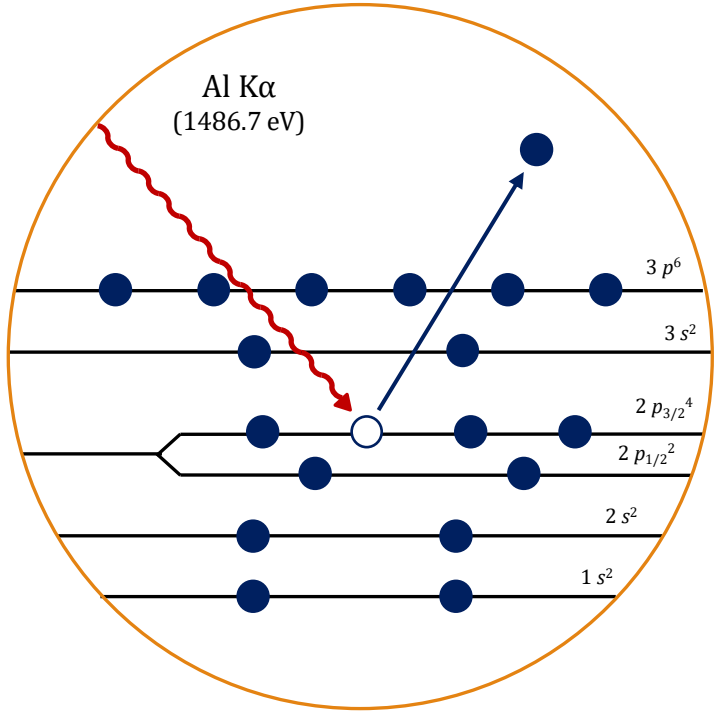
X-Ray Photoelectron Spectroscopy



Aalto University
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XPS

X-Ray Photoelectron Spectroscopy

OUTLINE:

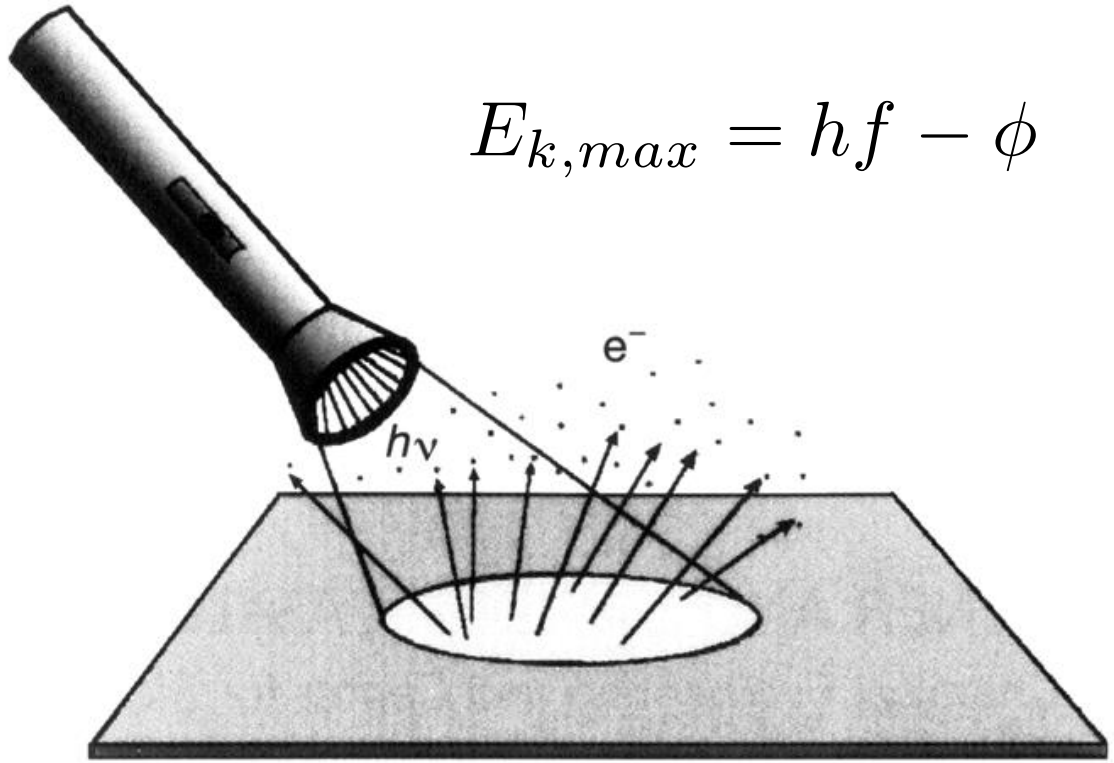
1. Background
   1. Phenomenon
   2. Instrumentation
2. Typical measurement data
   1. Qualitative analysis & spectral features
   2. Peak identification
3. Analysis and results
   1. Quantitative analysis & effects of sample
   2. Chemical environment & peak fitting
4. Technical issues & Auxiliary features
   1. Ion beam sputtering & depth profiling
   2. Angle resolved XPS
   3. Surface charging & energy calibration
   4. Small area analysis and imaging

The photoelectric effect

Emission of electrons when light is shone onto a material:

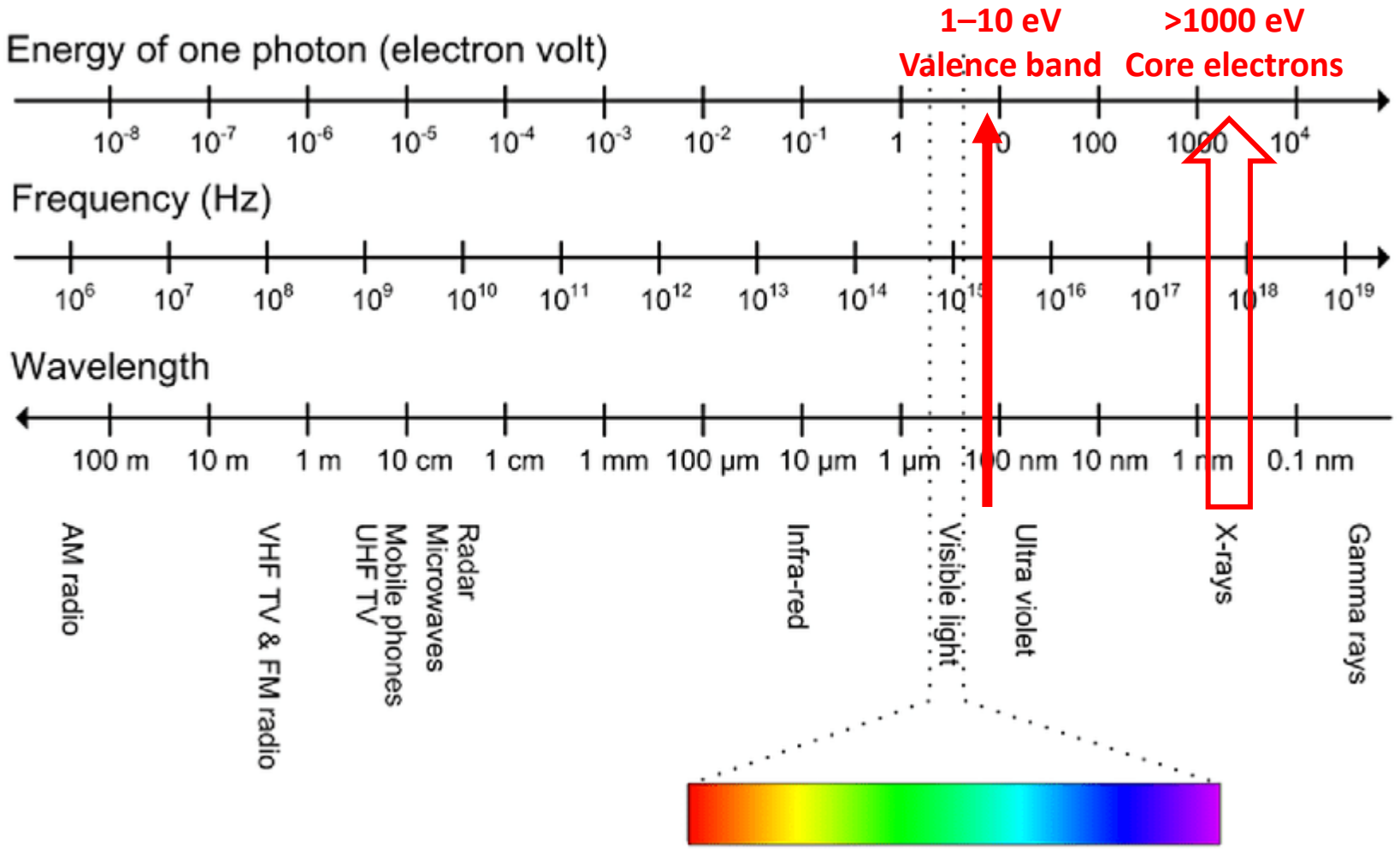
- Photoelectrons

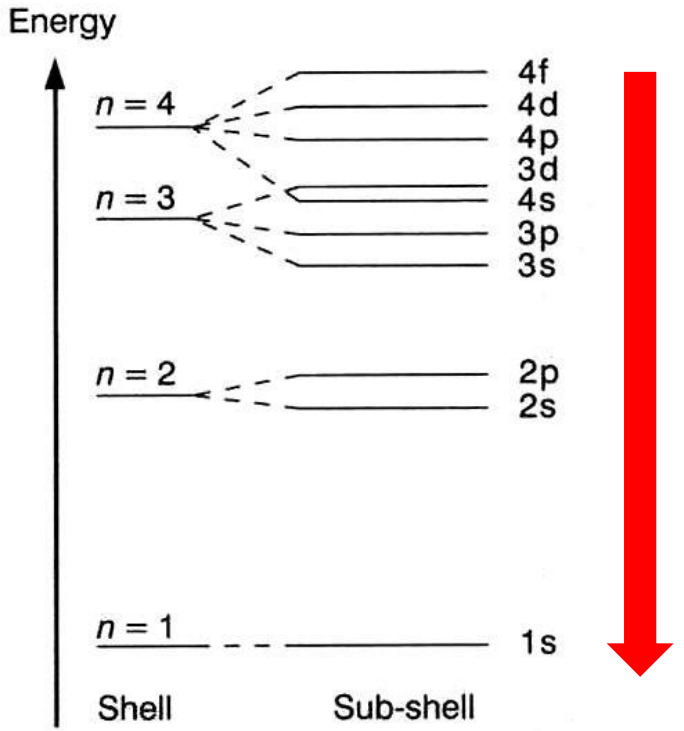
- Metal plate irradiated by UV light emits charged particles: H. Hertz, 1887
- Shown to be electrons: J. J. Thompson, 1899
- Theory on photon quanta: A. Einstein, 1905
- Verified through experiments: R. Millikan, 1915



$$E_{k,max} = hf - \phi$$

The electromagnetic spectrum



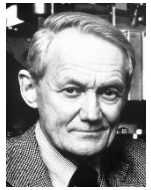


- Core levels have larger differences in energy!

Photoemission as an analytical tool

Electron Spectroscopy for Chemical Analysis (ESCA)

- Kai Siegbahn, 1957 (Nobel Prize 1981)

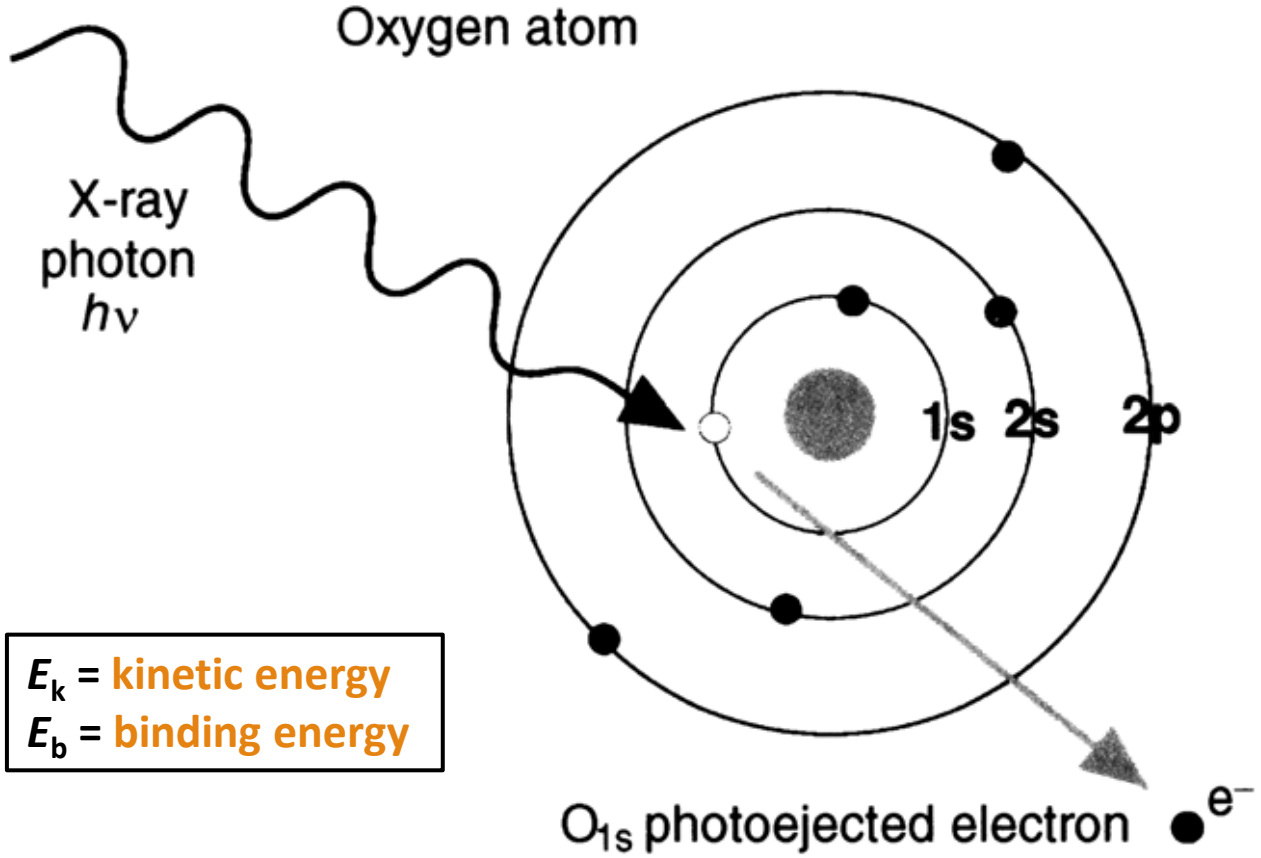


- Intensity of photoelectrons versus E_b or E_k
- Non-destructive analysis technique
- Elemental identification, surface stoichiometry, chemical environments, electronic structure, microscopy with chemical sensitivity…

Widely used technique for surface analysis:

- **XPS**: X-Ray Photoelectron Spectroscopy
- **ESCA**: Electron Spectroscopy for Chemical Analysis
- **UPS**: Ultraviolet Photoelectron Spectroscopy
- **PES**: Photoemission Spectroscopy

$$E_k = hf - (E_b + \phi)$$



E_k = **kinetic energy**
E_b = **binding energy**

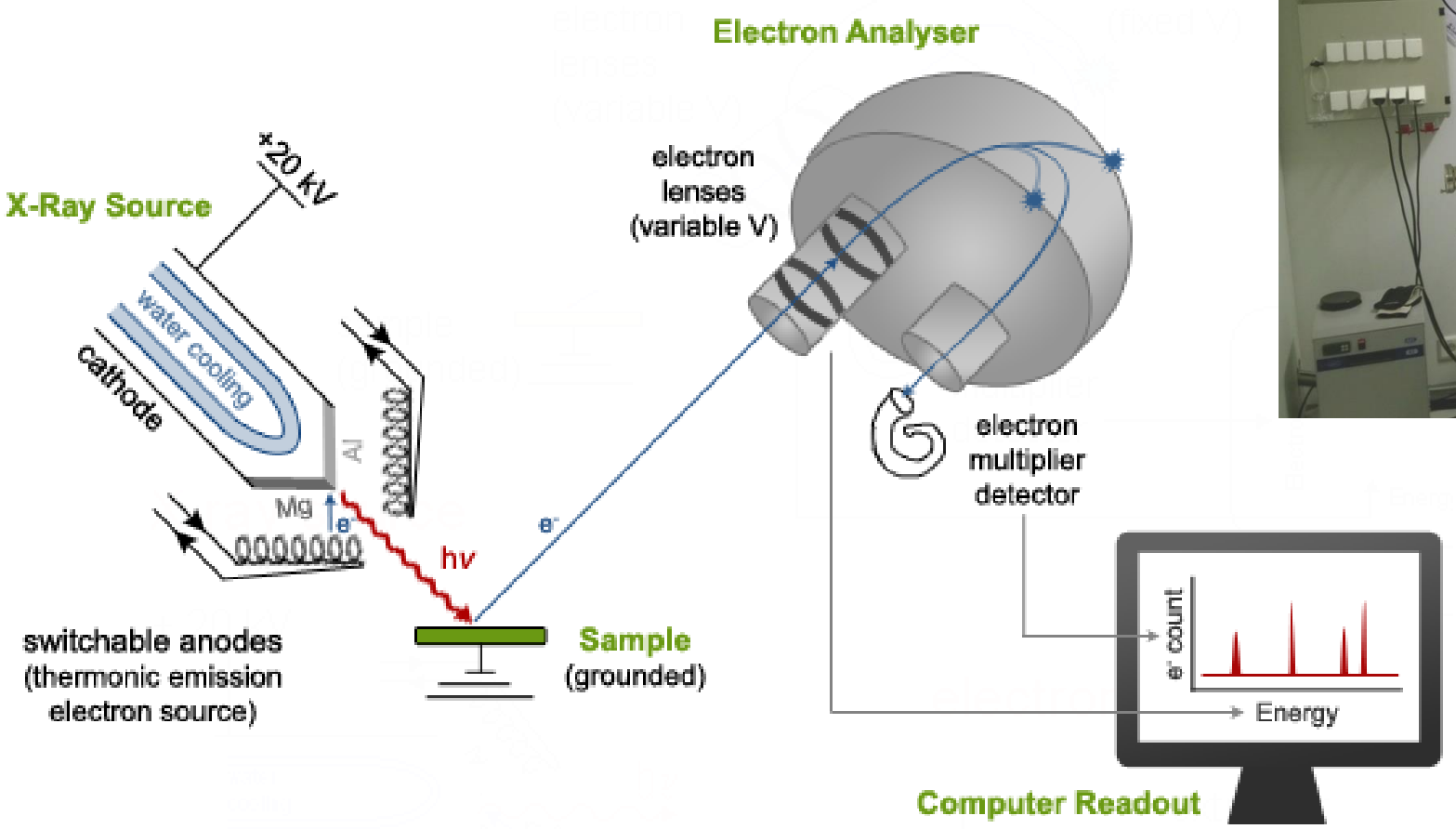
XPS in applied surface science

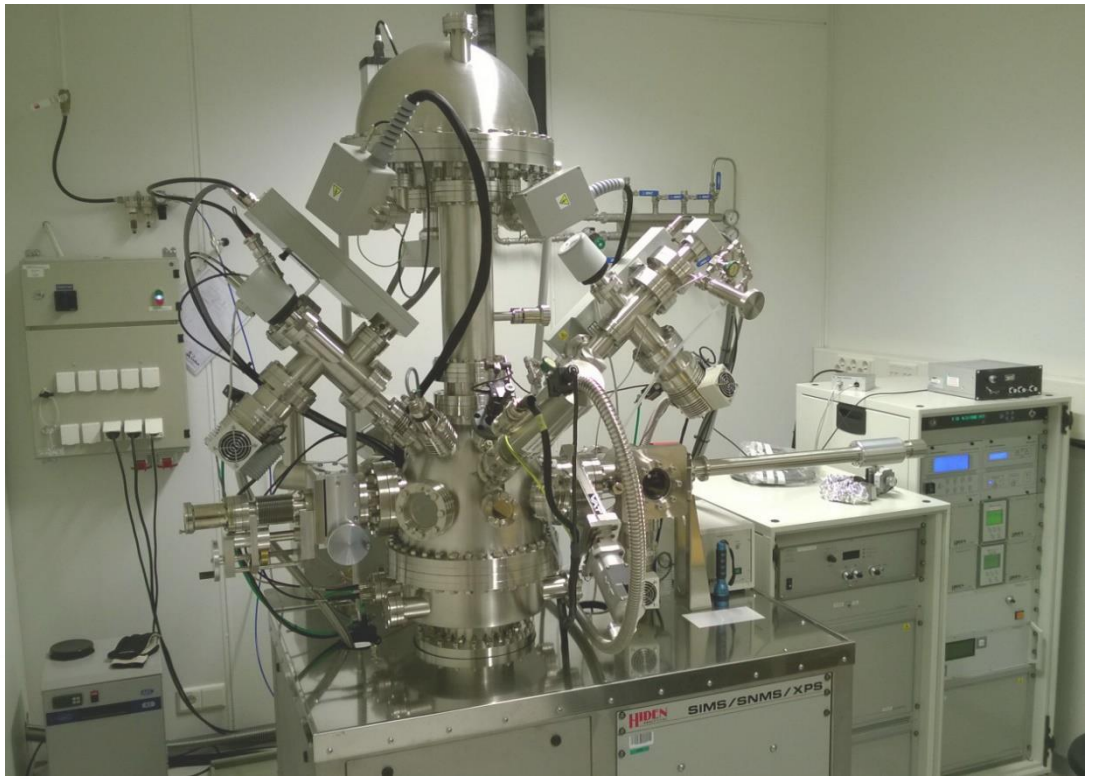
Quantification of elements at the surface of materials

- Analysis depth less than 10 nm
- Detection of all elements, except for hydrogen
- Chemical identification
- Surface distributions in the first 10 nm (such as films vs islands?)

