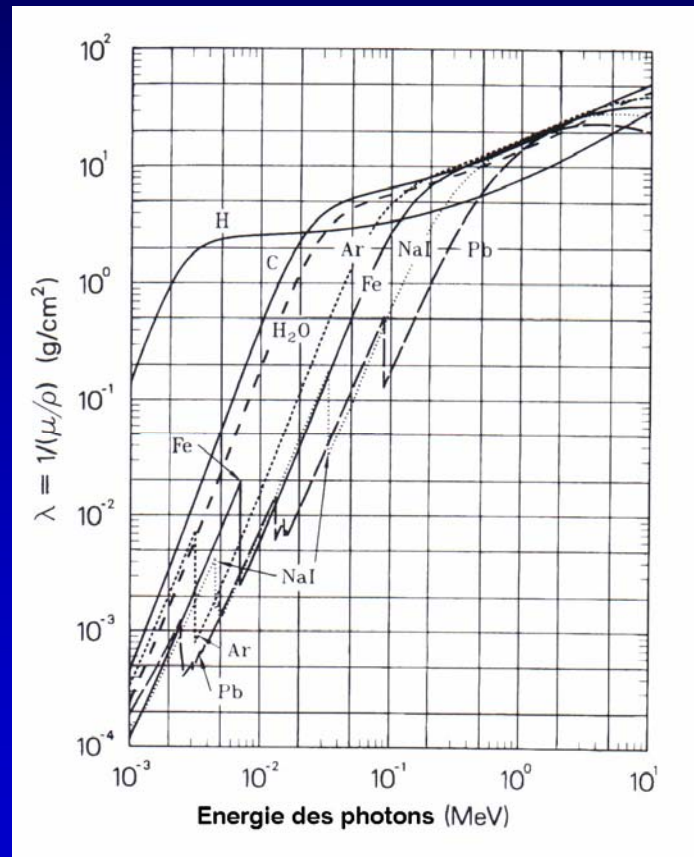
# LA SONDE PHOTONIQUE

The image is a composite of three main elements:

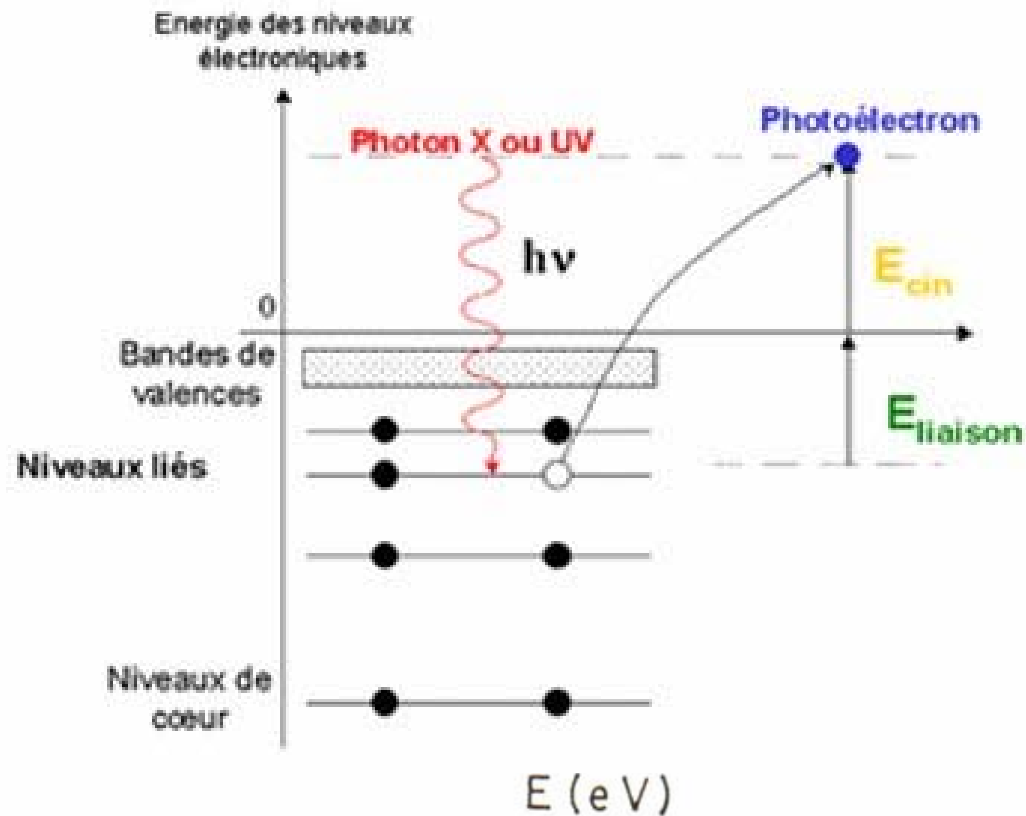
- Top Diagram:** A detailed cross-sectional view of an X-ray tube. It features a central filament (Cathode / Filament) and an anode, both housed within a high vacuum chamber. The chamber is protected by a Beryllium (Be) window and surrounded by a ceramic insulator. A coolant system is also shown. Labels include: Coolant, Be Window, Ceramic Insulator, Anode, High Vacuum, Focusing Cylinder, and Metal Tube Body. A green handwritten mark '2' is visible on the left side.
- Bottom Center:** A prominent yellow and red radiation warning sign with the text "CAUTION" at the top, a black radiation symbol in the center, and "X-RAY RADIATION" at the bottom.
- Bottom Background:** A portion of an electromagnetic spectrum chart. The vertical axis shows energy levels from  $10^{-19}$  eV to  $10^{20}$  MeV. The horizontal axis shows wavelengths from  $10^4$  m to  $10^{-13}$  m. Key regions are labeled: "Lasers à extrêmes", "Ultraviolet", "cristallographie", "rayons X « médicaux »", and "radiographie industrielle".

# SONDE MOINS FRAGILE?

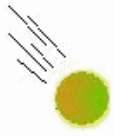
$$I = I_0 \exp\left(-\frac{\rho}{\lambda} x\right)$$



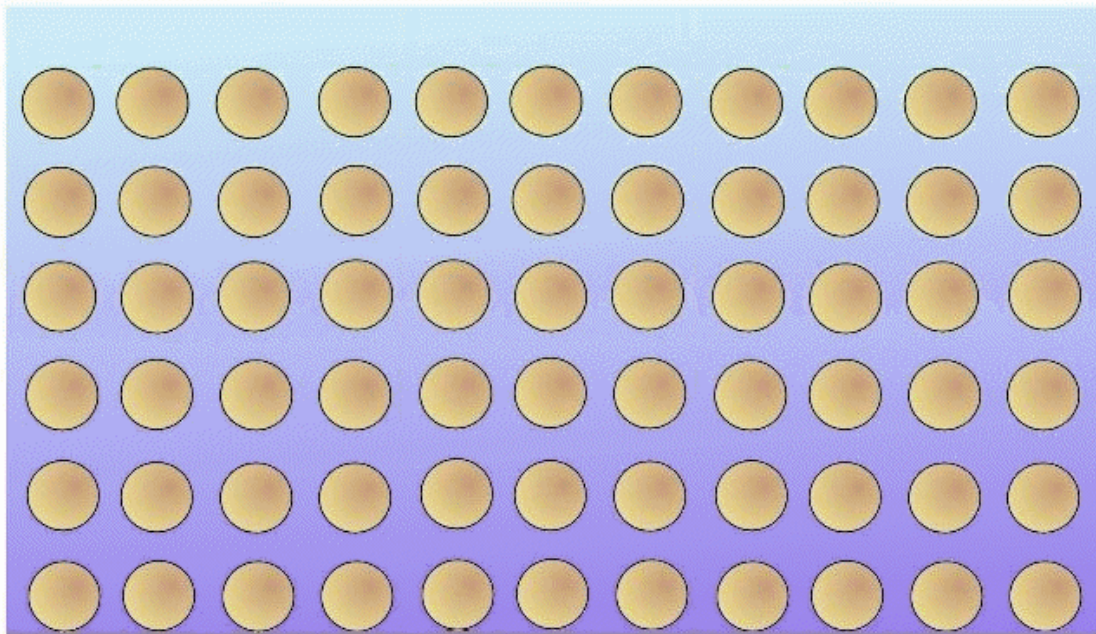
# L'EFFET PHOTOELECTRIQUE



# LA SONDE IONIQUE



Sputtering  
Emis. sec. ions



# LA SONDE IONIQUE

SRIM-2008.01

File Help, FAQ and Scientific Explanations

Help **Animate** Pause TRIM Change TRIM 100% ION ENERGY 0% Now: 216 of 999999 Ions