- Allows for insulating, conducting or heterogeneous samples
- Including composites and organic samples (even biological specimens)
- Easy sample preparation
- Non-destructive (no particle bombardment, only very soft X-rays)

Instrumentation



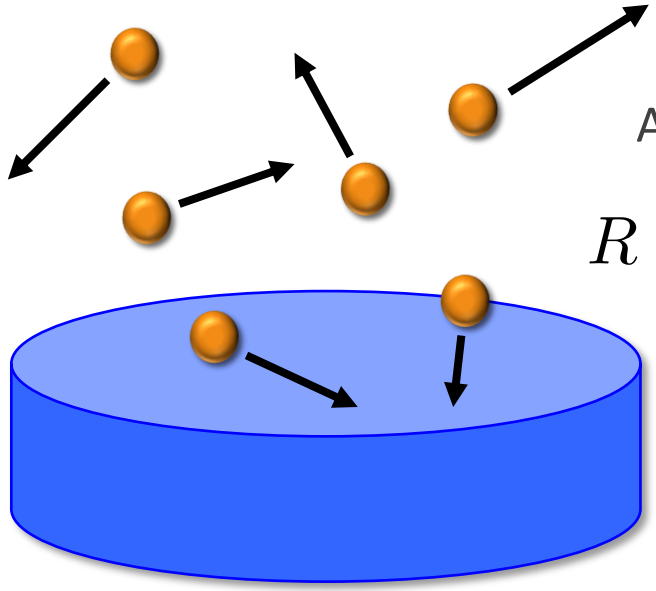


- X-ray source (typically Mg or Al anode)
- Electron energy analyzer
- Electronics & computer system

Vacuum chamber:

- Ar ion gun
- Low energy electron flood gun
- Cooling system

Degree of vacuum



Absorption rate:

$$R = \frac{p}{\sqrt{2\pi MkT}}$$

Improved vacuum:

- Increases the mean free path for photons and electrons
- Removes adsorbed gases from the sample
- Eliminates adsorption of contaminants on sample surface

Low vacuum	$10^{3} – 10^{0}$ mbar
Medium vacuum	$10^{0} – 10^{-3}$ mbar
High vacuum	$10^{-3} – 10^{-6}$ mbar
Very high vacuum	$10^{-6} – 10^{-9}$ mbar
Ultra-high vacuum	$10^{-9} – 10^{-12}$ mbar

Example:

- p = 10^{-6} mbar
- O_2 (M=32)
- T = 300 K

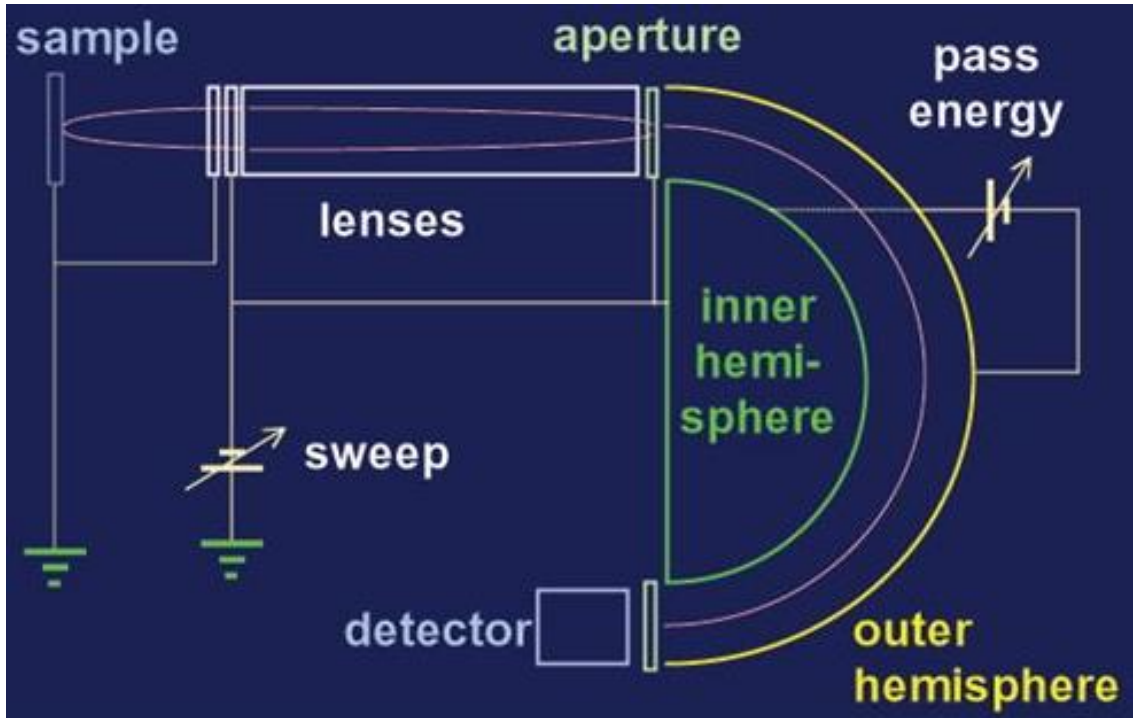
$$R = 4.7 \cdot 10^{14} \frac{1}{\mathrm{cm^2 s}}$$

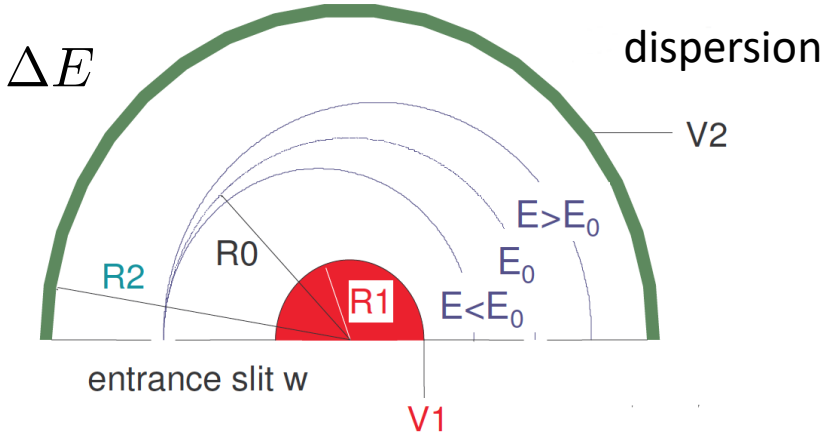
Complete coverage: $1\mathrm{ML} \sim 1 \cdot 10^{15} \mathrm{atoms/cm^2}$

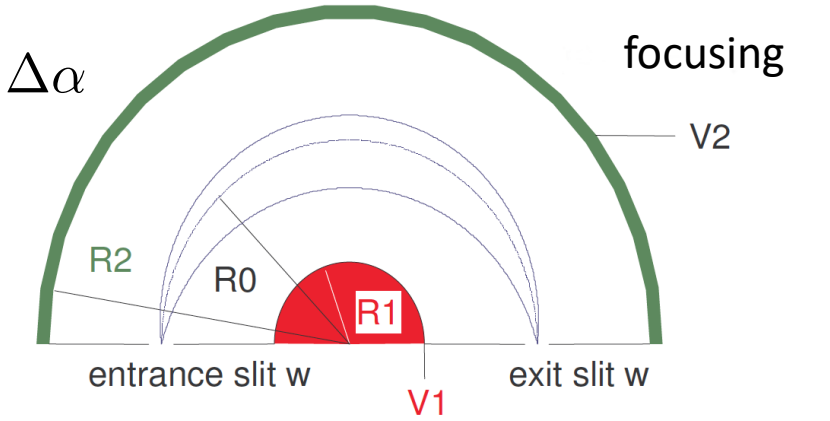
- Surface will be clean for about 1 second…

Analyzer

- Concentric hemispherical analyzer
- Lens system for focusing and retarding electronics – **pass energy** kept constant







Pass energy: $$E_0 = \frac{2(V_2 - V_1)}{R_0}\left(\frac{1}{R_1} - \frac{1}{R_2}\right)^{-1}$$

Energy resolution: $$\frac{\Delta E}{E_0} = \frac{\omega}{2R_0} + \frac{\alpha^2}{4}$$

- Decrease E_0 or increase R_0 – Better energy resolution!

AXIS 165 / AXIS Ultra^{DLD}

at Aalto CHEM 1995-2021 (L-S Johansson)

Cellulosic materials (ca 50 % of samples):

- Pulps surface analysis & process evaluations
- Paper coatings, contamination, fundamentals
- Model surfaces, mono/multicomponent film formation, and reaction dynamics
- Cellulose nanofibrils, whiskers& bacterial cellulose, fundamentals & applications
- Wood hydrothermal modification, adhesion
- Derivatisations TEMPO, click, CMC, silylation…
- Functional surfaces, bio-interfaces, biological surfaces, biomimetic materials
- Composites cellulose and derivatives, polymers, clay, lignin, chitosan, graphene, CNTs
- Textiles: flax, cotton, MMC, synthetic fibers
- Carburisedcelluloses: e.g. catalysis

Materials other than celluloses (50 % samples):

- Ultra-thin inorganic and organic films: ALD deposited, spin-coated, LB films, CVD, plasma, graphenes, CNTs, DLCs
- Surface analysis of metals, alloys, oxides, composites, polymers, powders, fibers, deposits
- Contamination analyses: e.g. semiconductor devices, quality control

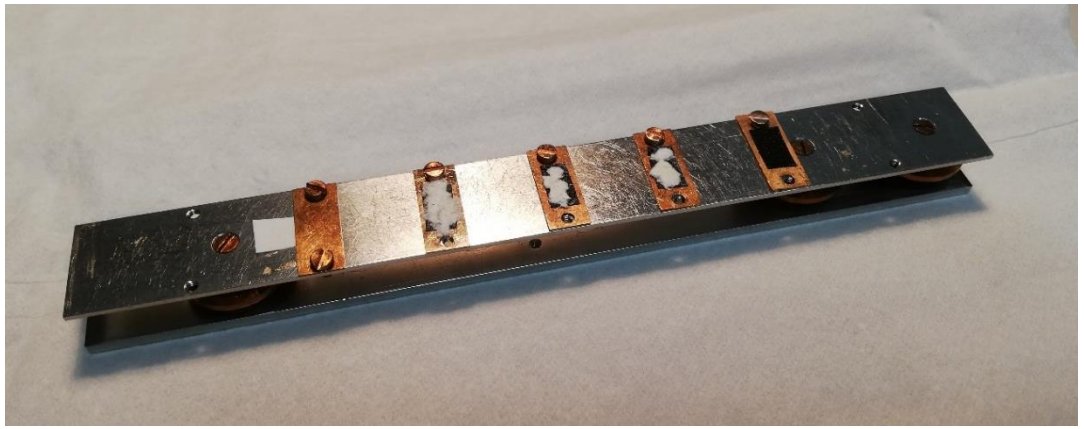
Limitations

XPS can only analyze the outermost surface (0-20 nm)

- It will not tell you the average sample composition
- Surface contamination is a big issue
- Samples must tolerate Ultra High Vacuum (<10^{-9} mbar)

Samples

- Almost any solid sample can be analyzed, provided it tolerates ultra high vacuum. Even insulating powders and fibers.
- Sample preparation: As little as possible.
- Samples are secured on the holder with springs or with vacuum compatible tape and then evacuated.



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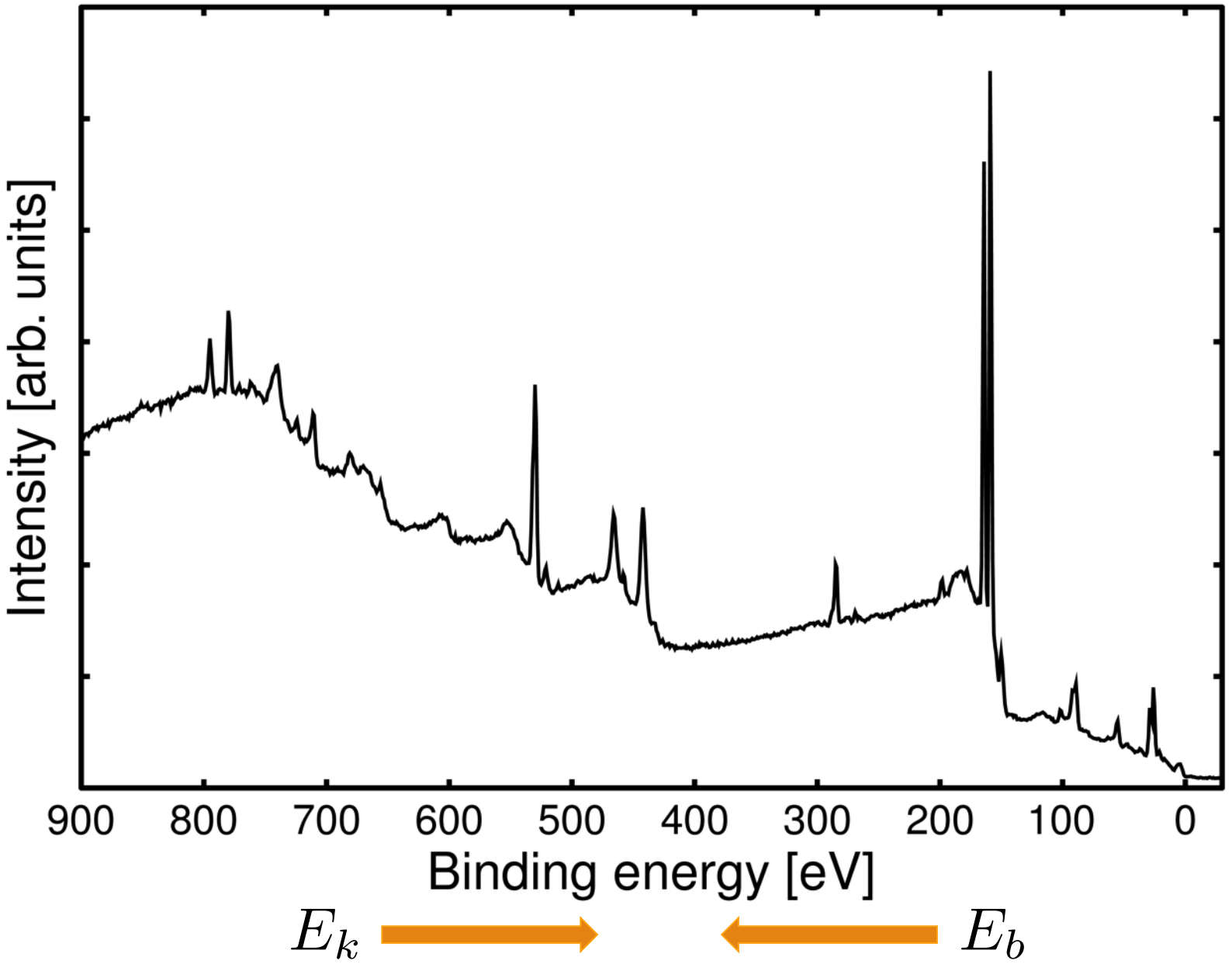
Experiment

Measurement:

- Retarding potential is step-wise decreased
- Dwell time for each step: a few 100 ms
- Number of electrons measured for each energy

Results:

- Photoemission spectrum
- High intensity peaks at core level binding energies
- **Survey spectra** – large range, low resolution
- **High-resolution spectra** – small range, high resolution



Binding energies

Core level energies are element specific:

- Each peak in the survey spectrum can be assigned to the binding energy of electrons from a specific energy level and element

Identification:

- Start with the strongest peaks – find energy level that matches (C 1s, O 1s + Auger lines are usually present)
- Compare other energy levels in element with spectrum – assign peaks
- Usually **fixed ratios** between **peak heights** for same element
- If there is a strong peak, but the other lines for that element do not appear – try to find another element!

Table 4.2. Binding energies of some elements

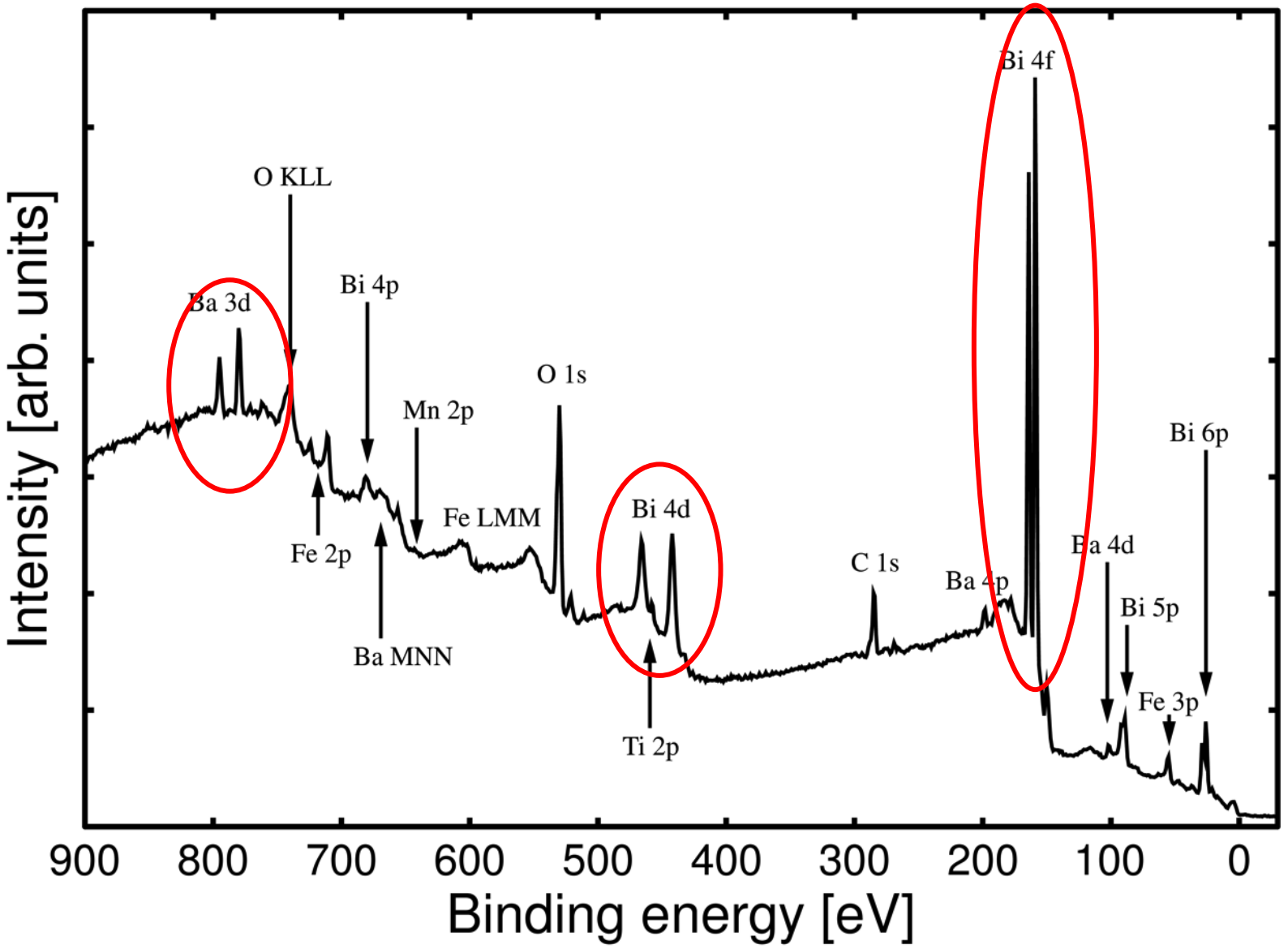
Z	El	$1s_{1/2}$ K	$2s_{1/2}$ L_1	$2p_{1/2}$ L_2	$2p_{3/2}$ L_3	$3s_{1/2}$ M_1	$3p_{1/2}$ M_2	$3p_{1/2}$ M_3	$3d_{3/2}$ M_4	$3d_{5/2}$ M_5
1	H	14								
2	He	25								
3	Li	55								
4	Be	111								
5	B	188			5					
6	C	284			6					
7	N	399			9					
8	O	532	24		7					
9	F	686	31		9					
10	Ne	867	45		18					
11	Na	1072	63		31	1				
12	Mg	1305	89		52	2				
13	Ml	1560	118	74	73	1				
14	Si	1839	149	100	99	8				
15	P	2149	189	136	135	16	10			
16	S	2472	229	165	164	16	8			
17	Cl	2823	270	202	200	18	7			
18	Ar	3202	320	247	245	25	12			
19	K	3608	377	297	294	34	18			
20	Ca	4038	438	350	347	44	26		5	
21	Sc	4493	500	407	402	54	32		7	
22	Ti	4965	564	461	455	59	34		3	
23	V	5465	628	520	513	66	38		2	
24	Cr	5989	695	584	757	74	43		2	
25	Mn	6539	769	652	641	84	49		4	
26	Fe	7114	846	723	710	95	56		6	
27	Co	7709	926	794	779	101	60		3	
28	Ni	8333	1008	872	855	112	68		4	
29	Cu	8979	1096	951	932	120	74		2	
30	Zn	9659	1194	1044	1021	137	90		9	
31	Ga	10367	1299	1144	1117	160	106		20	
42	Mo	20000	2866	2625	2520	505	410	393	208	205
46	Pd	24350	36304	3330	3173	670	559	531	340	335
48	Ag	25514	3806	3523	3351	718	602	571	373	367
73	Ta*	67416	11681	11136	11544	*566	*464	*403	*24	*22
79	Au*	80724	14352	13733	14208	*763	*643	*547	*88	*84

* 4s, 4p et 4f levels indicated, respectively

Survey

- Peaks can now be labeled
- When all peaks are accounted for, elemental constituents have been found

- Some features are not necessarily discrete peaks from core level electrons:
- Double peaks
- Broad peaks in bunches
- Etc…



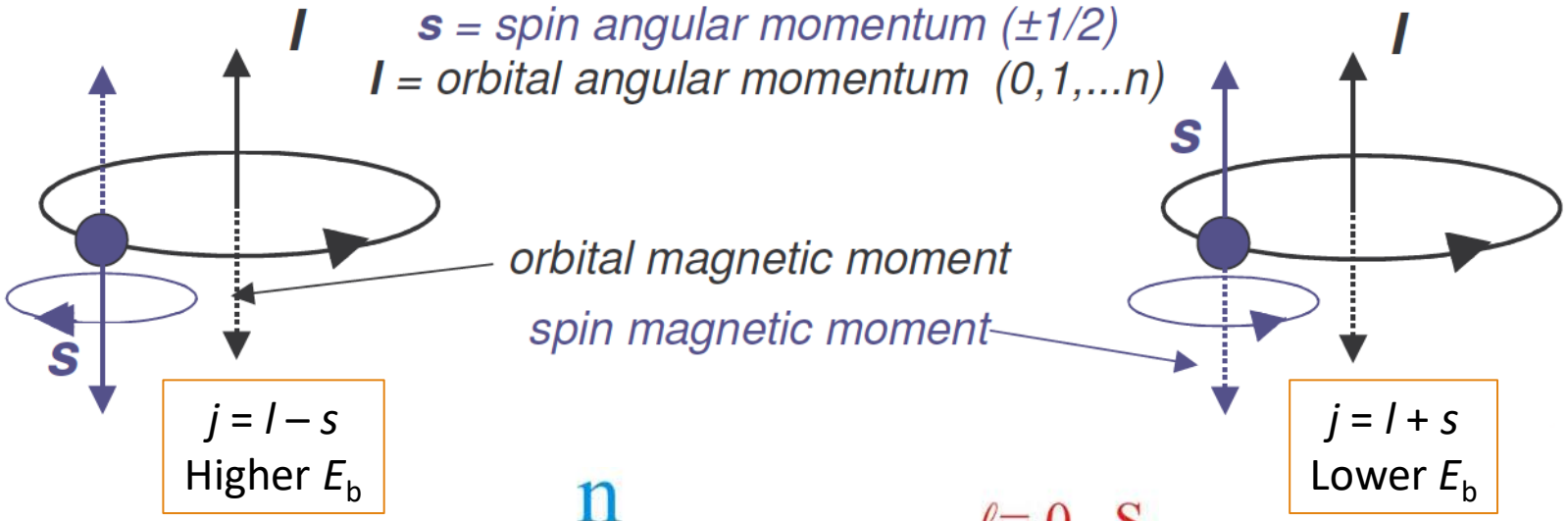
Spin-orbit splitting

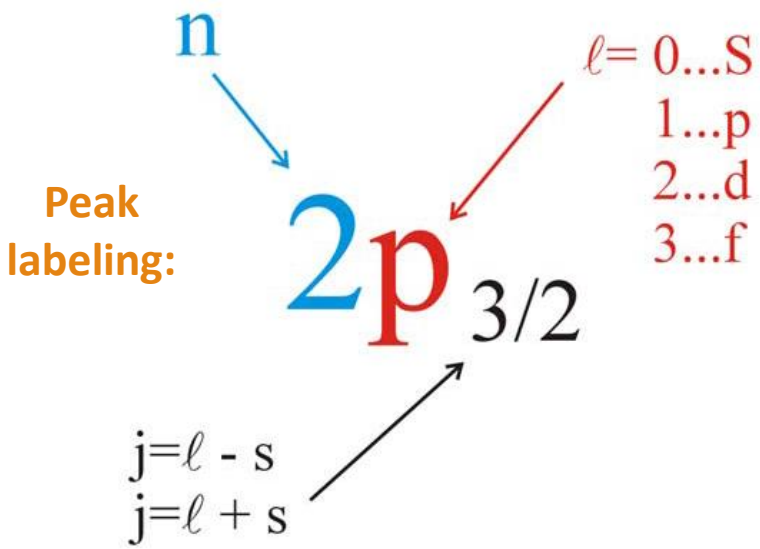
Before ionization
- Inner shells are filled
- No spin-orbit interactions