**ION**

Ion Type: U 238 amu  
 Ion Energy: 60 keV  
 Ion Angle: 0 degrees  
 Completed: 215 of 999999  
 SHOW LIVE DATA HELP

**Plots**

PLOT Window  
 0 A - 300 A  
 Max Target Depth: 300

**COLLISION PLOTS**

XY Longitudinal All  
 YZ Longitudinal None  
 XY Ions Only Tile  
 YZ Lateral Clear  
 Background color White/Black

**DISTRIBUTIONS**

File Plot

- Ion Distribution
- Ion/Recoil Distribution
- Lateral Range
- Ionization
- Phonons
- Energy to Recoils
- Damage Events
- Integral Sputtered Ions
- Differential Ions
- Ion Ranges (3D data)
- Backscattered Ions
- Transmitted Ions
- Collision Details

HELP

**TARGET DATA**

? U into Be/Au/Si [Beautiful Cascades] (3 layers, 3 atoms)

Layer Name	Density	Be (9)	Au (198)	Si (28)	Solid/Gas	Stop Corr.
1 Beryllium	1,850	1,00000	0,00000	0,00000	Solid	1
2 Gold	14,200	0,00000	1,00000	0,00000	Solid	1
3 Silicon	2,320	0,00000	0,00000	1,00000	Solid	1

	Be (9)	Au (198)	Si (28)
Lattice Binding Energy	2,1	2,2	2,3
Surface Binding Energy	3,1	3,2	3,3
Displacement Energy	21	22	23

**Calculation Parameters**

Backscattered Ions: 0  
 Transmitted Ions: 32  
 Vacancies/Ion: 1128,6

**ION STATS**

	Range	Straggle
Longitudinal	174 A	47 A
Lateral Proj.	31 A	41 A
Radial	49 A	33 A

Type of Damage Calculation  
 ? Full Cascades

Stopping Power Version  
 ? SRIM-2003

**% ENERGY LOSS**

	Ions	Recoils
Ionization	11,46	28,54
Vacancies	0,23	4,08
Phonons	0,58	55,12

**SPUTTERING YIELD**

	Atoms/Ion	eV/Atom
TOTAL	7,544	
Be	7,53	79,01
Au	0,009302	62,23
Si	0,000000	0,00

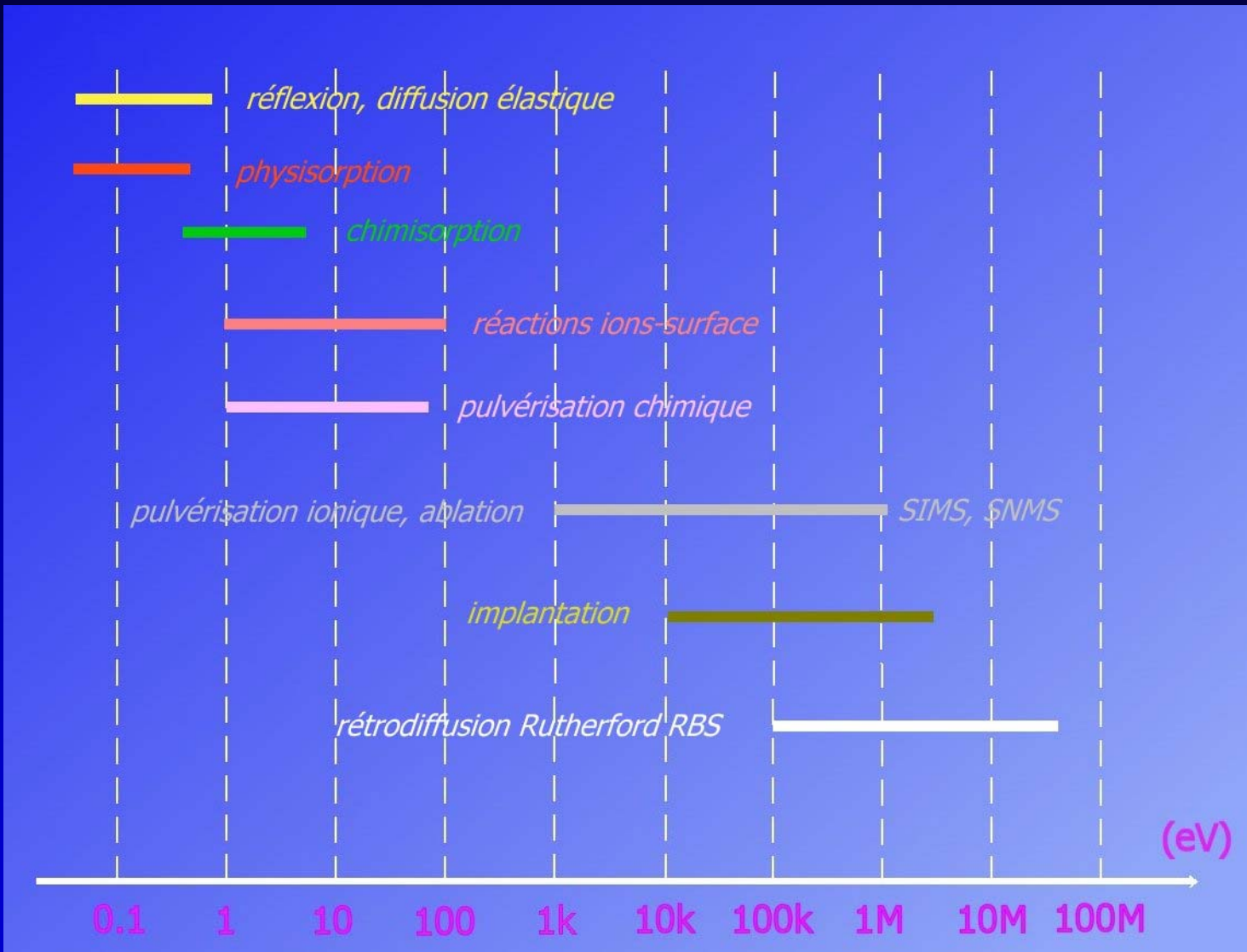
?  Save every 10000 ions  
 Random Number: 6910443  
 Counter:   
 HELP