After ionization
- Un-paired electrons
- Spin-orbit coupling taken into account
- Interaction between magnetic moments from electron spin and orbit will affect final energies

- Potential energy minimized for antiparallel moments – E_k of photoelectron higher for parallel spins: E_b lower

After photoionization:





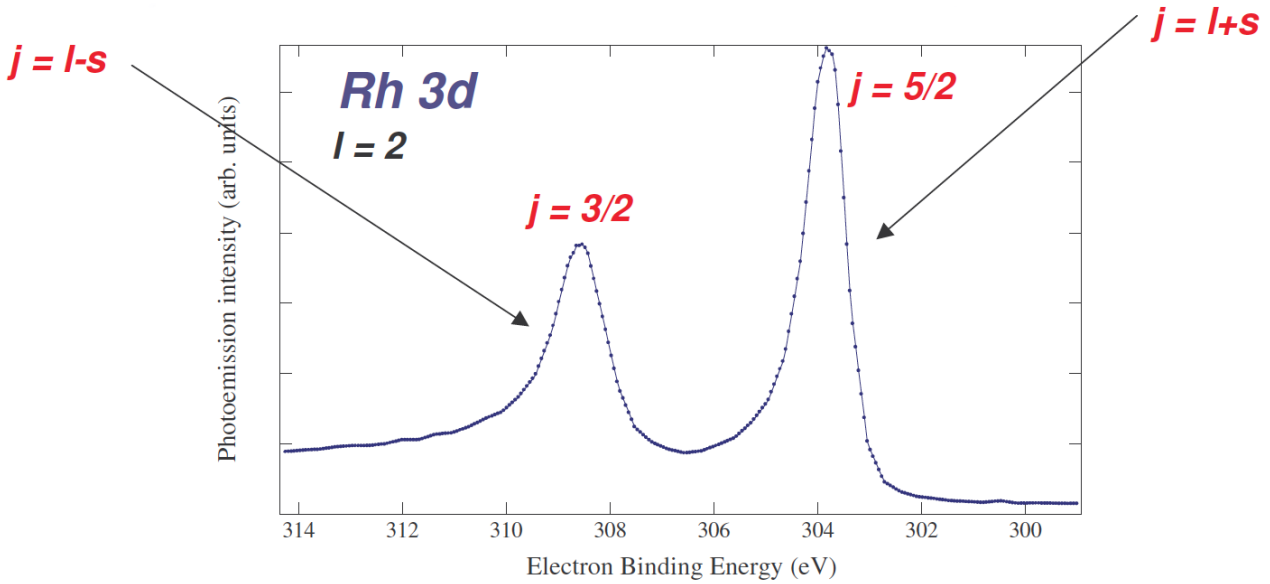
Doublet peak ratios

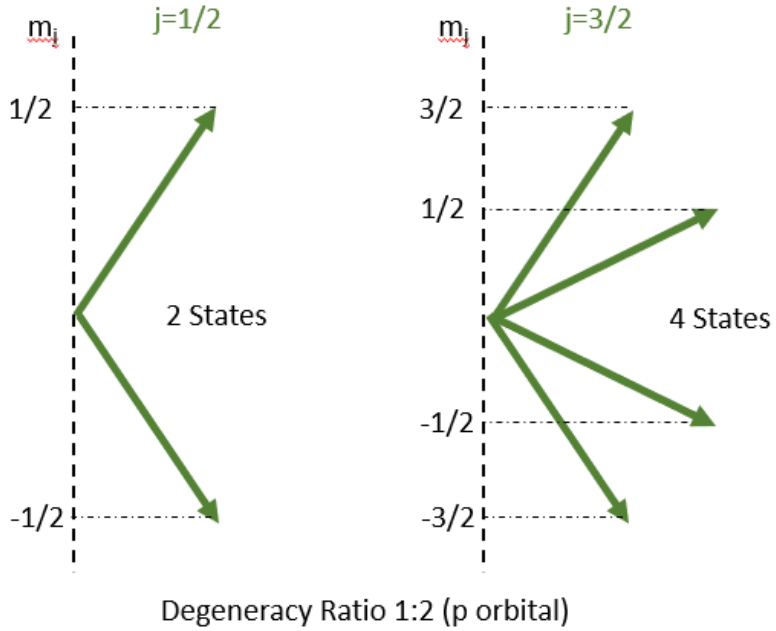
Spin-orbit splitting results in the formation of **doublets**

- Fixed area ratios between peaks!
  - Degeneracy of states: The total momentum *j* can have different orientations in space (m_l) with the same spin orbit-coupling energy

n	*l*	m_l
1	0	0
2	0	0
	1	-1, 0, +1
3	0	0
	1	-1, 0, +1
	2	-2, -1, 0, +1, +2

- Can be used for identification of elements
- For the same element ΔE_b will be approx. constant independent of compound



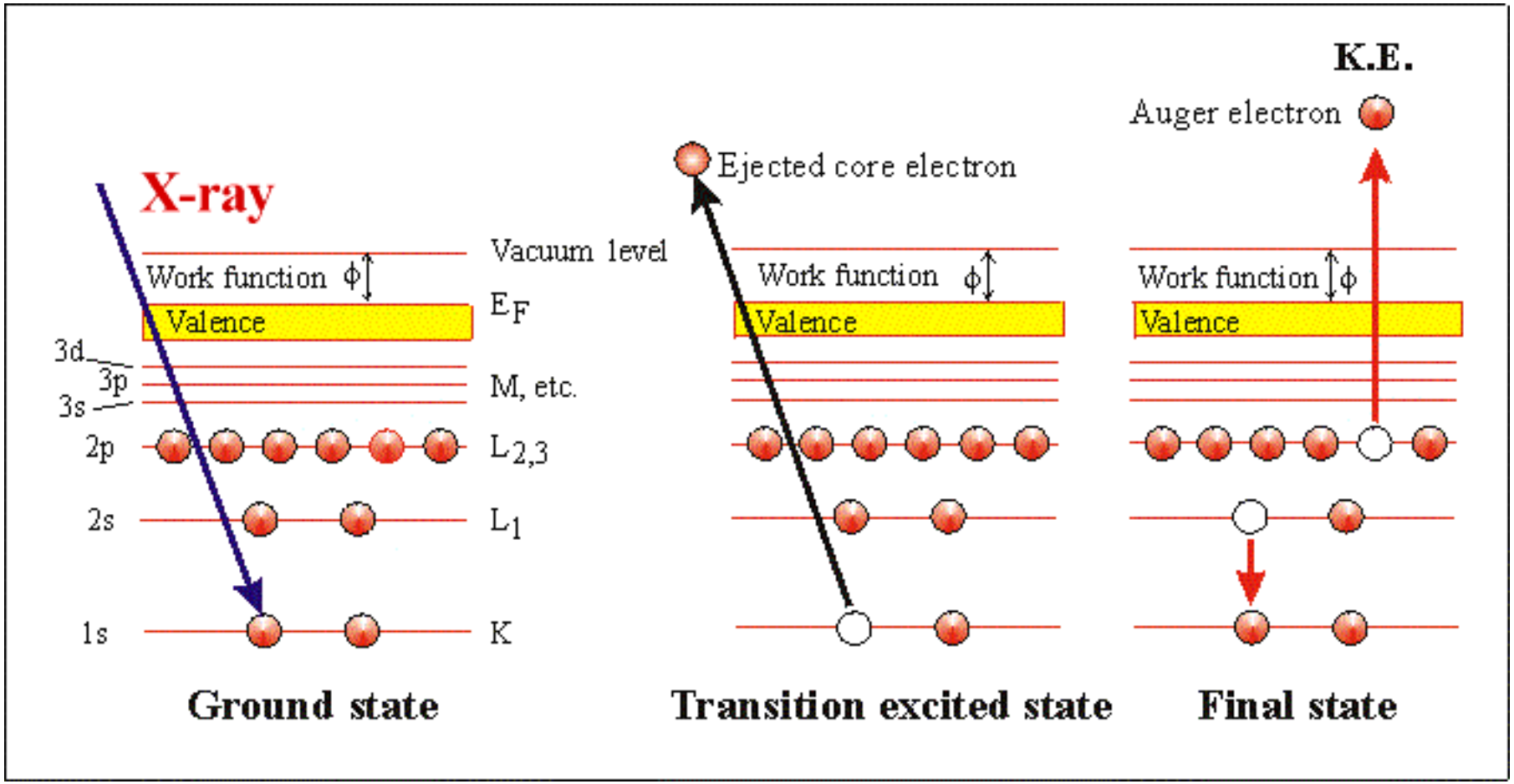


Degeneracy Ratio 1:2 (p orbital)

Orbital	Total Angular Momentum j	Degeneracy	Ratio
p	1/2	2	1:2
	3/2	4	
d	3/2	4	2:3
	5/2	6	
f	5/2	6	3:4
	7/2	8	

Auger electrons

- Atoms are in transitional excited states after core electrons are ejected
- Auger electrons can be emitted when excited states are relaxed
- E_k is independent of X-ray photon energy
- Position in E_b scale will depend on X-ray source



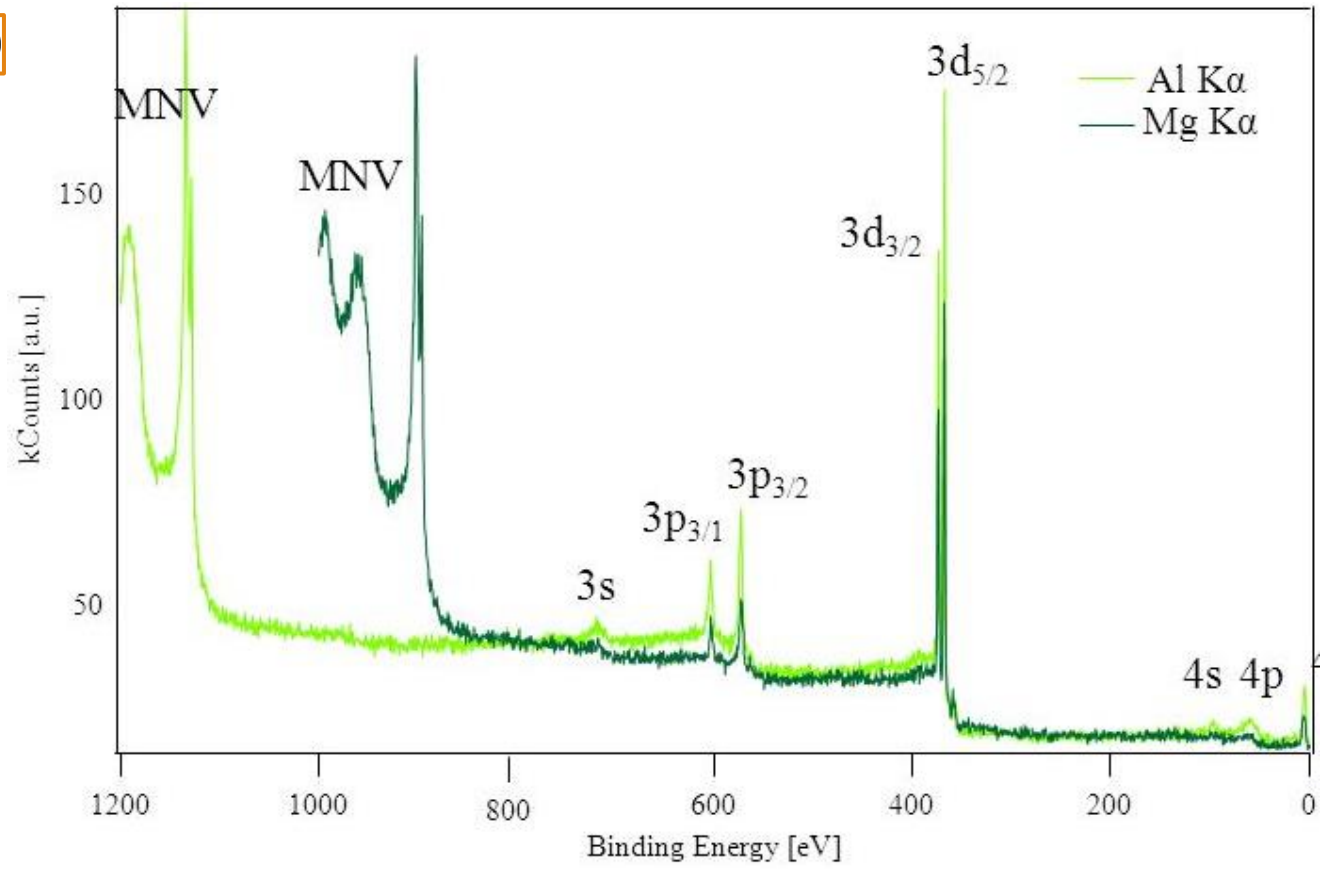
Characteristic X-rays

Different X-rays:

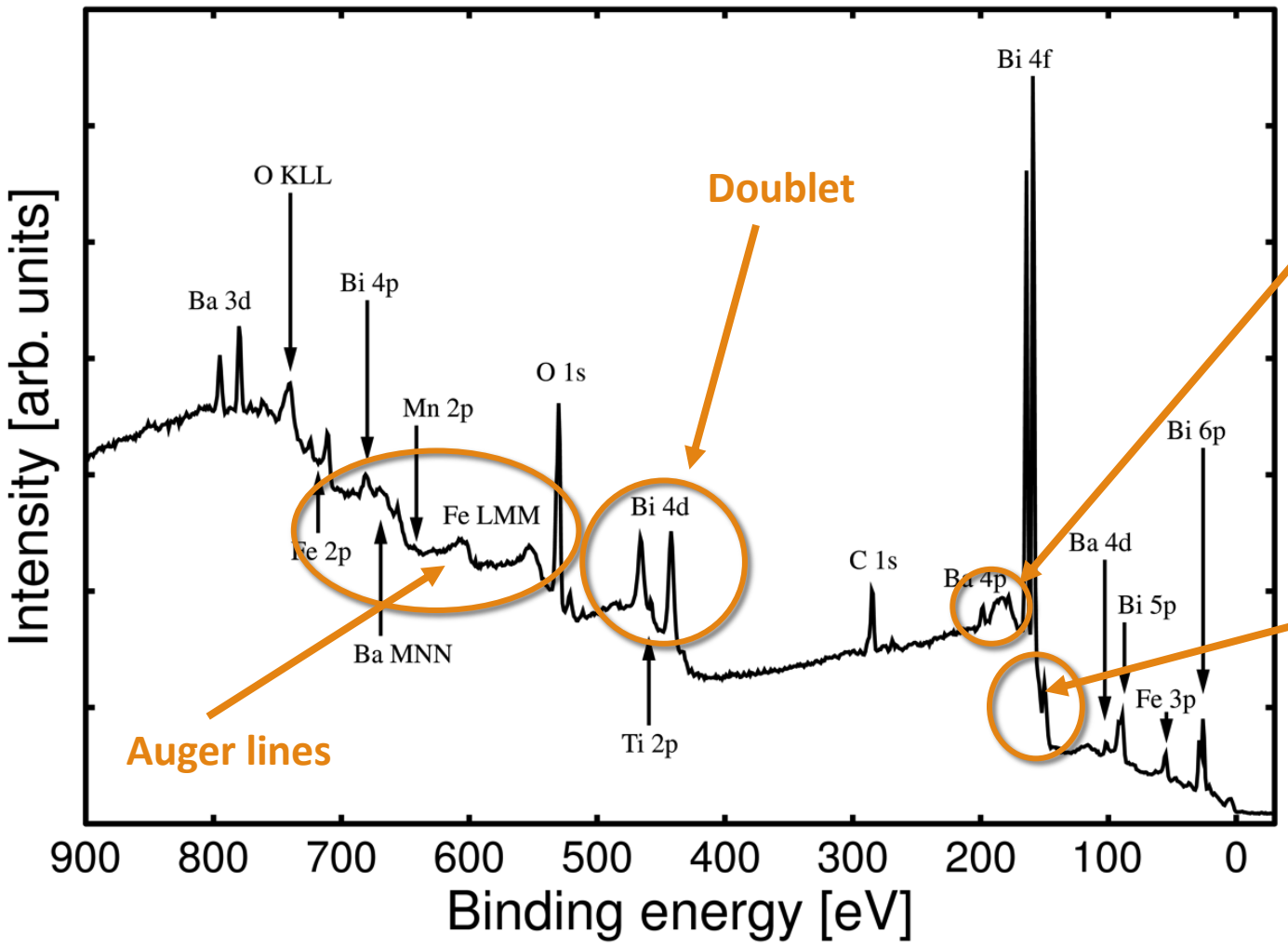
- Binding energy constant $E_k = hf - (E_b + \phi)$
- Auger transition ("binding") energy varies (kinetic energy for Auger electrons is constant)

Line	Energy (eV)	Width (eV)
Y M_ζ	132.3	0.47
Zr M_ζ	151.4	0.77
Cr L_α	572.8	3.0
Cu L_α	929.7	3.8
Mg K_α	1253.6	0.7
Al K_α	1486.6	0.85
Si K_α	1739.5	1.0
Cu K_α	8048.0	2.6

Typical Ag spectra:



Other features



Intrinsic loss features:

- Finite probability that the emitted core-shell electron will interact with a valence electron (that ends up in higher/unbound state) in the same atom – "**shake-up/off**" satellites, lower E_k

Extrinsic loss features:

- Photoelectrons travelling in a solid will interact with other electrons – lower E_k

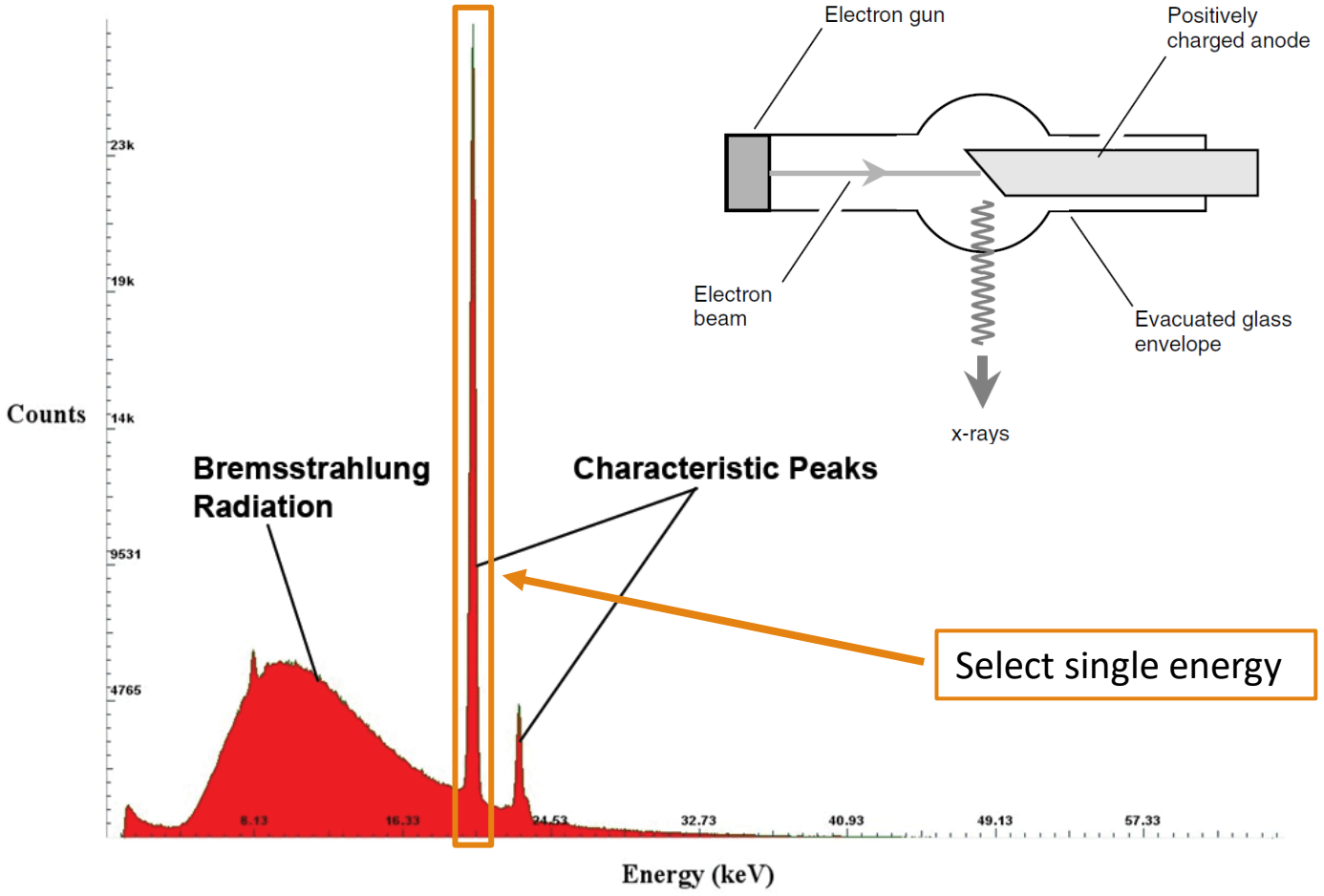
X-ray effects:

- **Satellites** – minor X-ray components from anode material – higher $E_0=hf$
- **Ghosts** – X-rays from other element (very rare)