**XY Longitudinal**

0 A - Target Depth - 300 A

Save Save As Print Label Clear

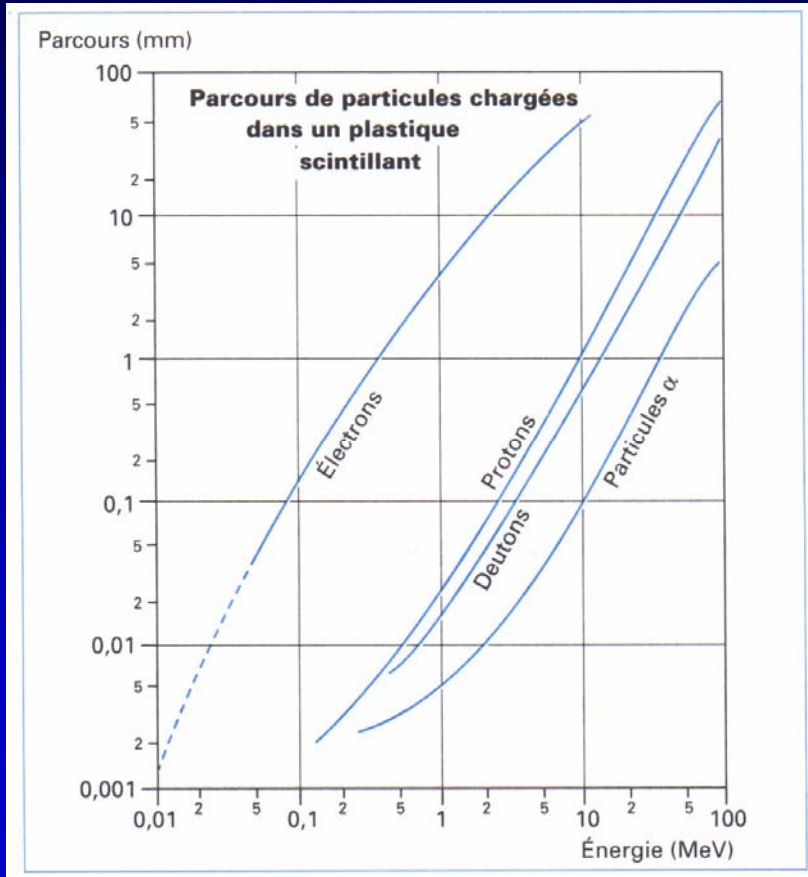
# SES PRODUITS





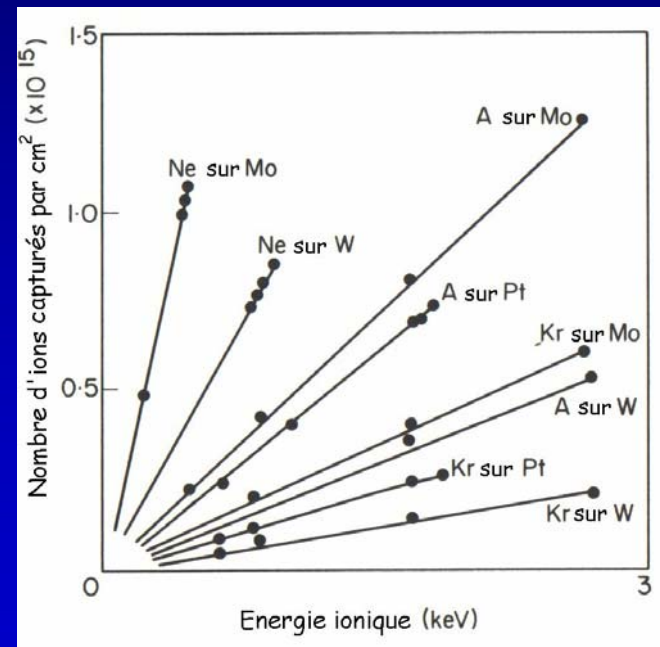
# LES PERTES D'ENERGIE

Principalement dues aux collisions électroniques



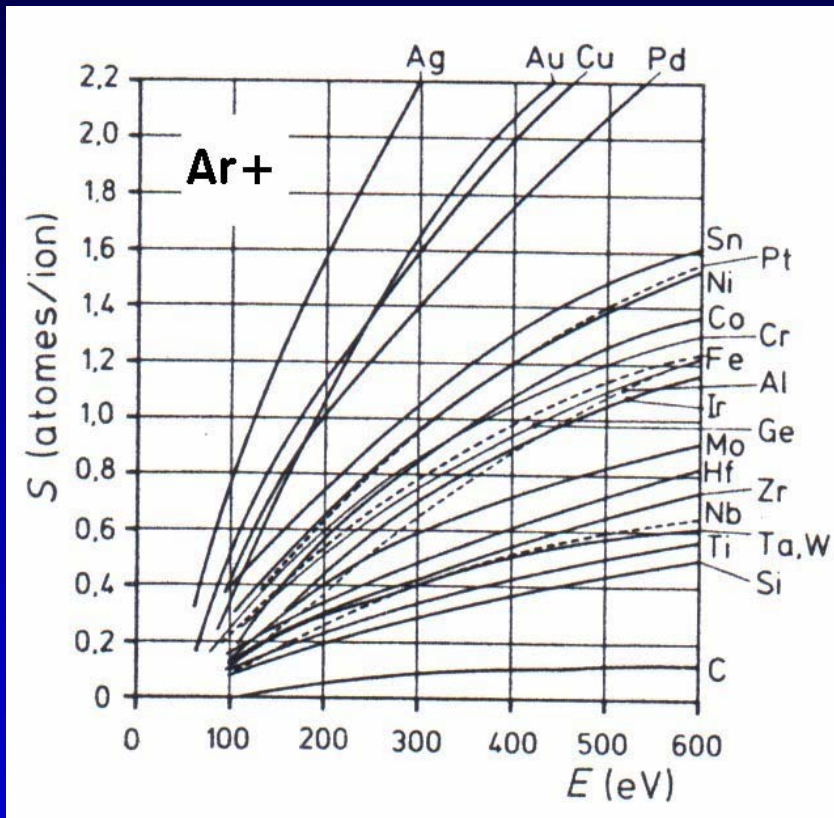
Parcours/Range

$$-\frac{dE}{dx}_{[MeV.cm^{-1}]} \approx 0.3071 \frac{Z_c \rho}{A \beta^2} \left( \text{Ln} \frac{2m_e c^2 \beta^2 \gamma^2}{\mathfrak{I}} - \beta^2 \right)$$

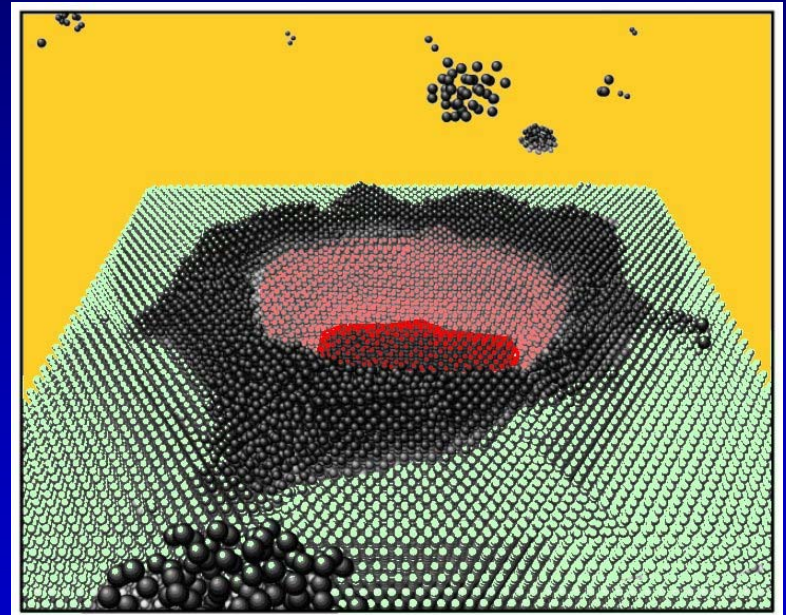


Implantation

# LA PULVERISATION



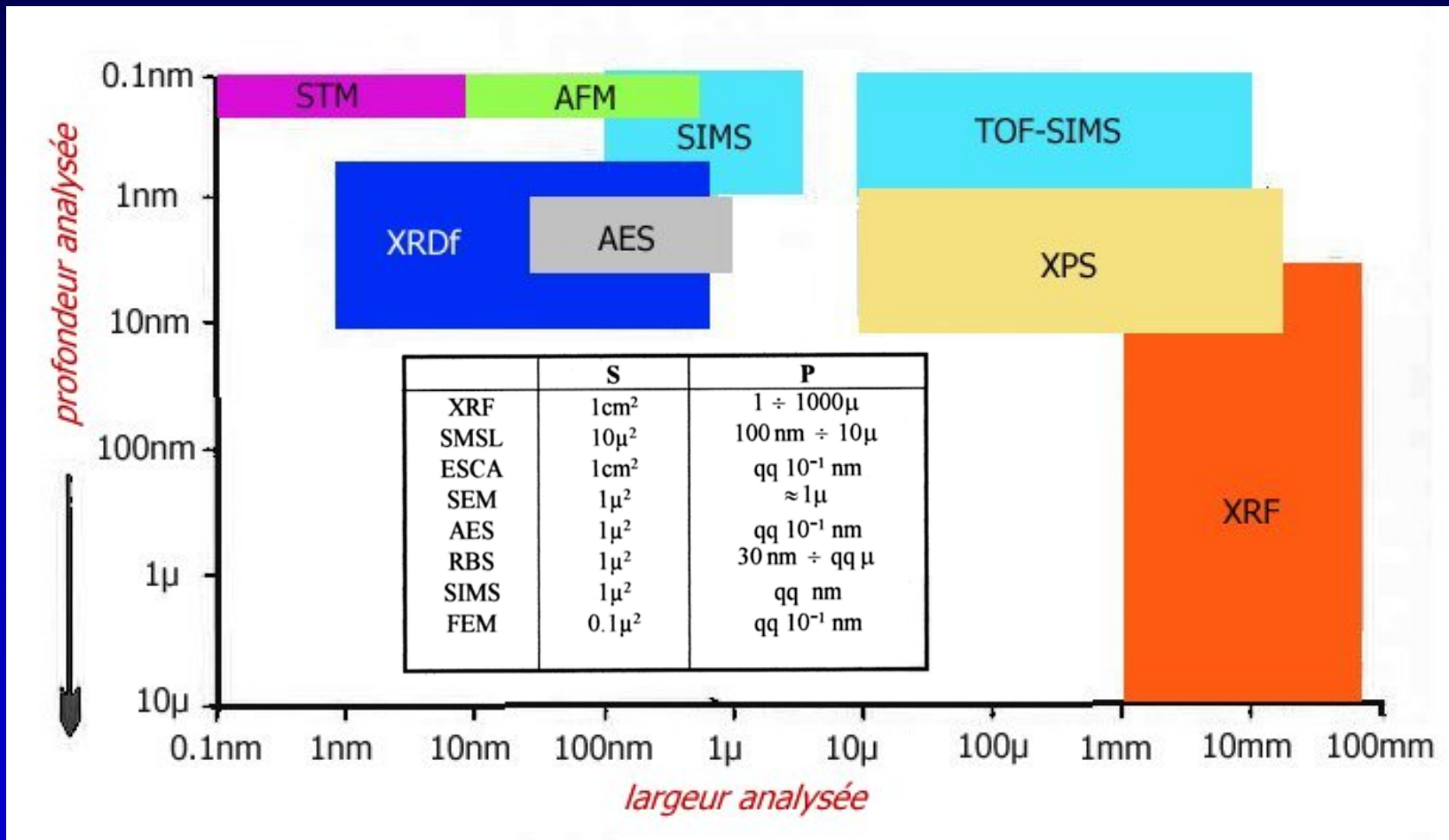
$$S = 76 \cdot 10^9 \alpha \alpha_i Z_i Z_c \frac{A_i}{A_i + A_c} \frac{Sn}{U[\text{eV}]}$$



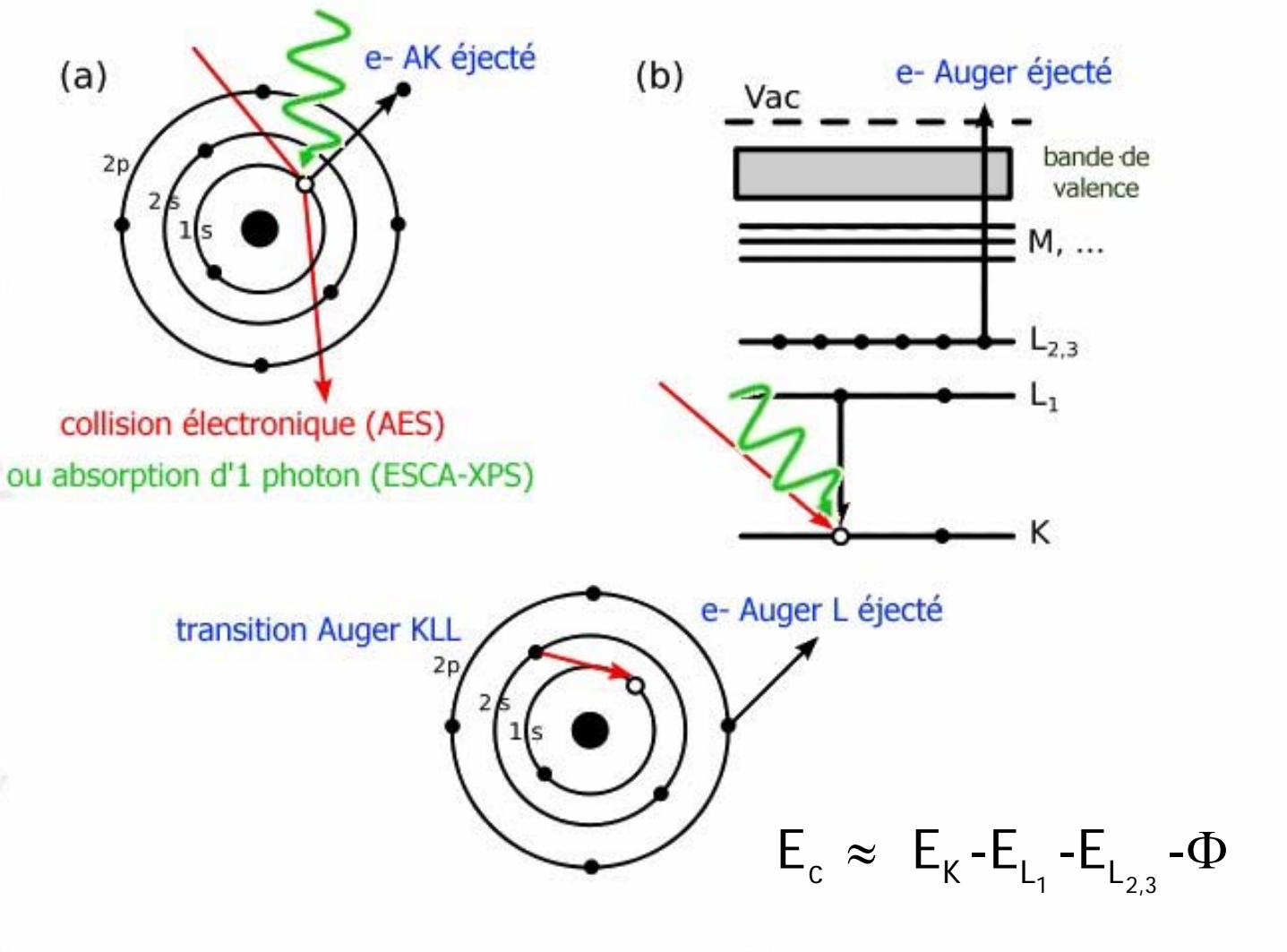
Accompagnée d'une émission d'ions secondaires  $\approx 1/1000$