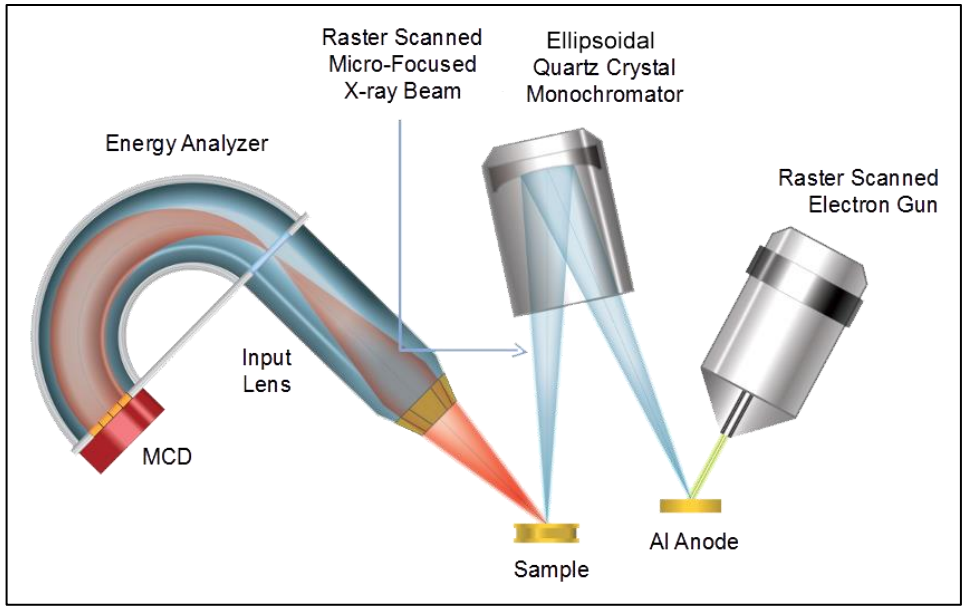
Satellites of Mg K_α

Line	α_{12}	α_3	α_4	α_5	α_6	β
Separation (eV)	0.0	8.4	10.2	17.5	20	48.5
Relative Intensity	100	8.0	4.1	0.55	0.45	0.5

X-Ray production



- X-ray tubes:
  - Continuous Bremsstrahlung
  - Characteristic peaks that depend on the anode material
- Unnecessarily large X-ray load & unwanted satellites in the spectra
- Solution: Monochromator



X-Ray monochromator

Advantages of X-monochromator:

- Narrow peak width, focusing of beam
- Reduced background, no satellite or ghost peaks

Disadvantage:

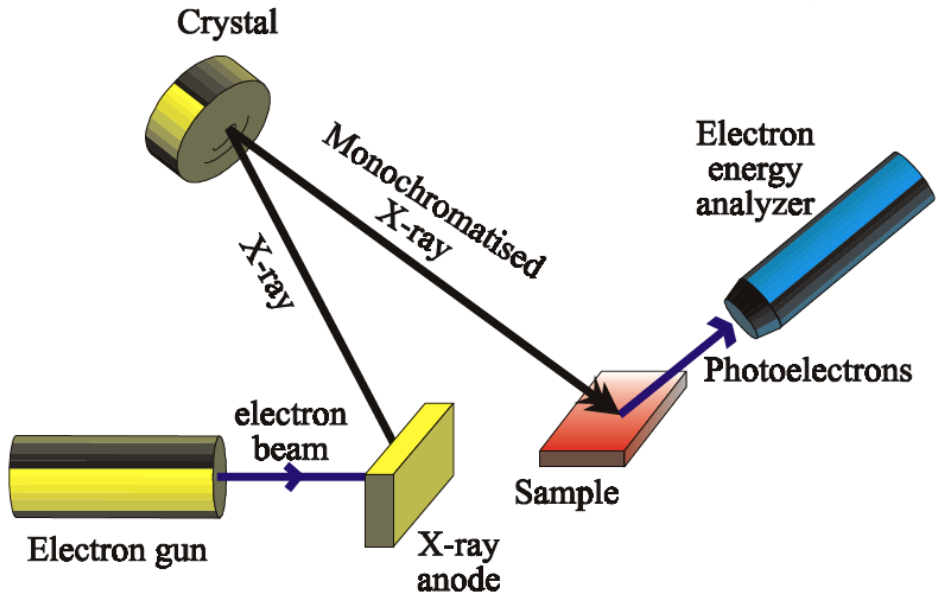
- 10-40 times lower intensity

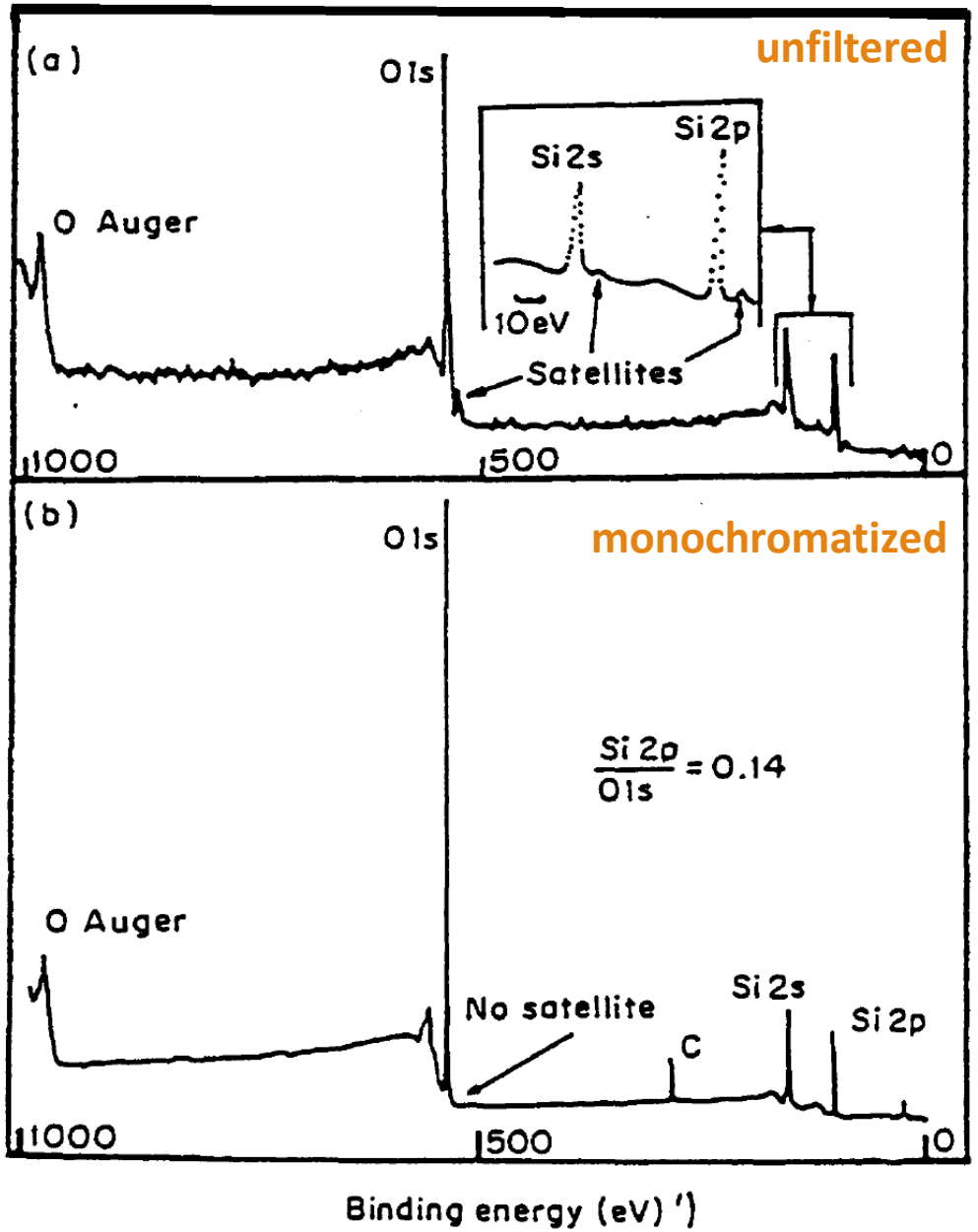
Bragg diffraction:

$$n\lambda = 2d\sin\theta$$

For Al K_α:
λ = 8.3 Å

Quartz $(10\bar{1}0)$ planes:
d = 4.25 Å
θ = 78.5°





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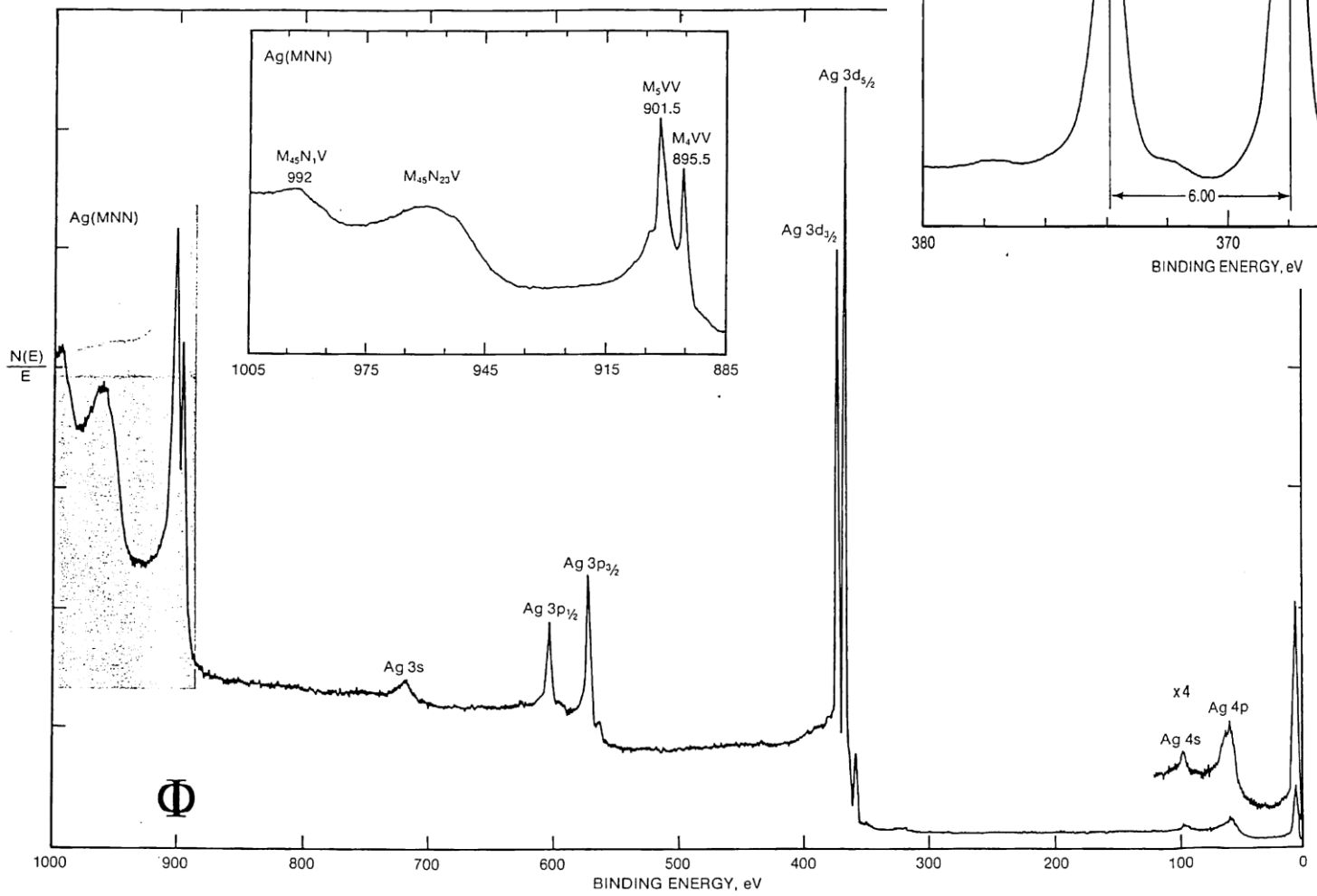
Reference spectra

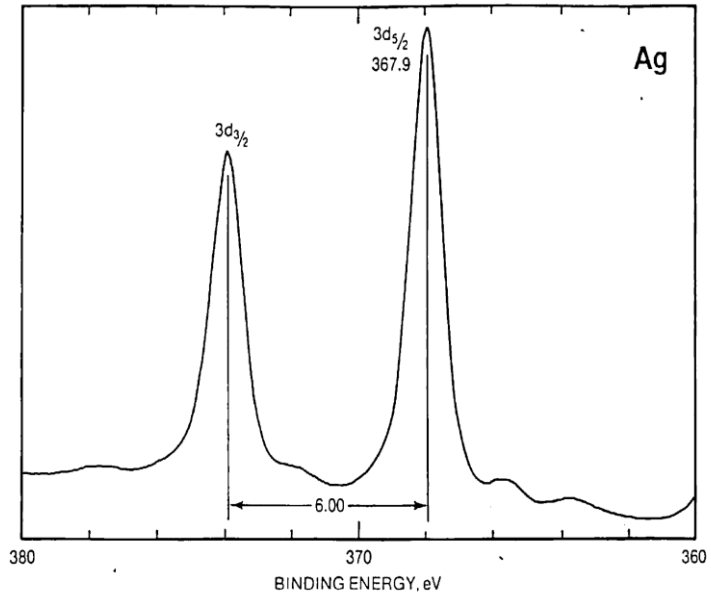
HANDBOOK OF
X-RAY PHOTOELECTRON
SPECTROSCOPY

A Reference Book of Standard Data
For Use In
X-Ray Photoelectron Spectroscopy

Handbooks with reference data:

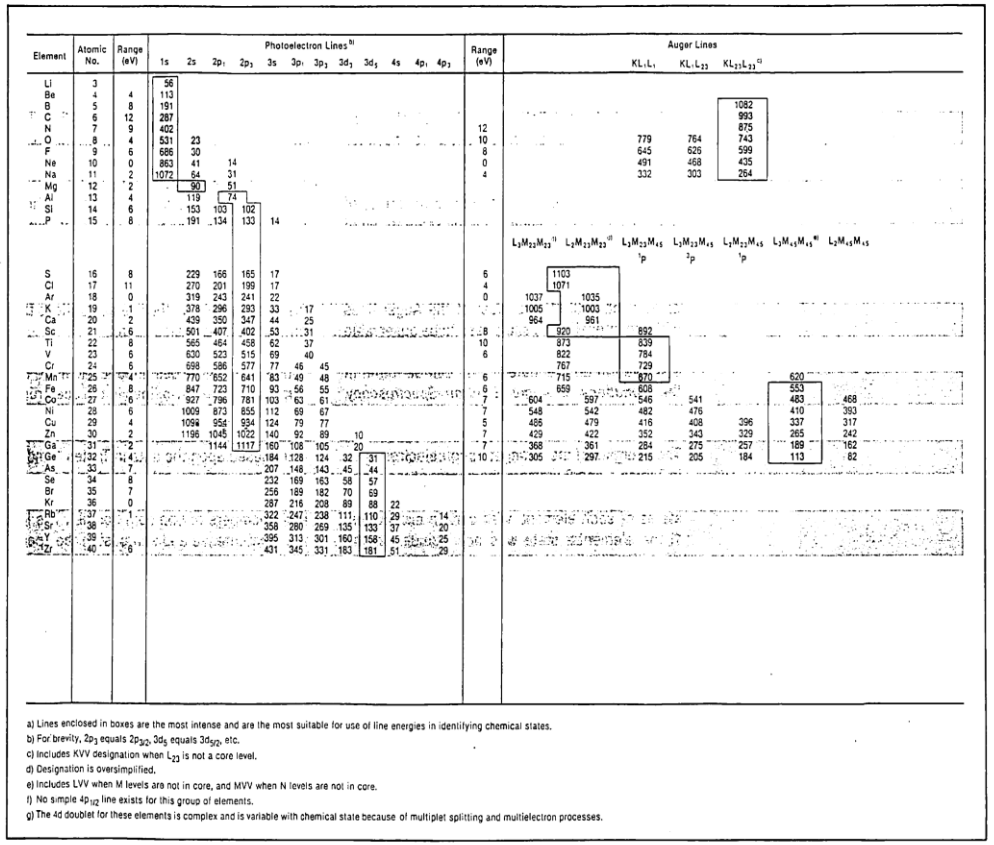
- Vital for identification of elements
- Reference survey and high-resolution spectra





Reference tables

Table 1. Line Positions[a] from Mg X-rays, by Element



a) Lines enclosed in boxes are the most intense and are the most suitable for use of line energies in identifying chemical states.
b) For brevity, $2p_3$ equals $2p_{3/2}$, $3d_5$ equals $3d_{5/2}$, etc.
c) Includes KVV designation when L_{23} is not a core level.
d) Designation is oversimplified.
e) Includes LVV when M levels are not in core, and MVV when N levels are not in core.
f) No simple $4p_{1/2}$ line exists for this group of elements.
g) The 4d doublet for these elements is complex and is variable with chemical state because of multiplet splitting and multielectron processes.

Table 3. Line Positions from Mg X-rays, in Numerical Order

17	$Hf4f_7$ (2)	102	$Si2p_3$ (1)	206	$Nb3d_5$ (3)	359	$Lu4p_3$ (53)	575	$Te3d_5$ (10)	863	Ne 1s
23	O 2s	105	$Ga3p_3$ (3)	208	$Kr3p_3$ (8)	359	$Hg4d_5$ (20)	577	$Cr2p_3$ (9)	872	Cd (A)
25	$Ta4f_7$ (2)	108	$Ce4d_5$ (4)	213	$Hf4d_5$ (11)	362	Gd (A)	594	Ce (A)	875	N (A)
30	F 2s	110	$Rb3d_5$ (1)	229	S 2s	364	$Nb3p_3$ (15)	599	F (A)	882	$Ce3d_5$ (18)
31	$Ge3d_5$ (1)	113	Be 1s	229	$Ta4d_5$ (12)	368	$Ag3d_5$ (6)	618	$Cd3p_3$ (34)	897	Ag (A)
34	$W4f_7$ (2)	113	Ge (A)	230	$Mo3d_5$ (3)	378	K 2s	619	$I3d_5$ (11)	920	Sc (A)
40	V 3p	114	Pr 4d	238	$Rb3p_3$ (9)	380	$U4f_7$ (11)	632	La (A)	928	Pd (A)
41	Ne 2s	118	$Tl4f_7$ (4)	241	$Ar2p_3$ (2)	385	$Tl4d_5$ (21)	641	$Mn2p_3$ (11)	930	$Pr3d_5$ (20)
43	$Re4f_7$ (2)	119	Al 2s	245	$W4d_5$ (12)	396	$Mo3p_3$ (17)	657	Ba (A)	934	$Cu2p_3$ (20)
44	$As3d_5$ (1)	120	Nd 4d	263	$Re4d_5$ (14)	402	N 1s	666	$In3p_3$ (38)	954	Rh (A)
45	$Cr3p_3$ (1)	124	$Ge3p_3$ (4)	264	Na (A)	402	Eu (A)	670	Mn (A)	961	Ca (A)
48	$Mn3p_3$ (1)	132	Sm 4d	265	Zn (A)	402	$Sc2p_3$ (5)	672	$Xe3d_5$ (13)	970	U (A)
50	$I4d_5$ (2)	133	$P2p_3$ (1)	269	$Sr3p_3$ (11)	405	$Cd3d_5$ (7)	677	$Th4d_5$ (37)	980	$Nd3d_5$ (21)
51	Mg 2p	133	$Sr3d_5$ (2)	270	Cl 2s	410	Ni (A)	684	Cs (A)	981	Ru (A)
52	$Os4f_7$ (3)	136	Eu 4d	279	$Os4d_5$ (15)	413	$Pb4d_5$ (22)	686	F 1s	993	C (A)
55	$Fe3p_3$ (1)	138	$Pb4f_7$ (5)	282	$Ru3d_5$ (4)	435	Ne (A)	710	$Fe2p_3$ (13)	1003	K (A)
56	Li 1s	143	$As3p_3$ (5)	284	$Tb4p_3$ (33)	439	Ca 2s	711	Xe (A)	1005	Th (A)
57	$Se3d_5$ (1)	150	Tb 4d	287	C 1s	440	Sm (A)	715	$Sn3p_3$ (42)	1022	$Zn2p_3$ (23)
61	$Co3p_3$ (2)	153	Si 2s	293	$Dy4p_3$ (36)	443	$Bi4d_5$ (24)	724	$Cs3d_5$ (14)	1035	Ar (A)
62	$Ir4f_7$ (3)	154	Dy 4d	293	$K2p_3$ (3)	445	$In3d_5$ (8)	729	Cr (A)	1071	Cl (A)
63	$Xe4d_5$ (2)	158	$Y3d_5$ (2)	297	$Ir4d_5$ (16)	458	$Ti2p_3$ (6)	737	I (A)	1072	Na 1s
64	Na 2s	159	$Bi4f_7$ (5)	301	$Y3p_3$ (12)	463	$Ru3p_3$ (22)	739	$U4d_5$ (42)	1082	B (A)
67	$Ni3p_3$ (2)	161	Ho 4d	306	$Ho4p_3$ (39)	483	Co (A)	743	O (A)	1083	$Sm3d_5$ (27)
69	$Br3d_5$ (1)	163	$Se3p_3$ (6)	309	$Rh3d_5$ (5)	486	$Sn3d_5$ (8)	765	Te (A)	1088	Nb (A)
73	$Pt4f_7$ (3)	165	$S2p_3$ (1)	316	$Pt4d_5$ (17)	498	$Rh3p_3$ (24)	768	$Sb3p_3$ (46)	1103	S (A)
74	Al 2p	169	Er 4d	319	Ar 2s	501	Sc 2s	780	$Ba3d_5$ (15)	1117	$Ga2p_3$ (27)
75	$Cs4d_5$ (2)	180	Tm 4d	320	$Er4p_3$ (42)	515	$V2p_3$ (8)	781	$Co2p_3$ (15)	1136	$Eu3d_5$ (30)
77	$Cu3p_3$ (2)	181	$Zr3d_5$ (2)	331	$Zr3p_3$ (14)	519	Nd (A)	784	V (A)	1155	Bi (A)
85	$Au4f_7$ (4)	182	$Br3p_3$ (7)	333	$Tm4p_3$ (45)	530	$Sb3d_5$ (9)	794	Sb (A)	1162	Pb (A)
87	$Zn3p_3$ (3)	185	$Yb4d_5$ (9)	335	$Th4f_7$ (9)	531	O 1s	819	Sn (A)	1169	Tl (A)
88	$Kr3d_5$ (1)	189	Ga (A)	336	$Au4d_5$ (18)	534	$Pd3p_3$ (27)	822	$Te3p_3$ (51)	1176	Hg (A)
90	$Ba4d_5$ (2)	191	B 1s	337	$Pd3d_5$ (5)	553	Fe (A)	834	$La3d_5$ (17)	1184	Au (A)
90	Mg 2s	191	P 2s	337	Cu (A)	555	Pr (A)	839	Ti (A)	1186	$Gd3d_5$ (33)
100	$Hg4f_7$ (4)	197	$Lu4d_5$ (10)	342	$Yb4p_3$ (50)	565	Ti 2s	846	In (A)	1192	Pt (A)
101	$La4d_5$ (3)	199	$Cl2p_3$ (2)	347	$Ca2p_3$ (3)	573	$Ag3p_3$ (31)	855	$Ni2p_3$ (18)		

An A in parentheses denotes Auger line. Numbers in parentheses are spin doublet separations in electron volts. The sharpest Auger line and the two most intense photoelectron lines per element are included in the table. For brevity, $2p_3$ equals $2p_{3/2}$, $3d_5$ equals $3d_{5/2}$, etc.