Exaltée par l'oxygène

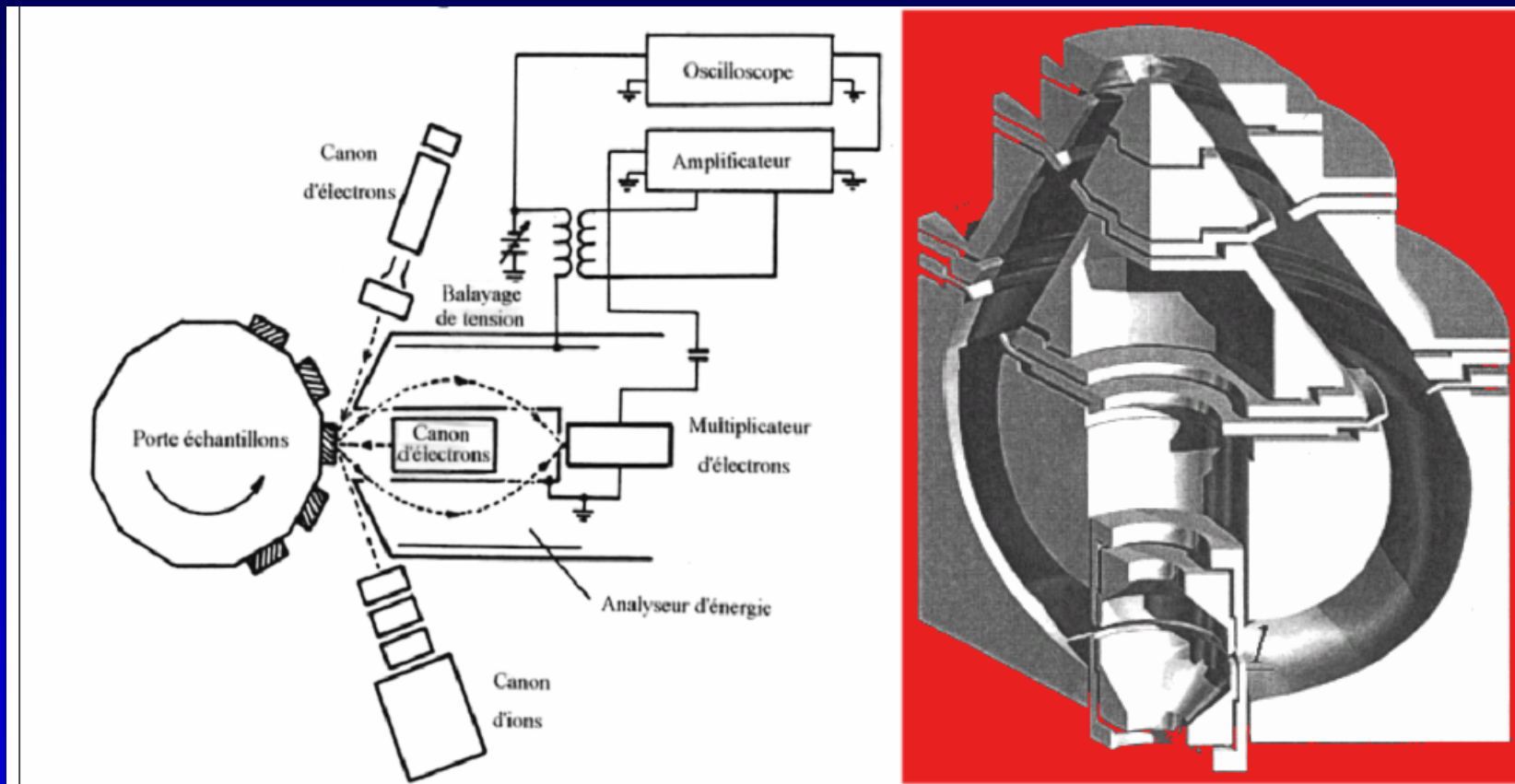
# SPECTROMETRIES DU VIDISTE



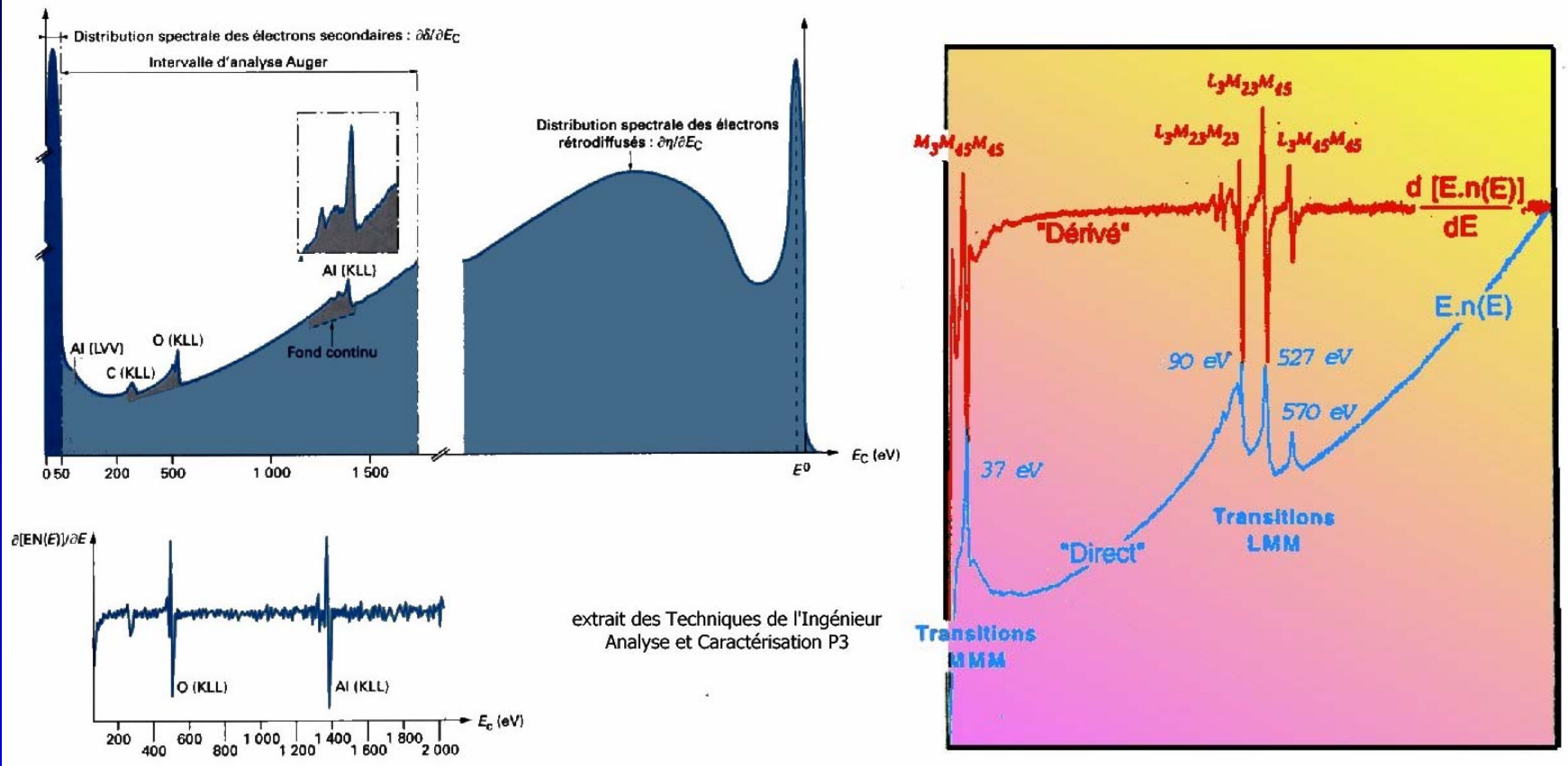
# LA SPECTROMETRIE AUGER AES



# LE DISPOSITIF

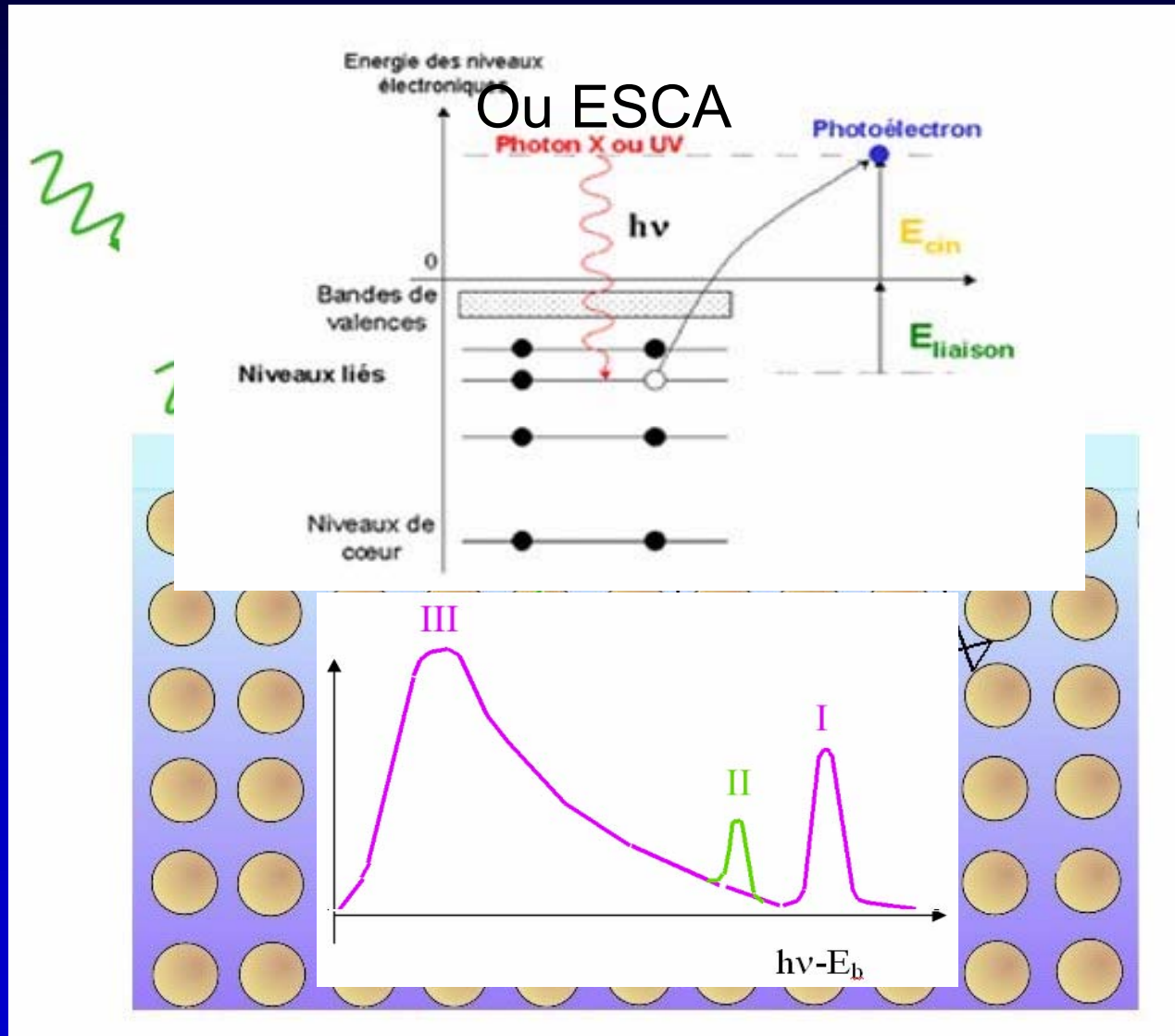


# LES SPECTRES

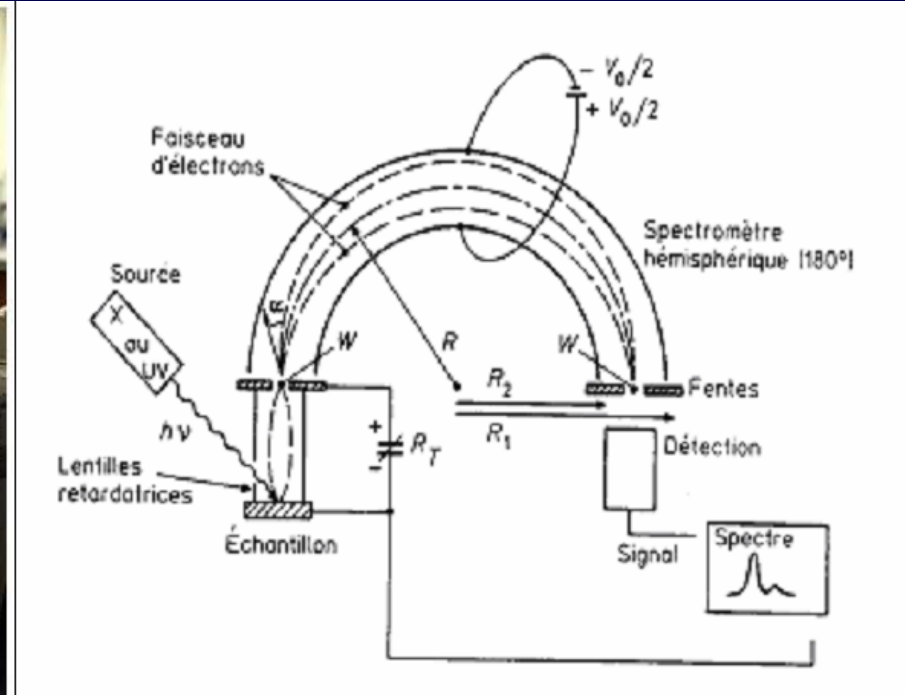
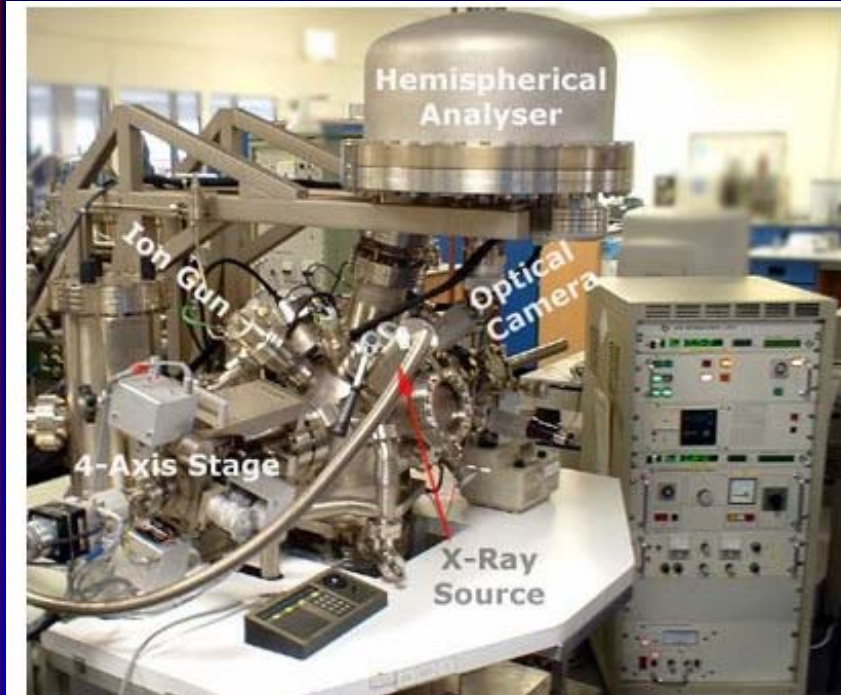


Problème avec les charges sur isolant!

# LA SPECTROMETRIE XPS



# LE DISPOSITIF

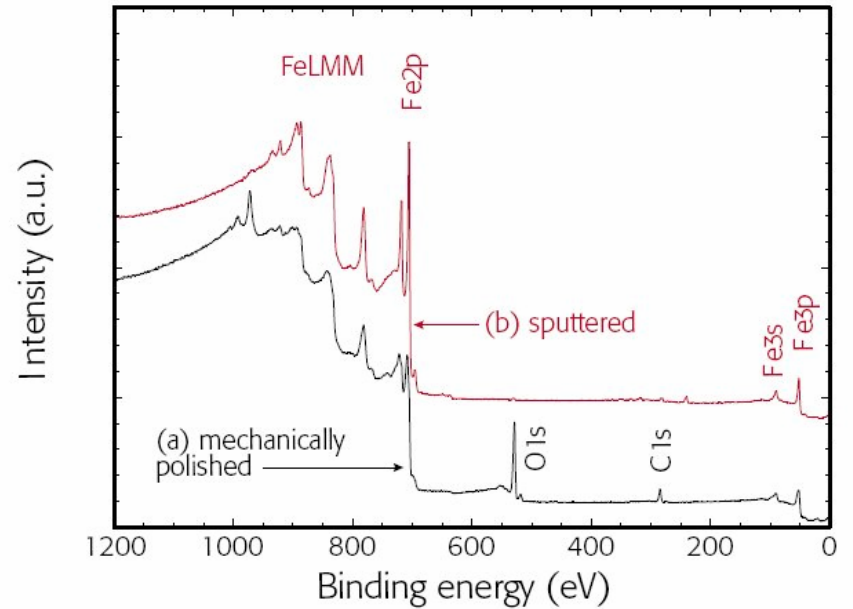
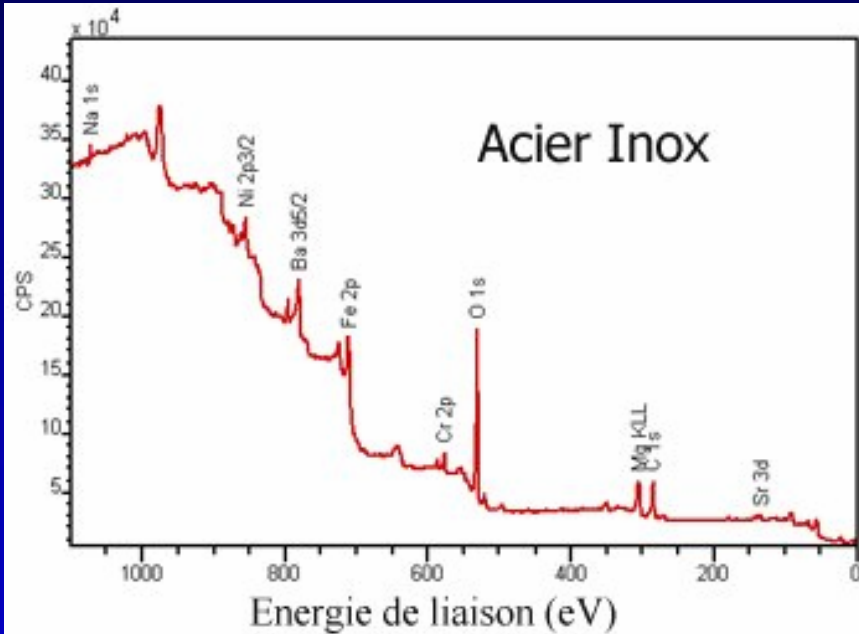