Survey spectra: example 1

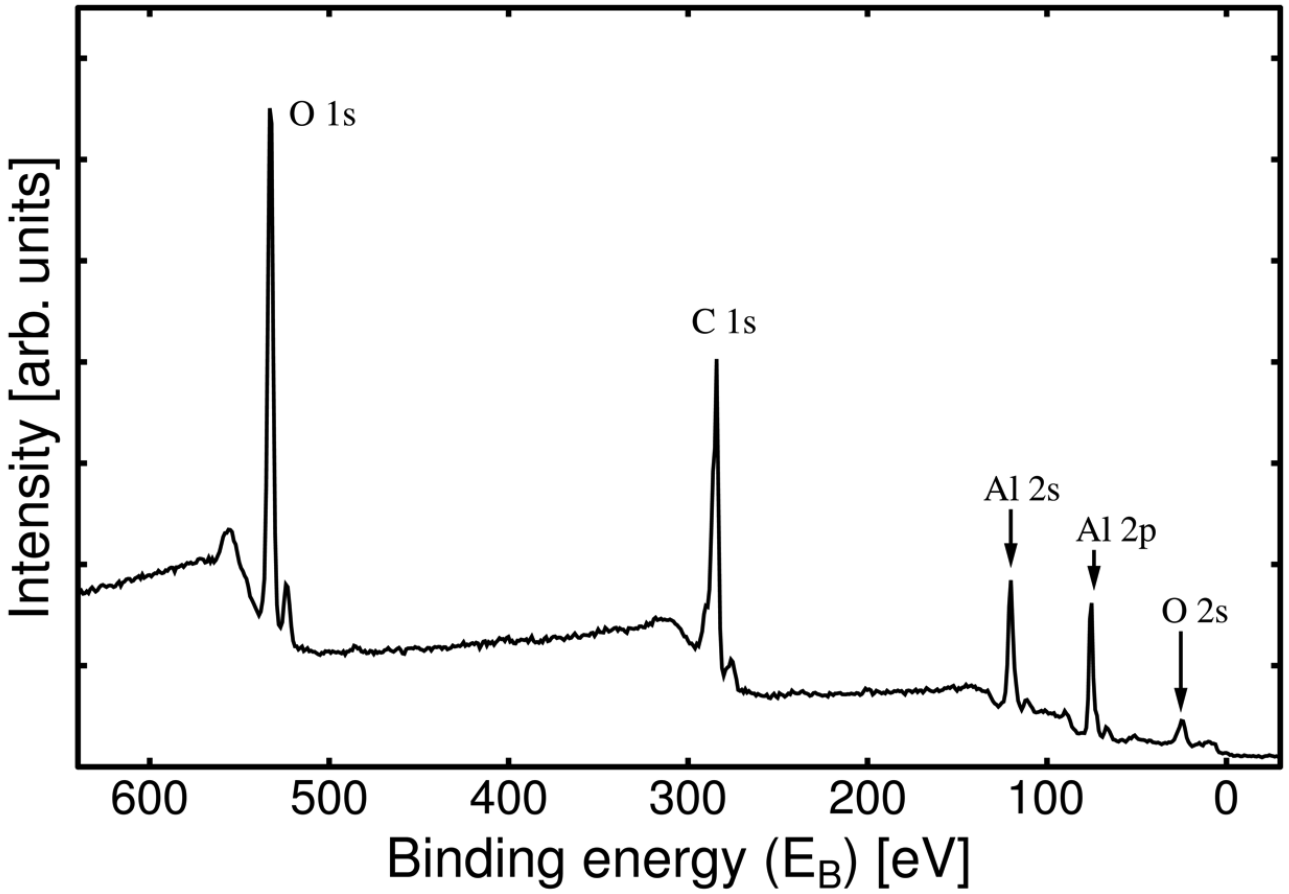


Table 3. Line Positions from Mg X-rays, in N

17 Hf 4f$_7$	(2)	102 Si 2p$_3$	(1)	206 Nb 3d$_5$	(3)	359 Lu 4p$_3$	(53)
23 O 2s		105 Ga 3p$_3$	(3)	208 Kr 3p$_3$	(8)	359 Hg 4d$_5$	(20)
25 Ta 4f$_7$	(2)	108 Ce 4d$_5$	(4)	213 Hf 4d$_5$	(11)	362 Gd (A)	
30 [illegible]		110 Rb 3d$_5$	(1)	229 S 2s		364 Nb 3p$_3$	(15)
31 Ge 3d$_5$	(1)	113 Be 1s		229 Ta 4d$_5$	(12)	368 Ag 3d$_5$	(6)
34 W 4f$_7$	(2)	113 Ge (A)		230 Mo 3d$_5$	(3)	378 K 2s	
40 V 3p		114 Pr 4d		238 Rb 3p$_3$	(9)	380 U 4f$_7$	(11)
41 Ne 2s		118 Tl 4f$_7$	(4)	241 Ar 2p$_3$	(2)	385 Tl 4d$_5$	(21)
43 Re 4f$_7$	(2)	119 Al 2s		245 W 4d$_5$	(12)	396 Mo 3p$_3$	(17)
44 As 3d$_5$	(1)	120 Nd 4d		263 Re 4d$_5$	(14)	402 N 1s	
45 Cr 3p$_3$	(1)	124 Ge 3p$_3$	(4)	264 Na (A)		402 Eu (A)	
48 Mn 3p$_3$	(1)	132 Sm 4d		265 Zn (A)		402 Sc 2p$_3$	(5)
50 I 4d$_5$	(2)	133 P 2p$_3$	(1)	269 Sr 3p$_3$	(11)	405 Cd 3d$_5$	(7)
51 Mg 2p		133 Sr 3d$_5$	(2)	270 Cl 2s		410 Ni (A)	
52 Os 4f$_7$	(3)	136 Eu 4d		279 Os 4d$_5$	(15)	413 Pb 4d$_5$	(22)
55 Fe 3p$_3$	(1)	138 Pb 4f$_7$	(5)	282 Ru 3d$_5$	(4)	435 Ne (A)	
56 Li 1s		143 As 3p$_3$	(5)	284 Tb 4p$_3$	(33)	439 Ca 2s	
57 Se 3d$_5$	(1)	150 Tb 4d		287 C 1s		440 Sm (A)	
61 Co 3p$_3$	(2)	153 Si 2s		293 Dy 4p$_3$	(36)	443 Bi 4d$_5$	(24)
62 Ir 4f$_7$	(3)	154 Dy 4d		293 K 2p$_3$	(3)	445 In 3d$_5$	(8)
63 Xe 4d$_5$	(2)	158 Y 3d$_5$	(2)	297 Ir 4d$_5$	(16)	458 Ti 2p$_3$	(6)
64 Na 2s		159 Bi 4f$_7$	(5)	301 Y 3p$_3$	(12)	463 Ru 3p$_3$	(22)
67 Ni 3p$_3$	(2)	161 Ho 4d		306 Ho 4p$_3$	(39)	483 Co (A)	
69 Br 3d$_5$	(1)	163 Se 3p$_3$	(6)	309 Rh 3d$_5$	(5)	486 Sn 3d$_5$	(8)
73 Pt 4f$_7$	(3)	165 S 2p$_3$	(1)	316 Pt 4d$_5$	(17)	498 Rh 3p$_3$	(24)
74 Al 2p		169 Er 4d		319 Ar 2s		501 Sc 2s	
75 Cs 4d$_5$	(2)	180 Tm 4d		320 Er 4p$_3$	(42)	515 V 2p$_3$	(8)
77 Cu 3p$_3$	(2)	181 Zr 3d$_5$	(2)	331 Zr 3p$_3$	(14)	519 Nd (A)	
85 Au 4f$_7$	(4)	182 Br 3p$_3$	(7)	333 Tm 4p$_3$	(45)	530 Sb 3d$_5$	(9)
87 Zn 3p$_3$	(3)	185 Yb 4d$_5$	(9)	335 Th 4f$_7$	(9)	531 O 1s	
88 Kr 3d$_5$	(1)	189 Ga (A)		336 Au 4d$_5$	(18)	534 Pd 3p$_3$	(27)
90 Ba 4d$_5$	(2)	191 B 1s		337 Pd 3d$_5$	(5)	553 Fe (A)	
90 Mg 2s		191 P 2s		337 Cu (A)		555 Pr (A)	
100 Hg 4f$_7$	(4)	197 Lu 4d$_5$	(10)	342 Yb 4p$_3$	(50)	565 Ti 2s	
101 La 4d$_5$	(3)	199 Cl 2p$_3$	(2)	347 Ca 2p$_3$	(3)	573 Ag 3p$_3$	(31)

An A in parentheses denotes Auger line. Numbers in parentheses are spin doublet separations in electron volts. The photoelectron lines per element are included in the table. For brevity, 2p$_3$ equals 2p$_{3/2}$, 3d$_5$ equals 3d$_{5/2}$, etc.

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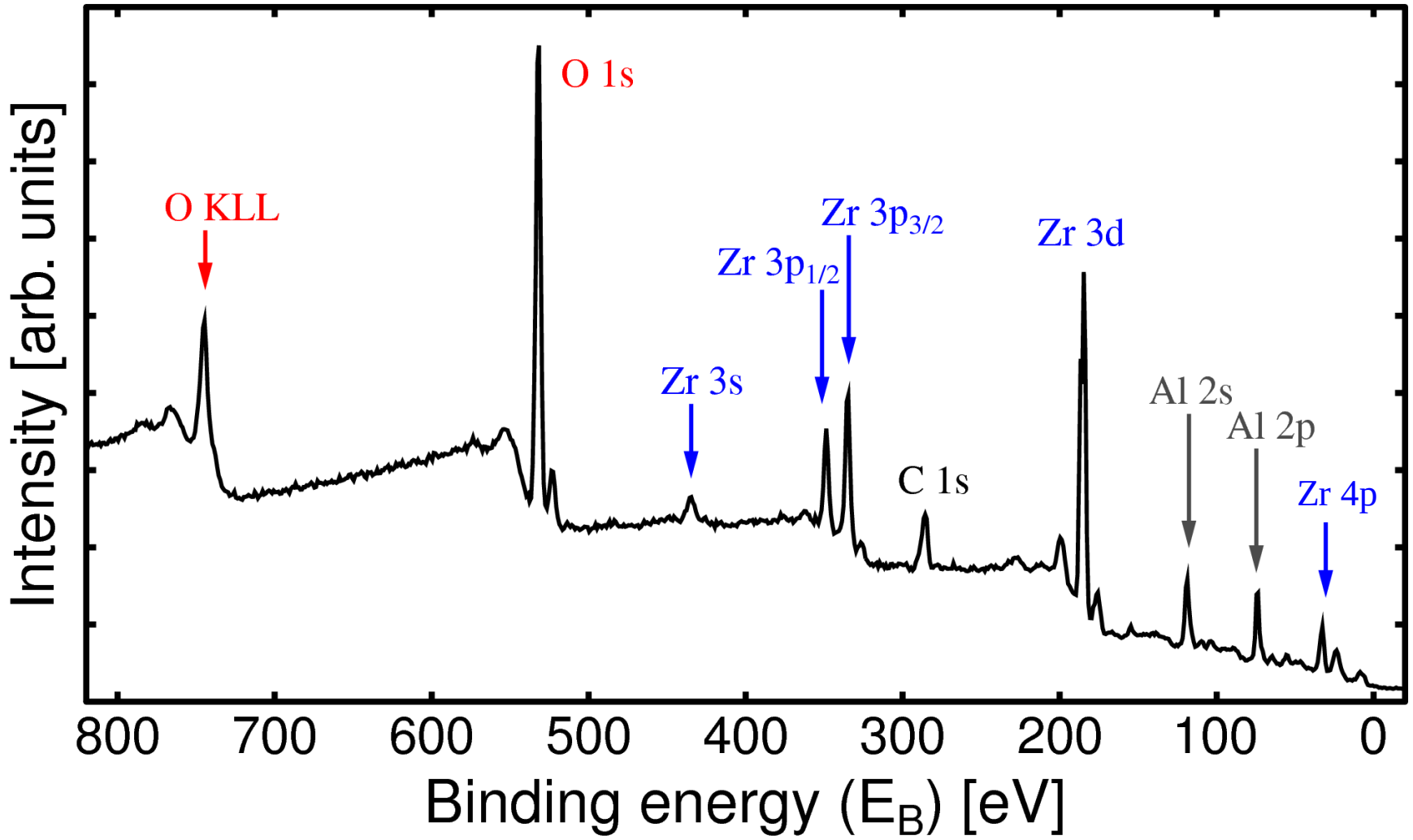
Example 2


O 1s
O KLL
Zr 3p3/2
Zr 3p1/2
Zr 3d
Zr 3s
Al 2s
Al 2p
C 1s
Zr 4p
Intensity [arb. units]
800
700
600
500
400
300
200
100
0
Binding energy (EB) [eV]

Aalto University
School of Chemical
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XPS

X-Ray Photoelectron Spectroscopy

OUTLINE:

1. Background
   1. Phenomenon
   2. Instrumentation
2. Typical measurement data
   1. Qualitative analysis & spectral features
   2. Peak identification
3. Analysis and results
   1. Quantitative analysis & effects of sample
   2. Chemical environment & peak fitting
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   1. Ion beam sputtering & depth profiling
   2. Angle resolved XPS
   3. Surface charging & energy calibration
   4. Small area analysis and imaging

Quantification

Peak intensity related to relative surface concentration:

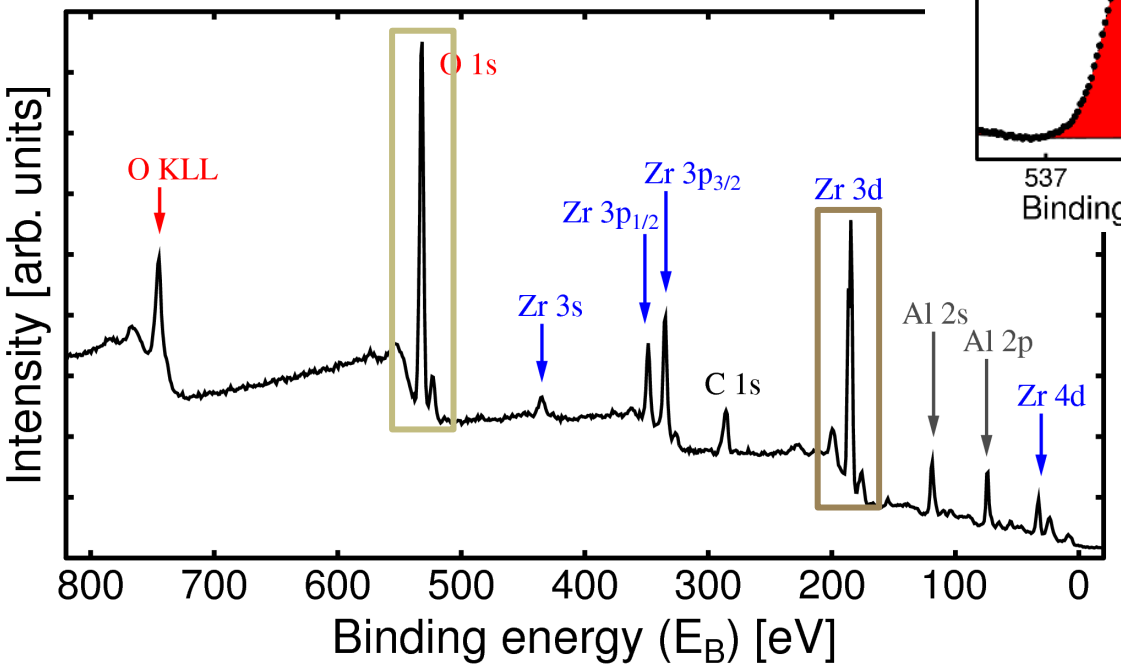
$$I_i \propto N_i a_i$$

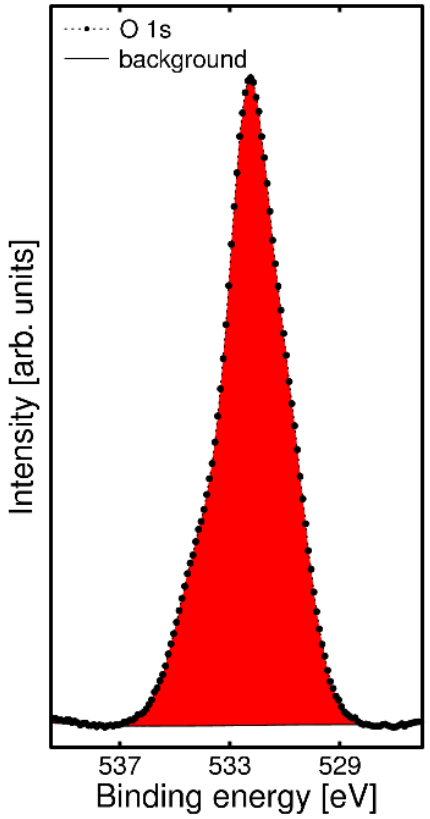
- I_i = peak intensity
- N_i = atomic concentration
- a_i = atomic sensitivity factor

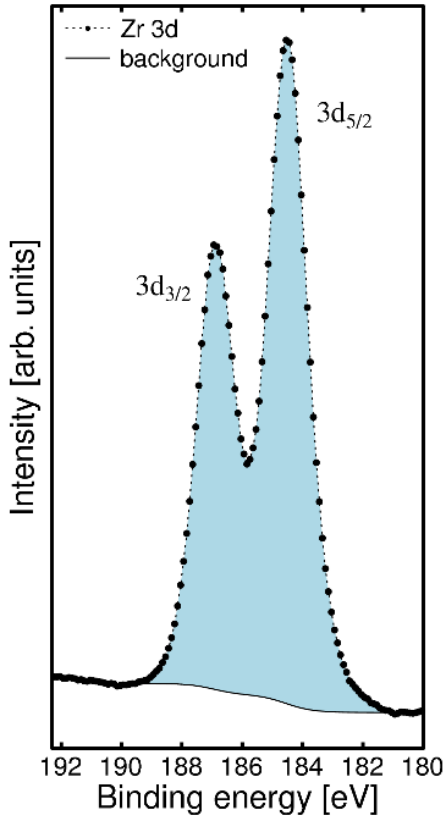
- Stoichiometry can be calculated using intensities and sensitivity factors
- Peak areas best measure of intensity

For multi-element surface layer:

$$N_A = \frac{I_A / a_A}{\sum_i I_i / a_i}$$







Stoichiometry:

Zr:	12.56 %
Al:	28.10 %
O:	41.46 %
C:	17.77 %

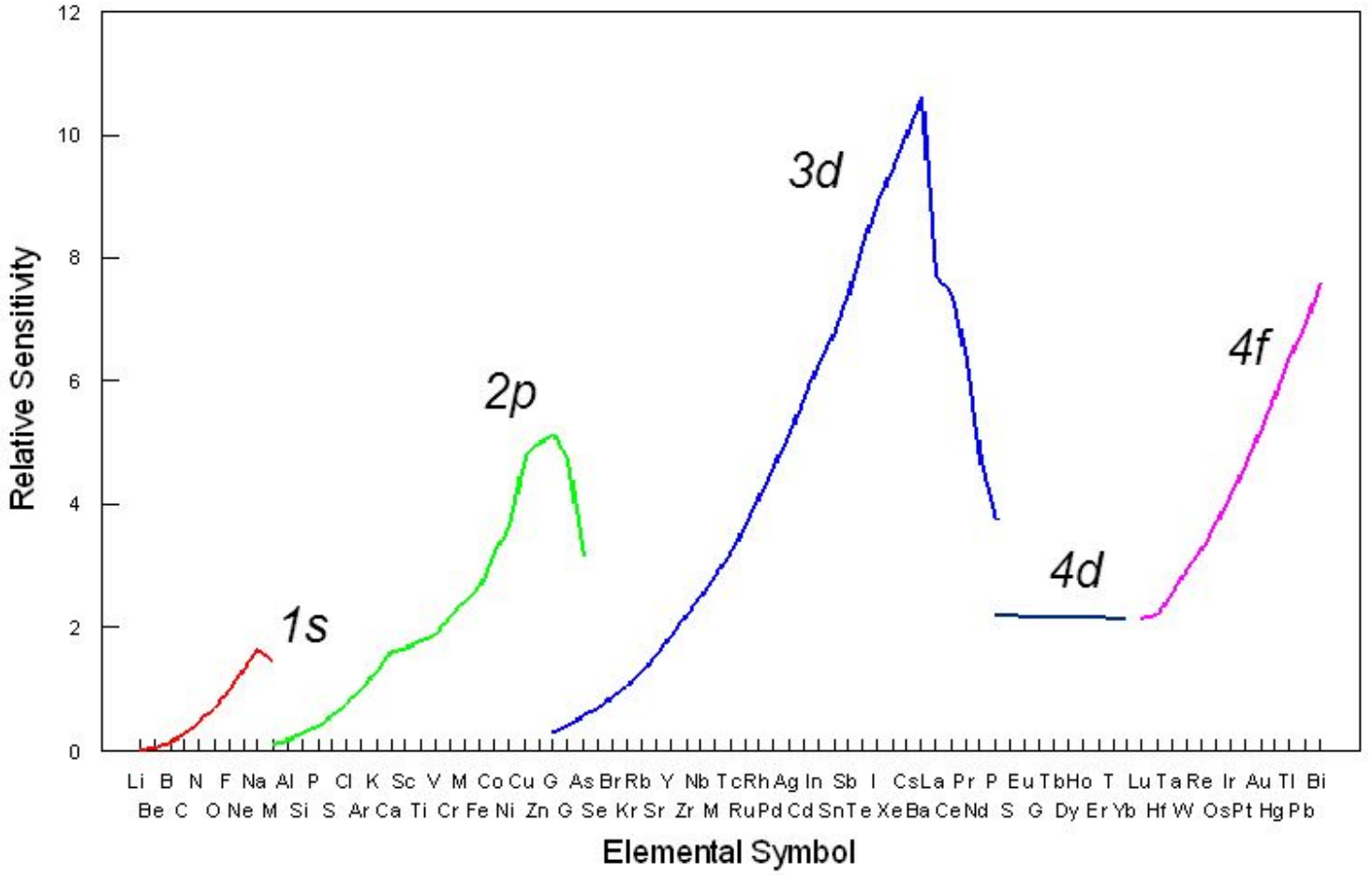
Atomic sensitivity factors (ASF)

Combination of several factors:

$$a_i = \sigma_i \lambda_i$$

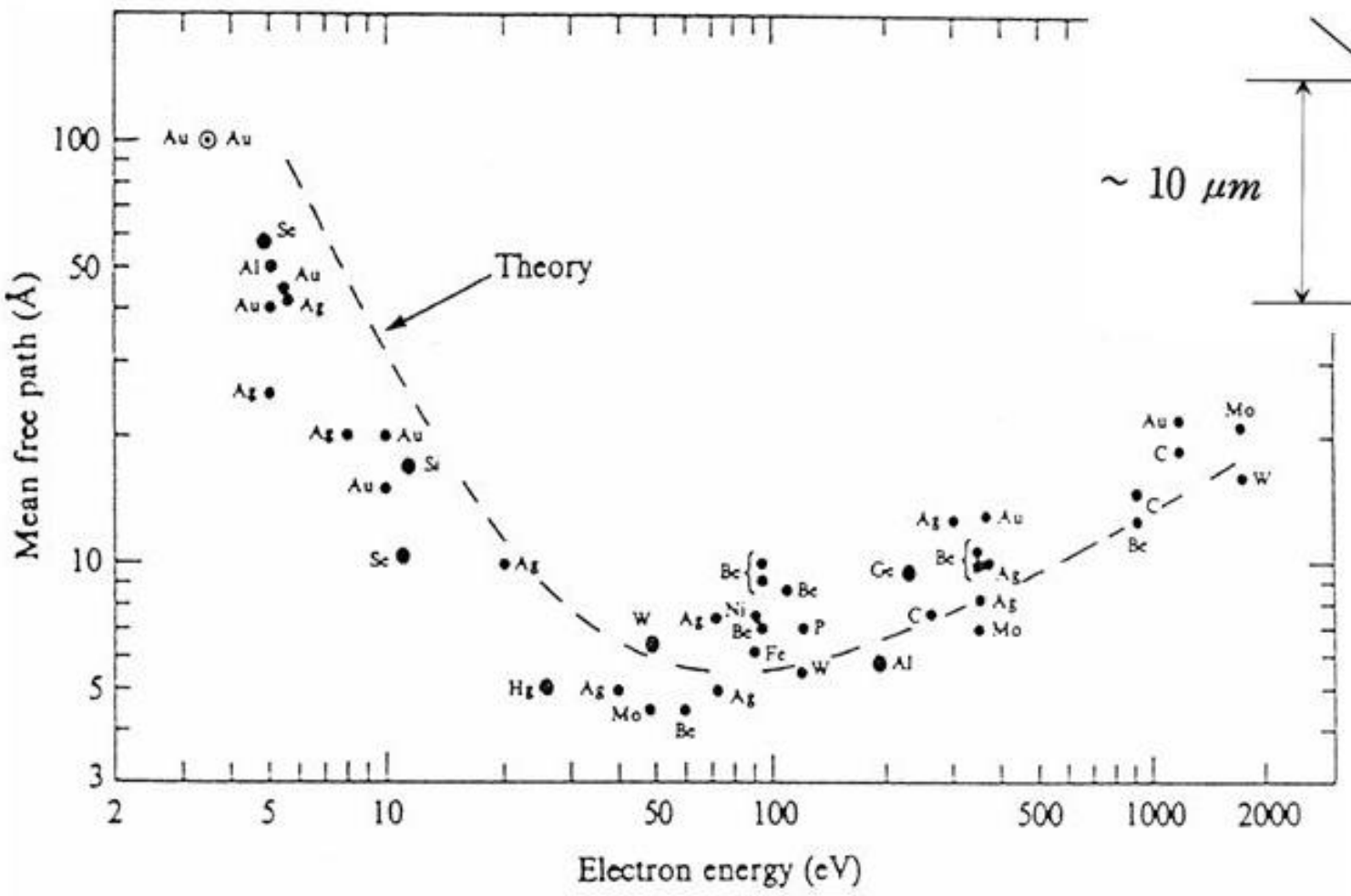
- σ_i: Scofield cross-sections (probability of X-ray producing photoelectron)
- λ_i: inelastic mean free path of photoelectron (likelihood electron will make it to the surface)

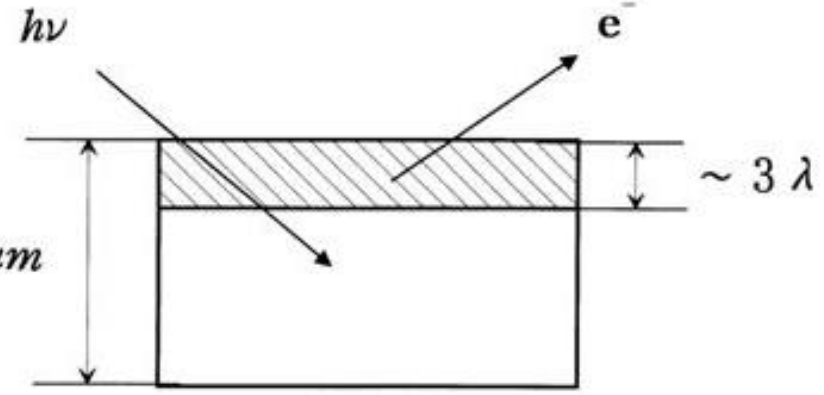
- ASF:s will vary greatly for different elements



Inelastic mean free path

$$I = I_0 e^{-\frac{d}{\lambda}}$$





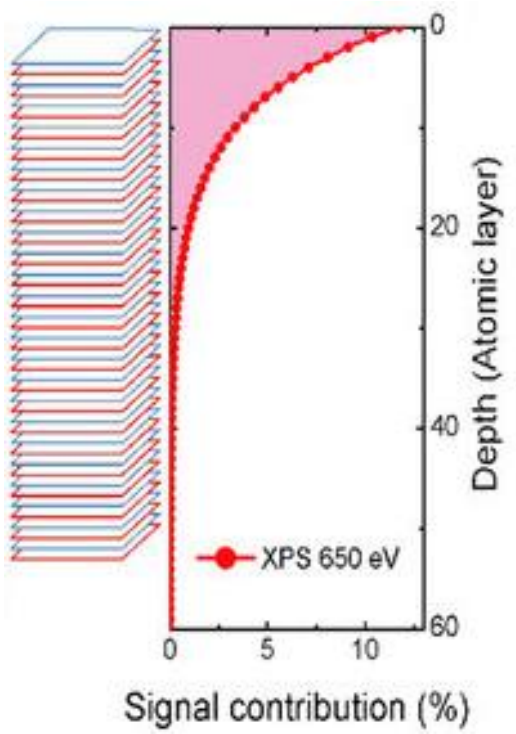
- 63 % of all electrons scattered within one λ
- 95 % scattered in 3λ – **sampling depth**

Loss processes:

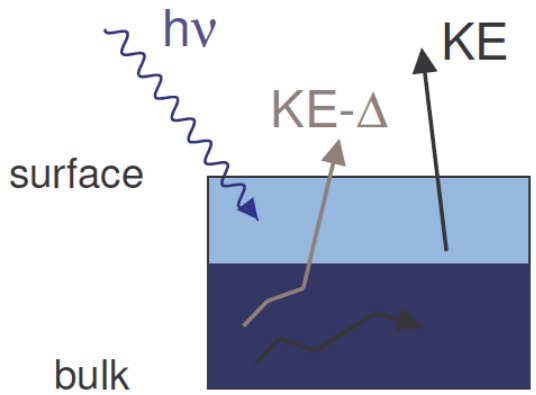
- Phonons: collective excitations of atoms (10 meV – 10 eV)
- Plasmons: collective excitations of electrons (5 eV – 20 eV)
- One electron excitations (50 eV –)

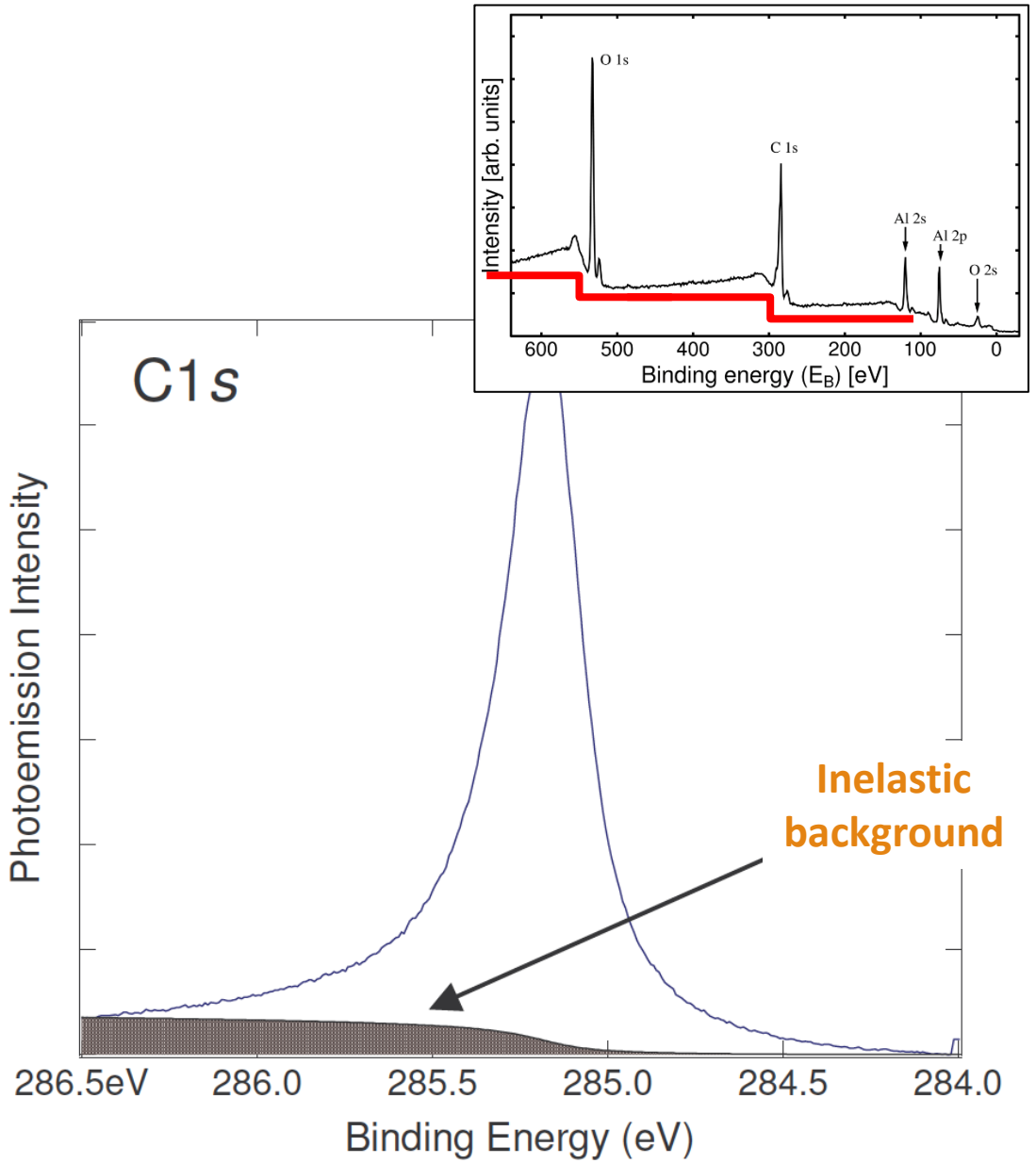
Inelastic background

- Core level peaks only account for a small part of all measured photoelectrons
- Exponential decrease in intensity with depth of photoionization



- Scattering losses result in a large increase in photoelectron intensity directly after each core level peak
- **Inelastic background**





Background removal

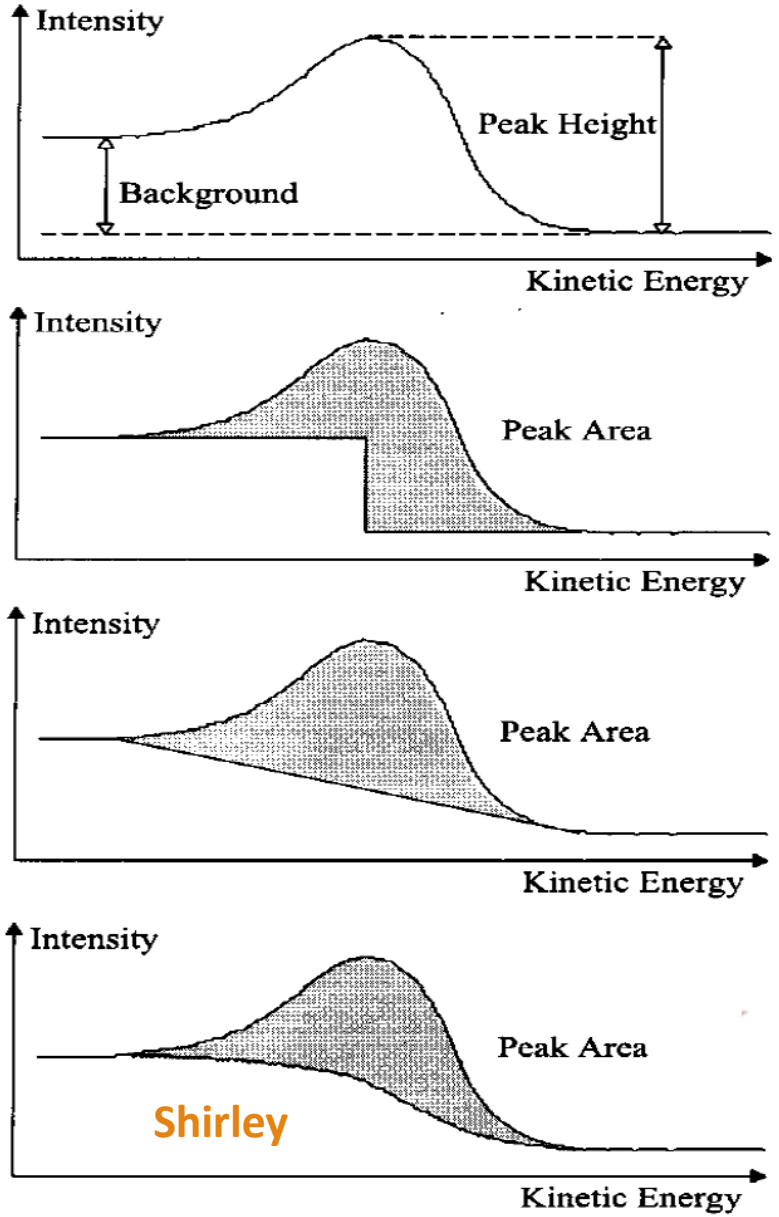
How is peak intensity measured?

- Peak heights can sometimes be used
- Result not very good – shapes not always the same

- **Area** is almost always used
- But background is not constant (nor linear) near peak

- **Shirley** background is most commonly used

- With ASF's: accuracy better than 15 %
- With standard samples on same instrument: ~5 %
- Reproducibility (precision) better than 2 %



Worst

Best

Surface morphologies

Traditional XPS quantification assumes:

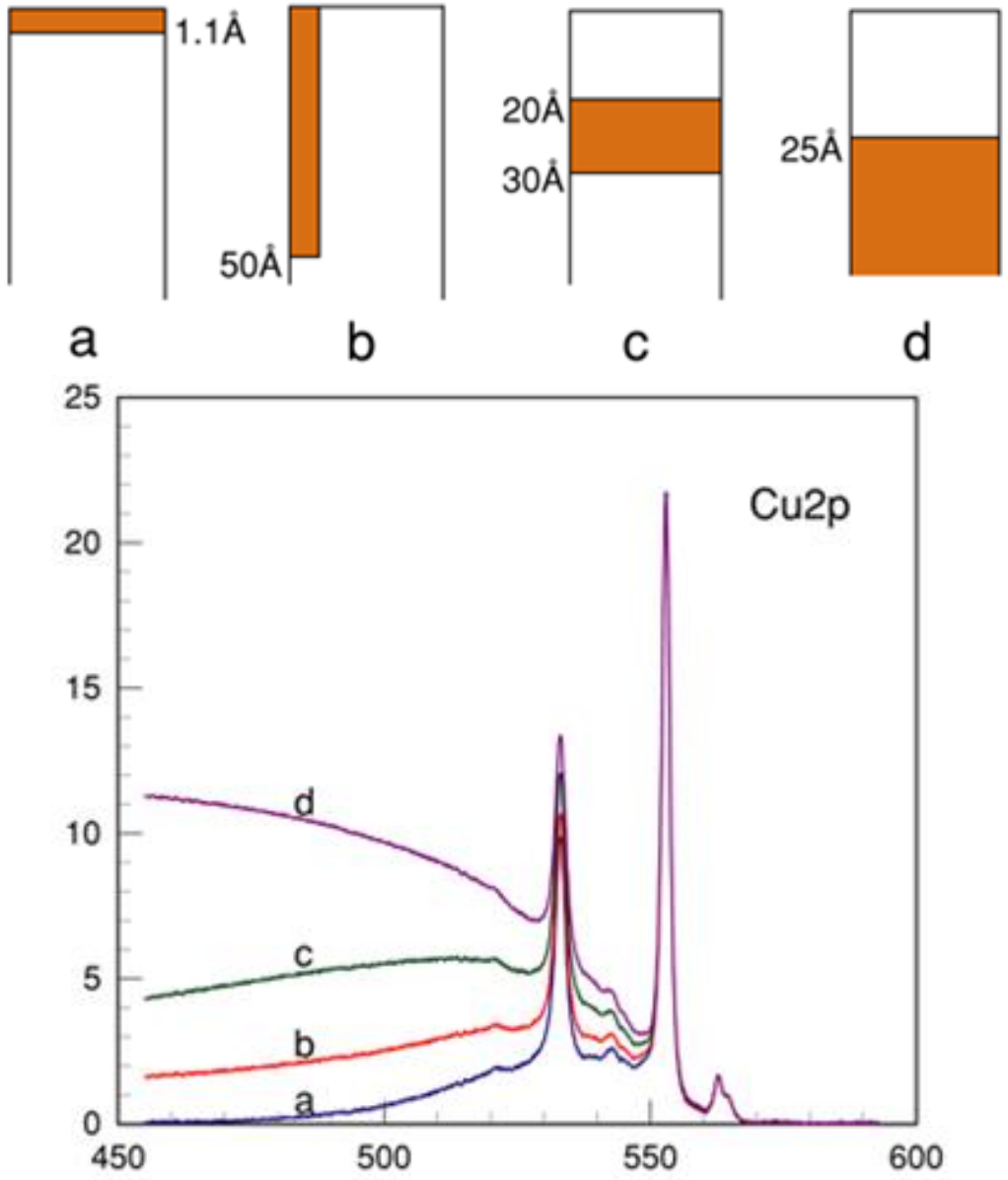
- Outer surface of sample is homogeneous
- Outer surface concentration is directly proportional to the main peak intensity

However, at a certain energy detected photoelectrons result from two process:

- *Intrinsic* electrons: energy from photoelectron process
- *Extrinsic* electrons: energy resulting from multiple scattering events (initial energy same as intrinsic)

Depending on the depth and lateral distribution of emitting atoms the extrinsic portion will change dramatically

- Extrinsic part (background) can give information on morphology, e.g. continuous film, clusters, etc…



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   4. Small area analysis and imaging

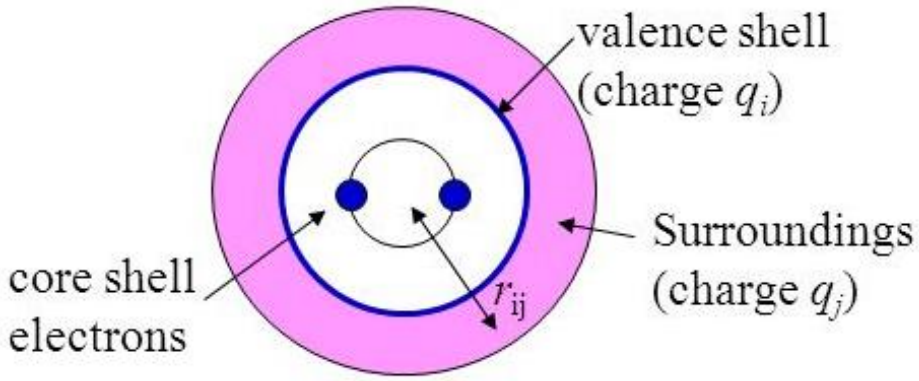
Chemical effect in XPS

Chemical shift:

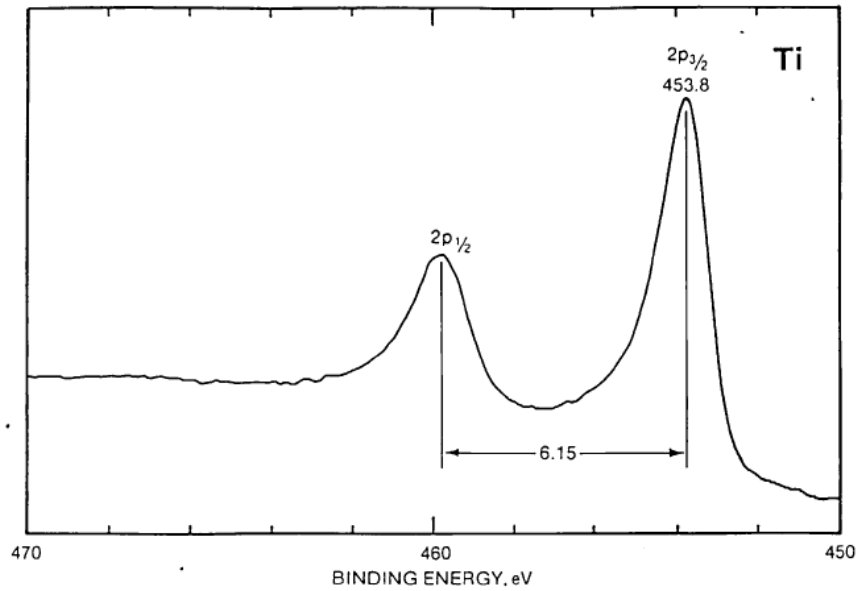
- Changes in the chemical bonding of an element will cause changes in the binding energy of core electrons

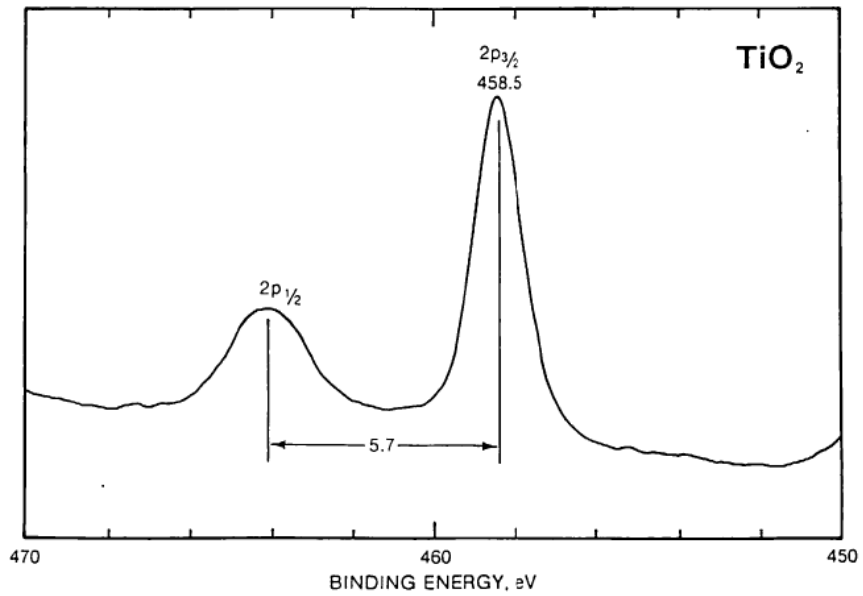
Core binding energies are determined by:

- Electrostatic interaction between electron and nucleus
- All other electrons (including valence) shield nuclear charge
- Removal or addition of electronic charge will alter this shielding



- Withdrawal of negative charge (oxidation) – increase in E_b
- Addition of negative charge – decrease in E_b

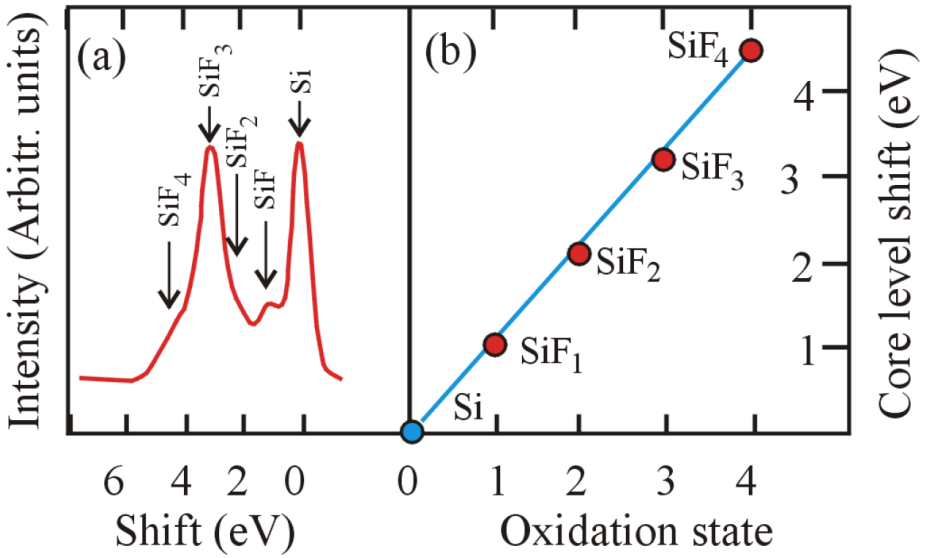


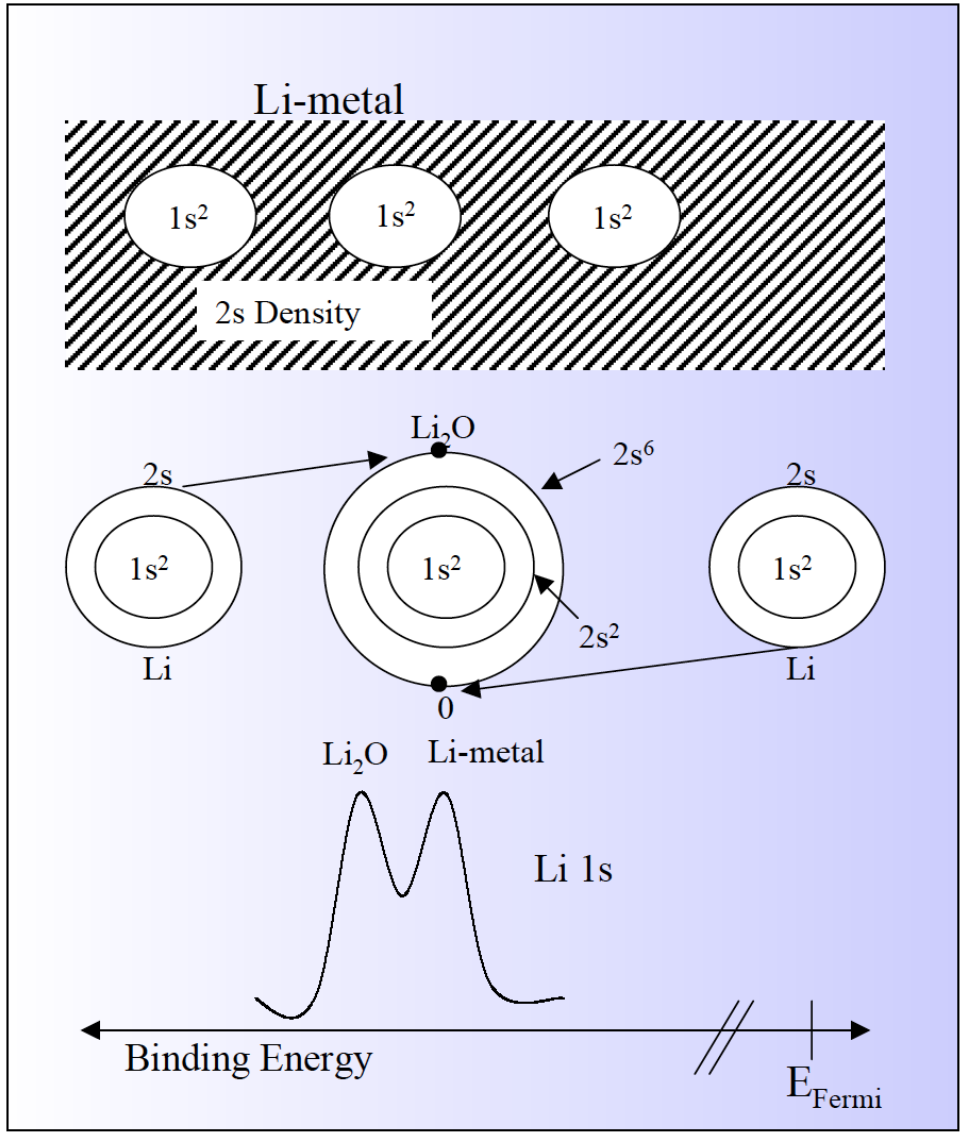


Chemical shift

Oxides compared to metals:

- Binding energy is lower in pure metals due to screening by conduction electrons
- Binding energy higher in metal oxides because electron density is lost to oxygen
- Ionic compounds: binding energy shift 1 eV / oxidation state!

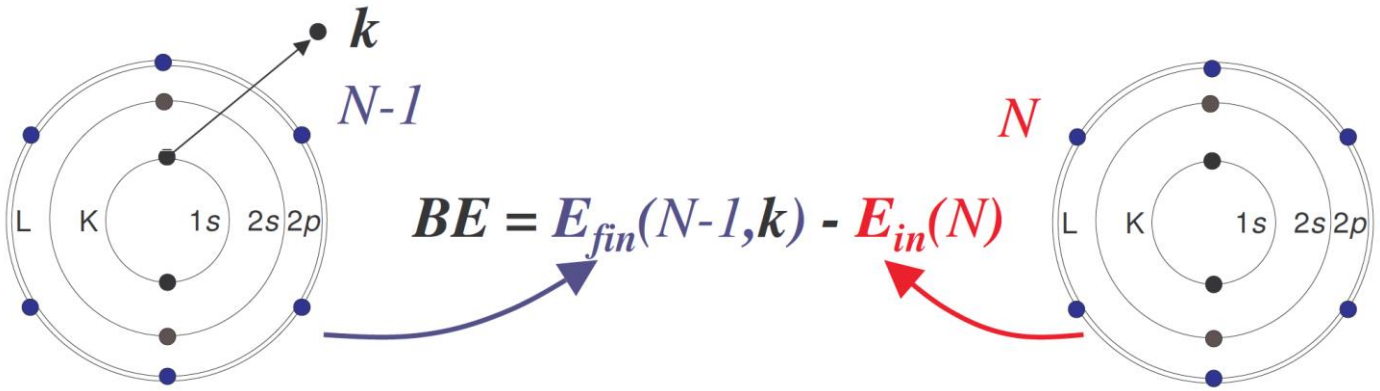




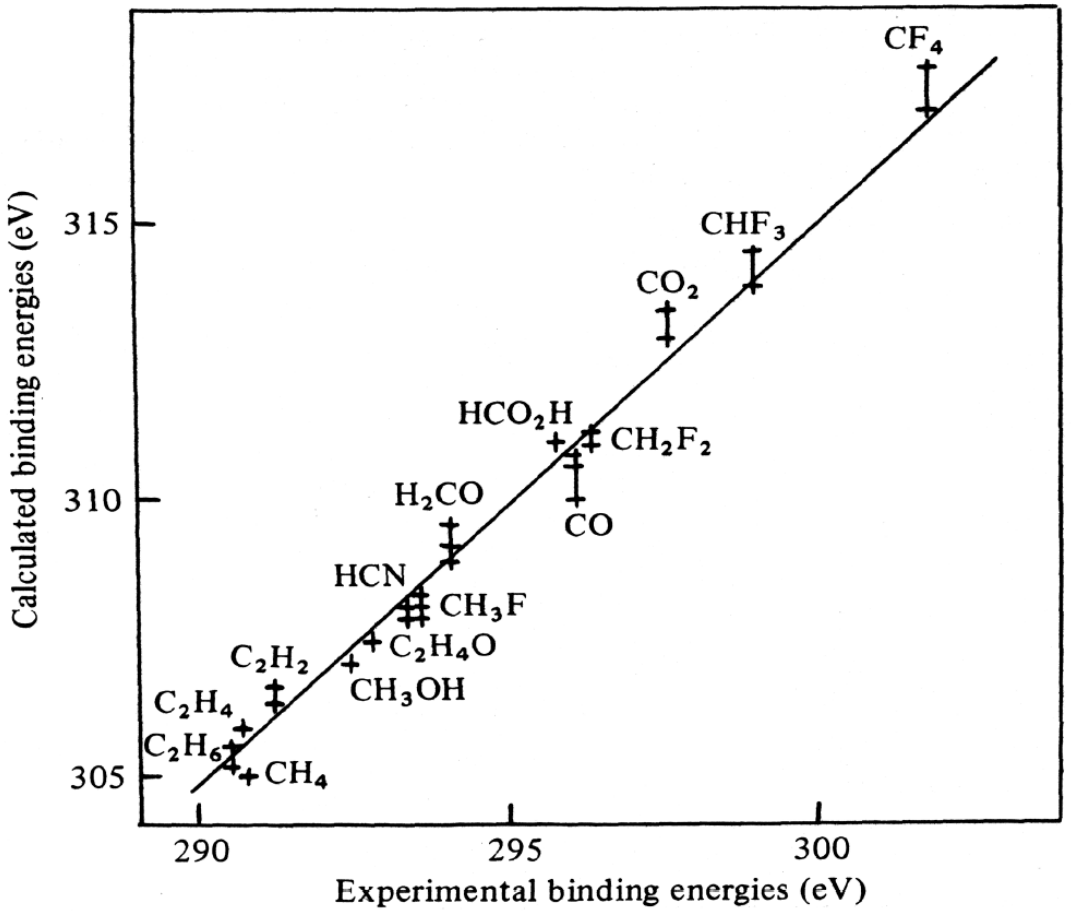
Calculations – Koopman's theorem

The binding energy of an electron is simply the difference between the initial state and the final state

- (atom with n electrons) - (atom with n-1 electrons and free electron)
- Only works if no electronic rearrangement followed photoemission
- Can be calculated with Hartree-Fock methods



$$BE = E_{fin}(N\text{-}1,k) - E_{in}(N)$$



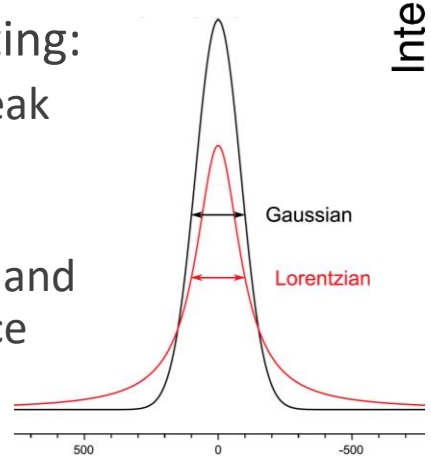
Peak fitting

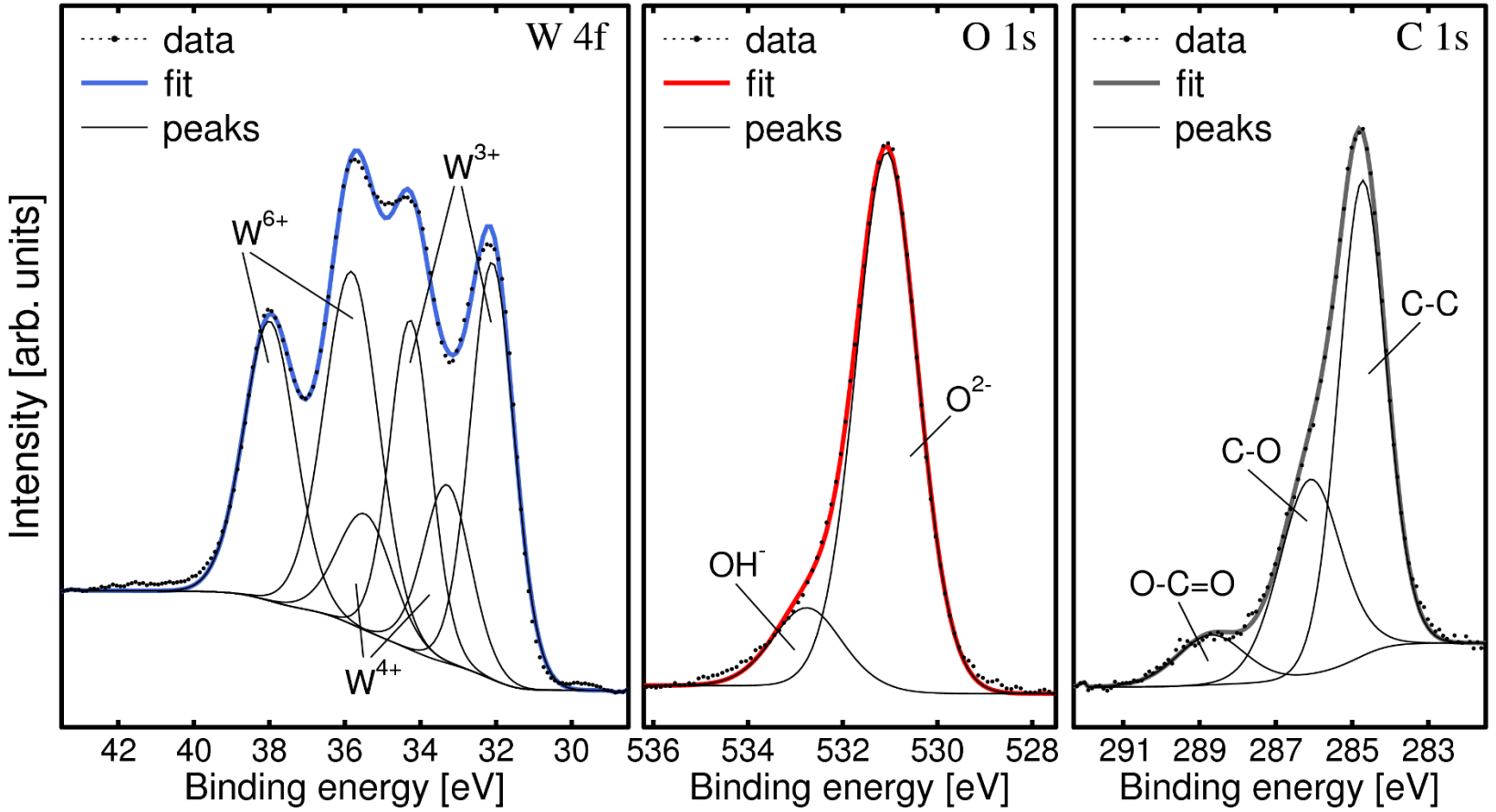
Measured peaks usually contain signals from atoms in many different chemical environments

- Chemical species can be de-convoluted from spectra using peak fitting algorithms
- Gaussian (70 %) –Lorentzian (30 %) peak shapes (other GL ratios also common)

Useful in peak fitting:

- Fixed ΔE_b and peak area ratios for doublets
- Known energies and FWHM (reference data)

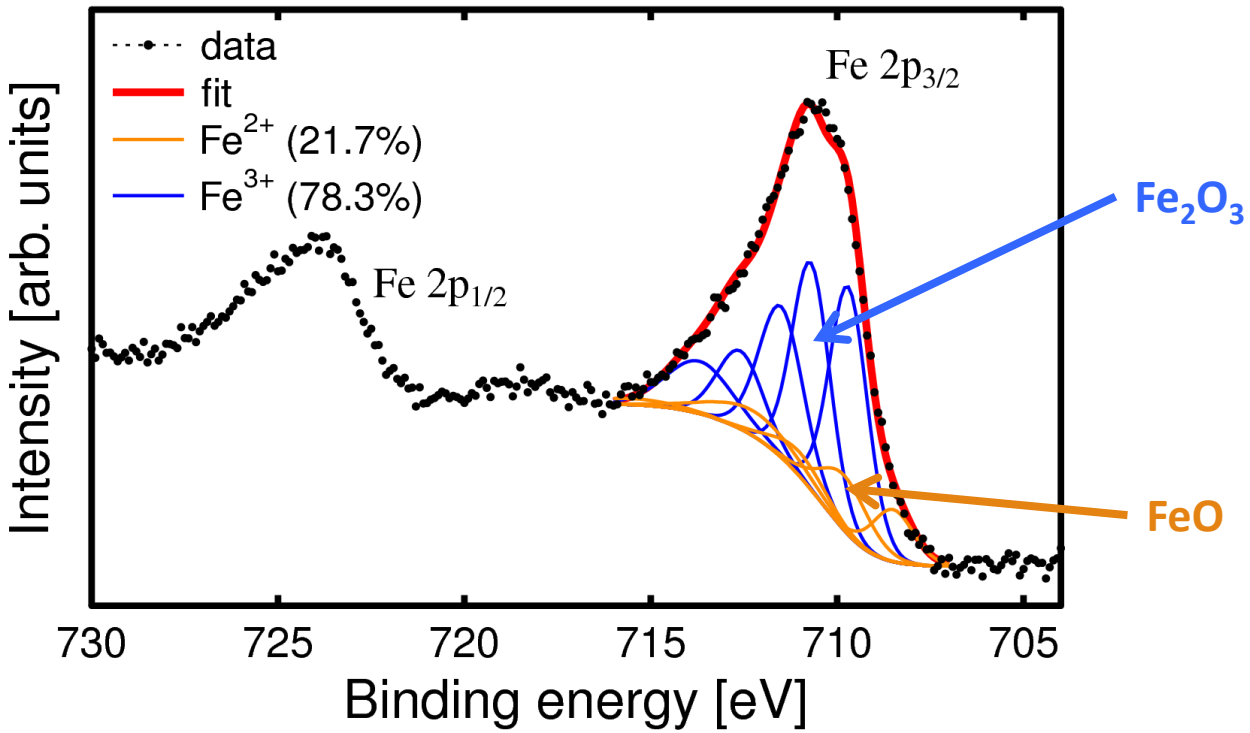


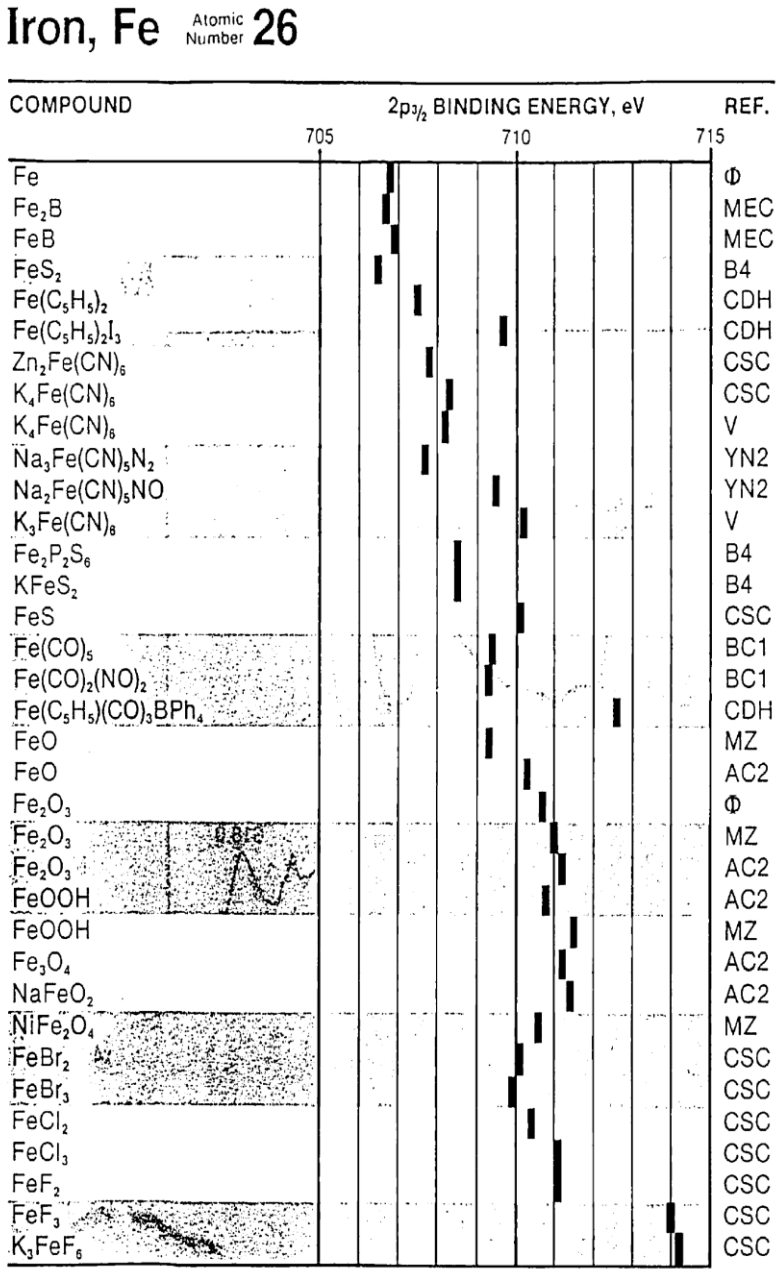


Multiplet splitting

Complex peak shapes are typical for many materials

- Usually occurs if there is one (or more) unpaired valence electron(s)
- A single compound will result in an asymmetric peak shape
- Several GL peaks have to be fitted in order to get reproducibility





NIST database

National Institute of Standards and Technology

- srdata.nist.gov/xps/
- Large database with reference XPS data
- Very useful for determining chemical states
- Literature references for all given data