Valable  $\forall$  matériau 1ppm

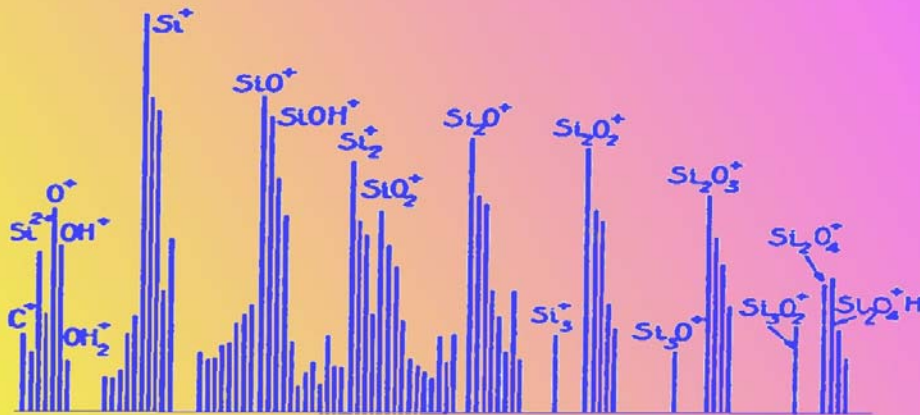
On utilise la raie  $K\alpha$  à  $8.34 \text{ \AA}$  -  $1486\text{eV}$



# LES SPECTRES



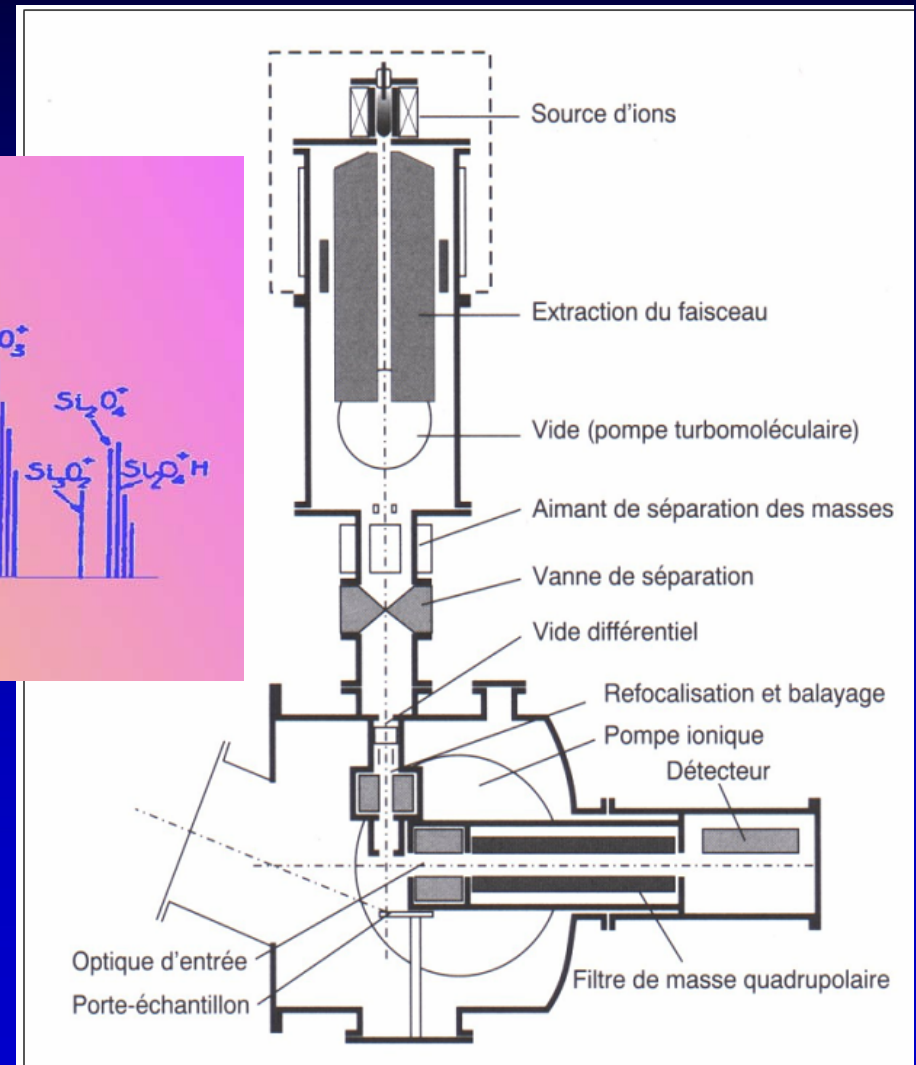
# LA SPECTROMETRIE SIMS



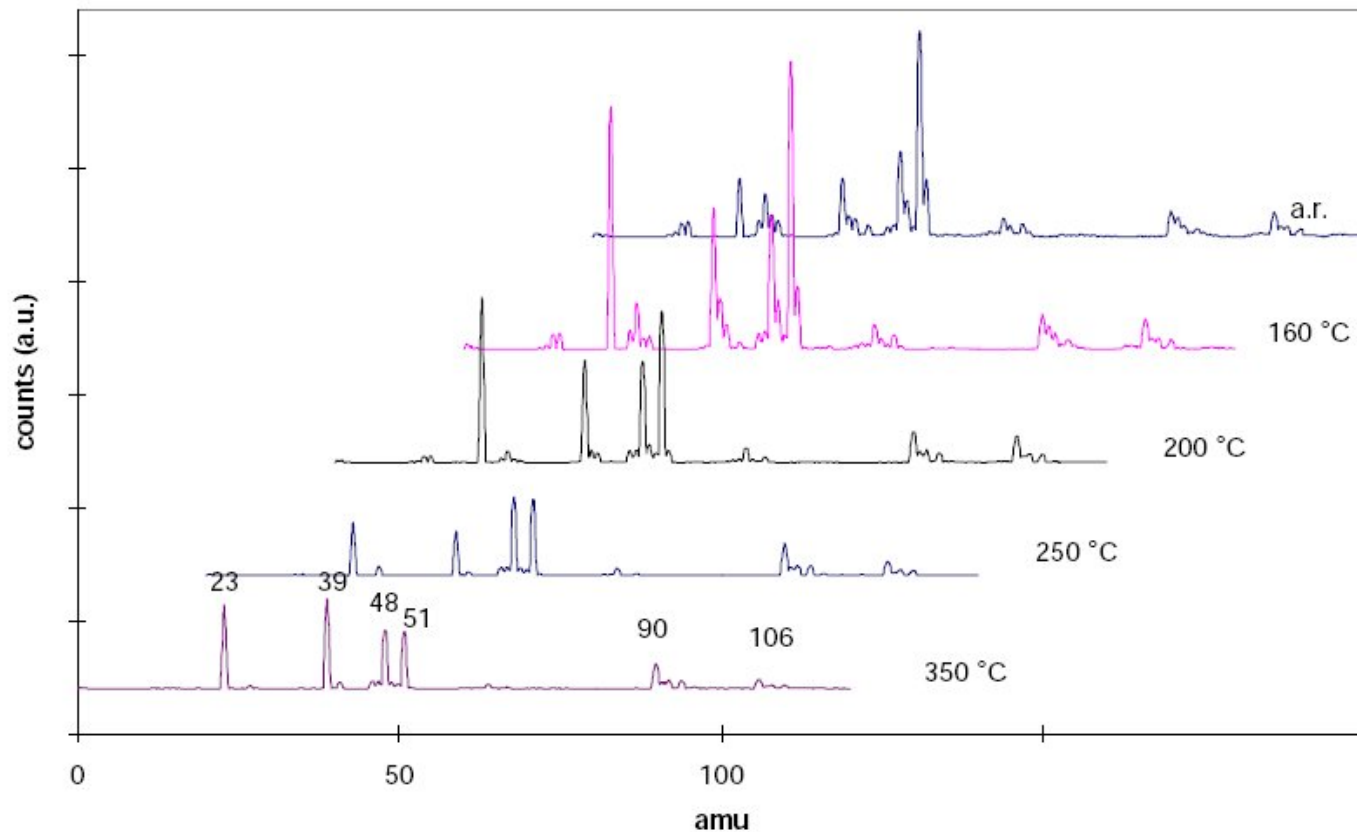
Méthode destructrice  
Identification aisée

0.1 ppb-0.1 ppm

profilage



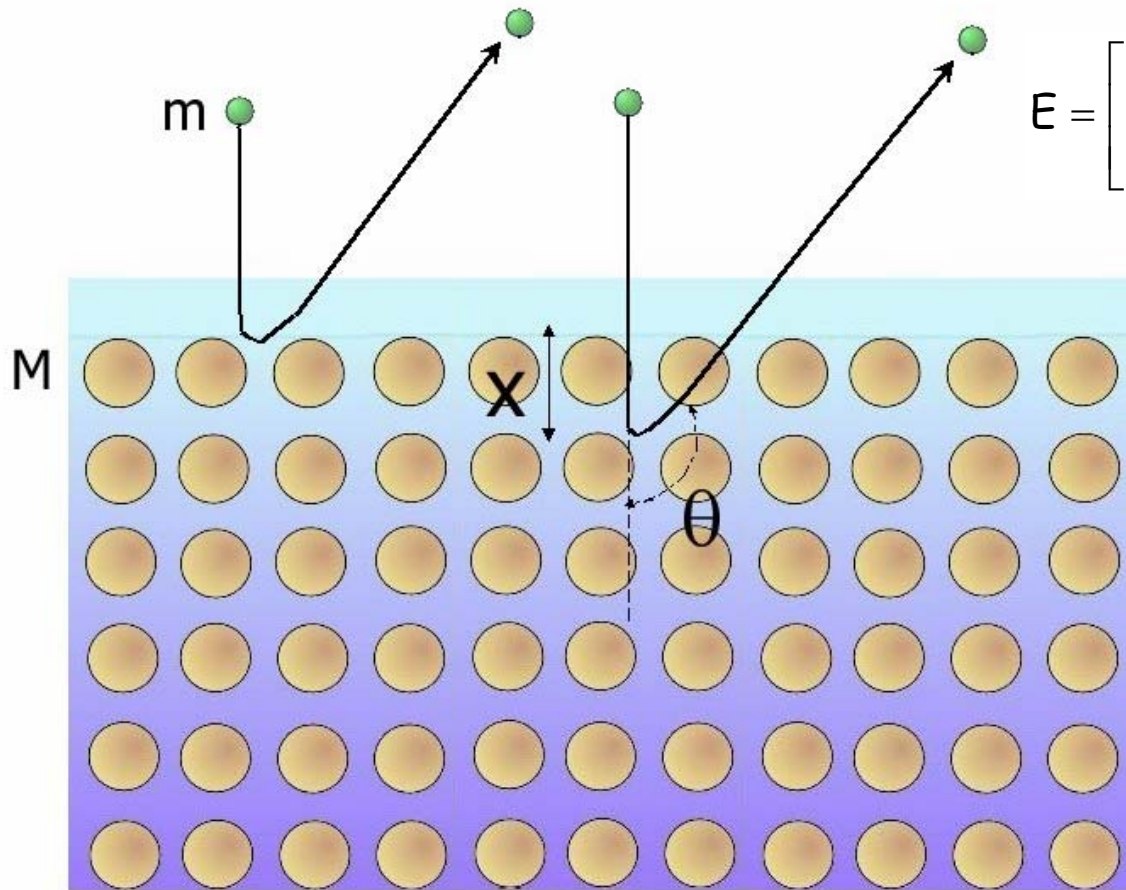
# LA SPECTROMETRIE SIMS



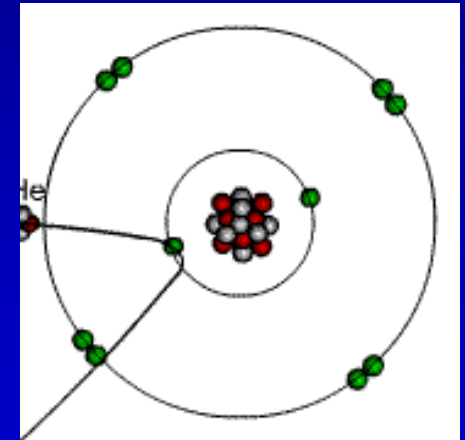
Positive secondary ion mass spectra as a function of 1h heating temperature. The main metal and metal oxide peaks are 48–Ti, 51–V, 90–Zr, 64–TiO, 67–VO and 106–ZrO. The peaks at 23 and 39 amu are characteristic for Na and K, respectively. The peaks at lower masses in the as received spectrum are mainly caused by hydrocarbon fragments (e.g. 15-CH<sub>3</sub>, 27-C<sub>2</sub>H<sub>3</sub>, 29-C<sub>2</sub>H<sub>5</sub>, 41-C<sub>3</sub>H<sub>5</sub>, 43-C<sub>3</sub>H<sub>7</sub>).

# LA SPECTROMETRIE RBS

Dite à recul élastique ou rétrodiffusion Rutherford



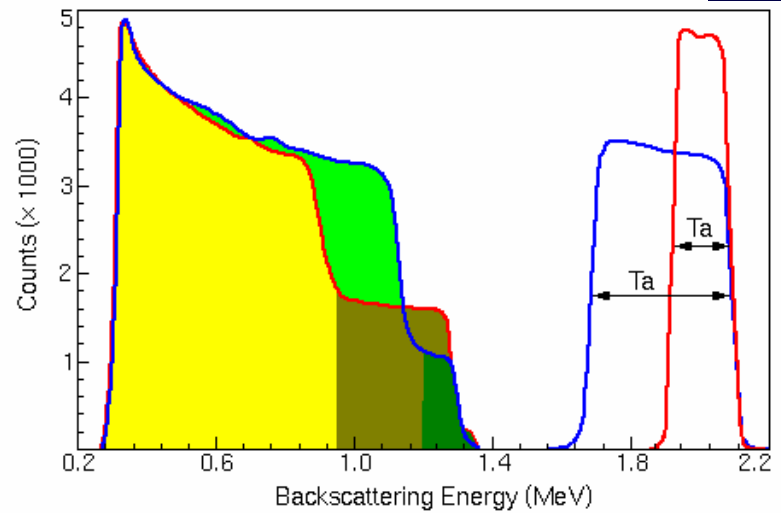
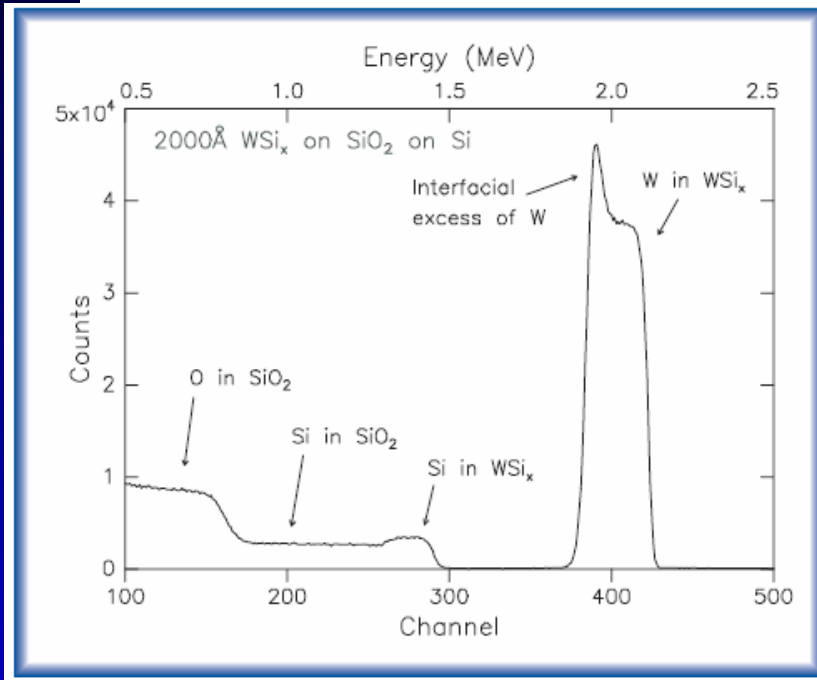
$$E = \left[ 1 - 2(1 - \cos \theta) \frac{mM}{(m + M)^2} \right] E_0$$



# LE DISPOSITIF



# LES SPECTRES



M1>M2

Non destructive pour quelques  $\mu$

Défauts réticulaires

# QUE CHOISIR?

TECHNIQUE	AVANTAGES	INCONVENIENTS
<i>AES</i>	Haute résolution spatiale Rapide Bonne précision avec les standards	Risque de dommages Problème de charges
<i>XPS</i>	Information chimique Faible dommages Bonne précision avec les standards Peu de problème de charge	Pauvre résolution spatiale Lente Ne détecte pas H
<i>SIMS</i>	Extrêmement sensible Détecte H Analyse des isotopes Très rapide	Quantification ardue Destructrice
<i>RBS</i>	Profilage en profondeur Non destructrice Quantification absolue Rapide	Requiert un accélérateur Pauvre résolution en profondeur Pas d'analyse qualitative

**Merci et bravo  
pour votre attention!!**