NIST X-ray Photoelectron Spectroscopy Database

NIST Standard Reference Database 20, Version 4.1

Data compiled and evaluated by

Alexander V. Naumkin, Anna Kraut-Vass, Stephen W. Gaarenstroom, and Cedric J. Powell

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Step 1. Choose type of data:

- (•) Binding Energy
- ( ) Auger Kinetic Energy
- ( ) Auger Parameter
- ( ) Doublet Separation
- ( ) Surface/Interface Core-Level Shift
- ( ) Chemical Shift:

Go to Step 2

Co	2p3/2	[N(C2H5)4]2CoBr4	780.10	Click
Co	2p3/2	[N(C2H5)4]2CoCl4	780.60	Click
Co	2p3/2	[N(C4H9)4]2[Co(NCC(S)C(S)CN)2]	780.00	Click
Co	2p3/2	[N(C4H9)4]2[Co(NCC(S)C(S)CN)2]	780.20	Click
Co	2p3/2	[N(CH3)4]2[CoSe(CN)4]	779.40	Click
Co	2p3/2	Al2CoO4	781.10	Click
Co	2p3/2	Al2CoO4	780.60	Click
Co	2p3/2	Al2CoO4	780.80	Click
Co	2p3/2	Co	778.30	Click
Co	2p3/2	Co	777.90	Click
Co	2p3/2	Co	778.32	Click
Co	2p3/2	Co	778.50	Click
Co	2p3/2	Co	778.10	Click
Co	2p3/2	Co	778.50	Click
Co	2p3/2	Co	778.20	Click
Co	2p3/2	Co	777.80	Click
Co	2p3/2	Co	778.00	Click
Co	2p3/2	Co	778.30	Click
Co	2p3/2	Co((C6H5)3PO)2(NO3)2	781.20	Click
Co	2p3/2	Co(NH3)6Cl3	781.10	Click
Co	2p3/2	Co(NH3)6Cl3	782.20	Click

Step 2. Select an element for binding energy:

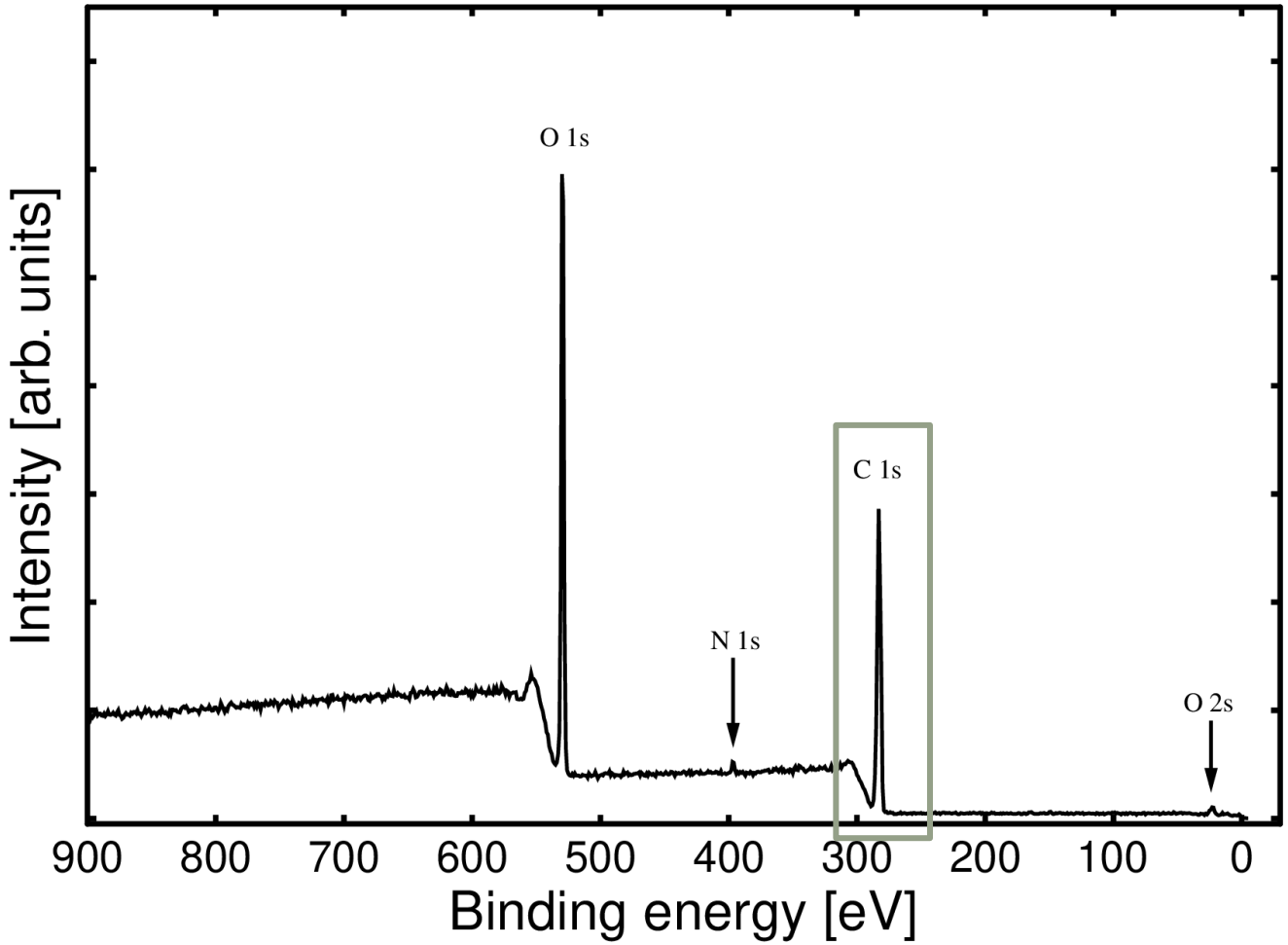
IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
^{1}H																	^{2}He
^{3}Li	^{4}Be				Metals							^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
^{11}Na	^{12}Mg				Transition metals							^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
^{19}K	^{20}Ca	^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{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	^{57}La	^{72}Hf	^{73}Ta	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	^{81}Tl	^{82}Pb	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
^{87}Fr	^{88}Ra	^{89}Ac	^{104}Rf	^{105}Db	^{106}Sg	^{107}Bh	^{108}Hs	^{109}Mt									
lanthanides			^{58}Ce	^{59}Pr	^{60}Nd	^{61}Pm	^{62}Sm	^{63}Eu	^{64}Gd	^{65}Tb	^{66}Dy	^{67}Ho	^{68}Er	^{69}Tm	^{70}Yb	^{71}Lu	
actinides			^{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	

Practical example – Cellulose

Large area survey scan from cellulose:

- Carbon and oxygen
- Elemental composition can be calculated
- O/C ratio measured
- Trace level impurities detected – nitrogen

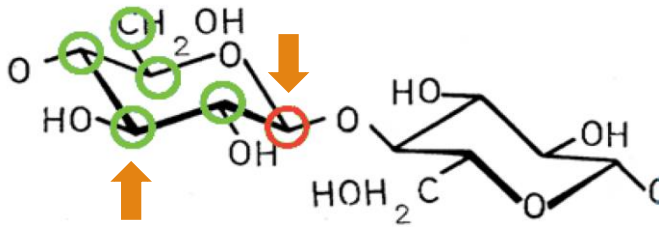
- Zooming in on individual peaks will give you a lot more information!



Practical example – Cellulose

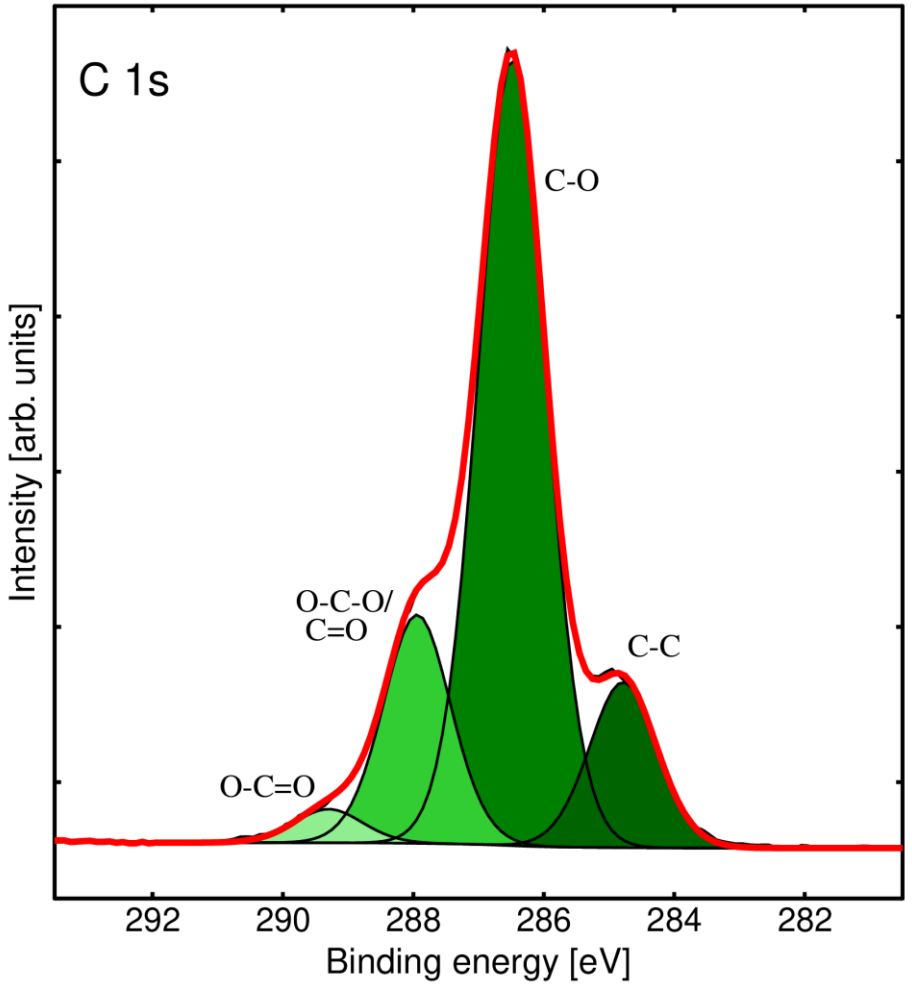
High resolution spectra:

- C 1s
- More components than a single Gaussian



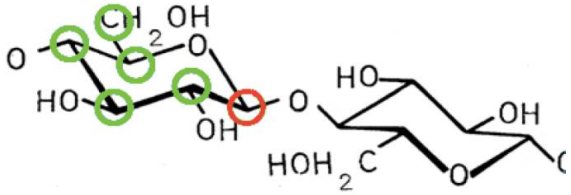
Understanding the material greatly improves the analysis

- Locating peaks
- Assigning peak energies



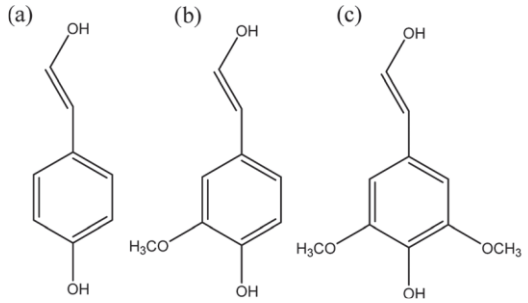
Cellulose vs lignin

Cellulose:

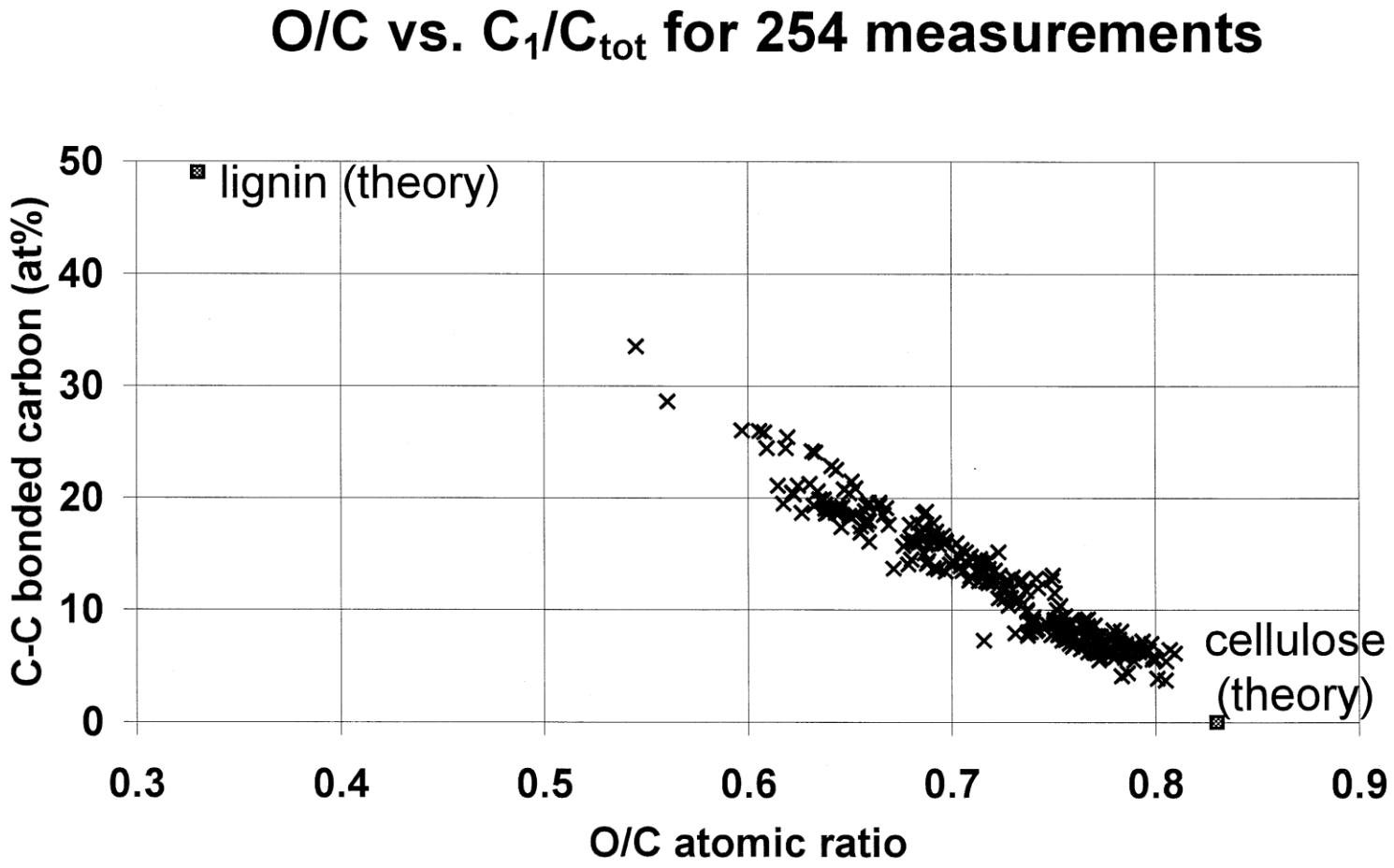


- O/C atomic ratio: 0.83
- C-C at.%: 0 %

Lignin (monolignols):



- O/C atomic ratio: 0.33
- C-C at.%: 49 %



[L.-S. Johansson, et al., Appl. Surf. Sci. 144-145 (1999) 92-95.]

Aalto University
School of Chemical
Engineering

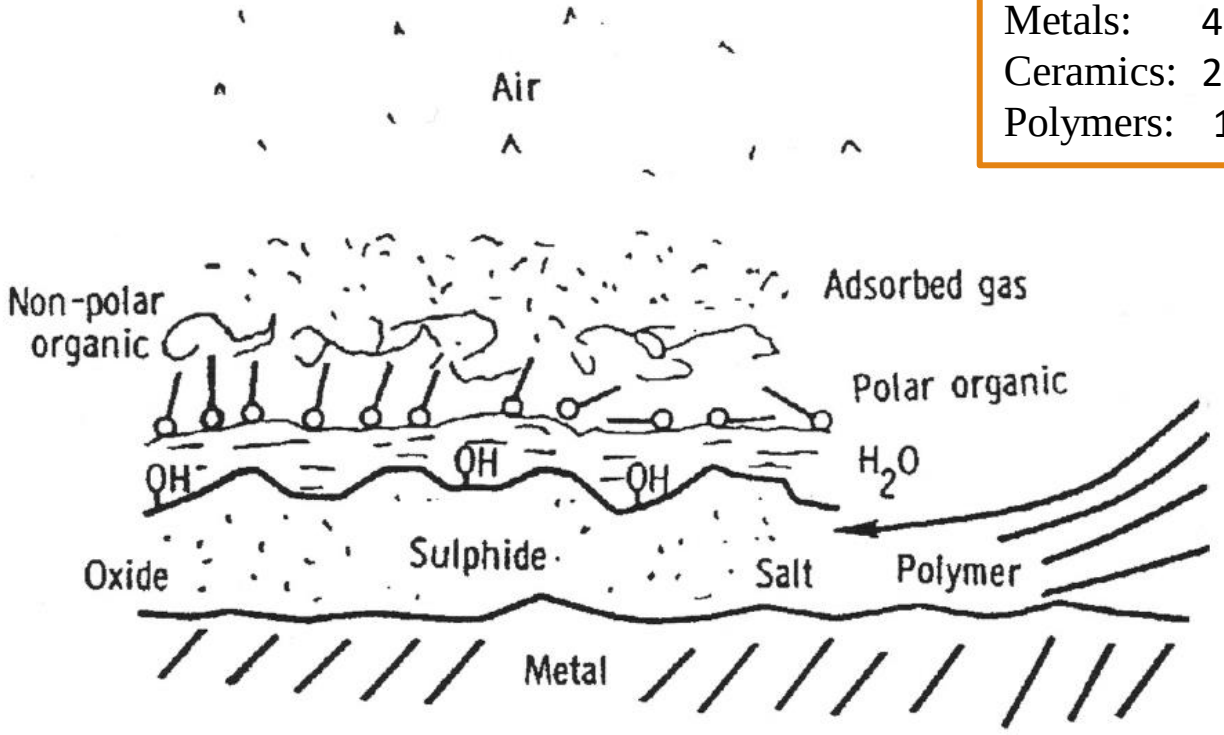
XPS

X-Ray Photoelectron Spectroscopy

OUTLINE:

1. Background
   1. Phenomenon
   2. Instrumentation
2. Typical measurement data
   1. Qualitative analysis & spectral features
   2. Peak identification
3. Analysis and results
   1. Quantitative analysis & effects of sample
   2. Chemical environment & peak fitting
4. Technical issues & Auxiliary features
   1. Ion beam sputtering & depth profiling
   2. Angle resolved XPS
   3. Surface charging & energy calibration
   4. Small area analysis and imaging

Surface contamination



Ambient C (at.-%):

Metals:	40 – 60 %
Ceramics:	20 – 40 %
Polymers:	1 – 10 %

Surface contamination is always a big problem

- Oxidation
- Advantageous carbon

Carbon contamination

- Exists on all samples that have not been prepared in vacuum!

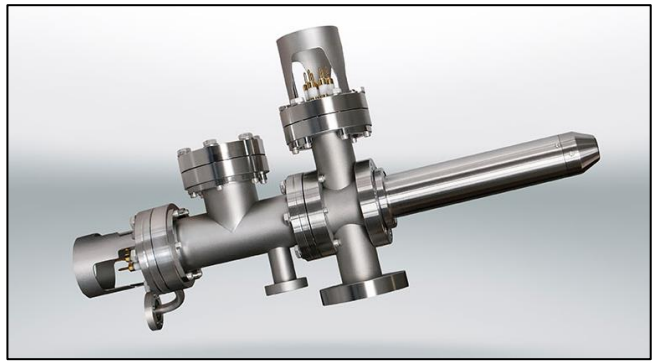
Sources:

- Organic molecules in air
- *In situ:*
  - Contamination due to pumping oil
  - Desorption from other samples in chamber

Ion beam sputtering

Ar-ion guns are often included in XPS-analysis chambers

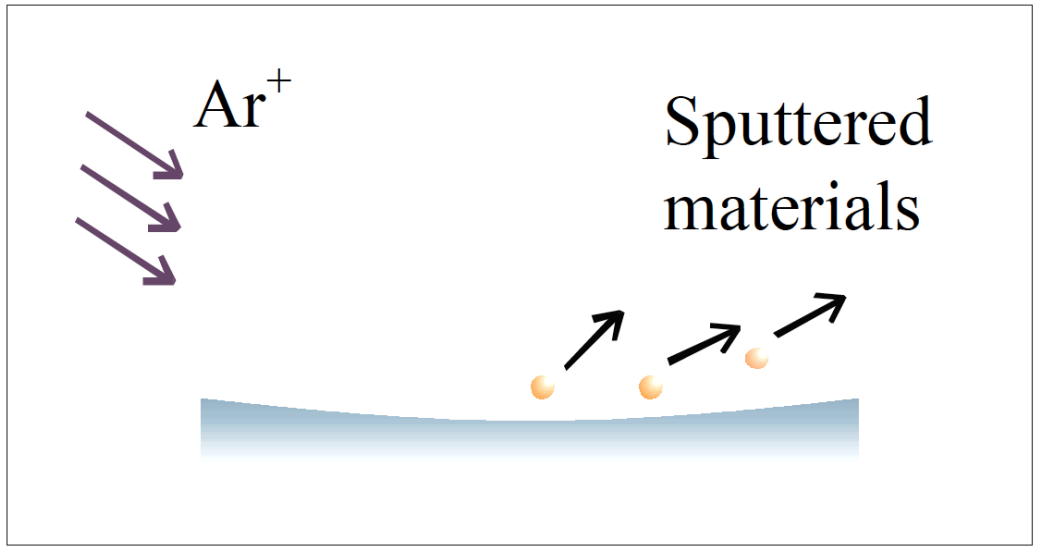
- Ion energies usually 0-10 keV



Removal of surface layers:

- Surface contamination
- Oxide removal
- Depth analysis

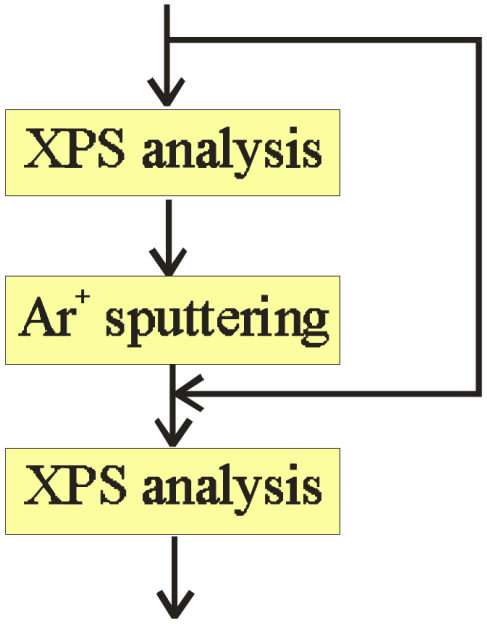
- NOTE: May affect surface chemistry and composition of materials
- Not always a good idea for XPS

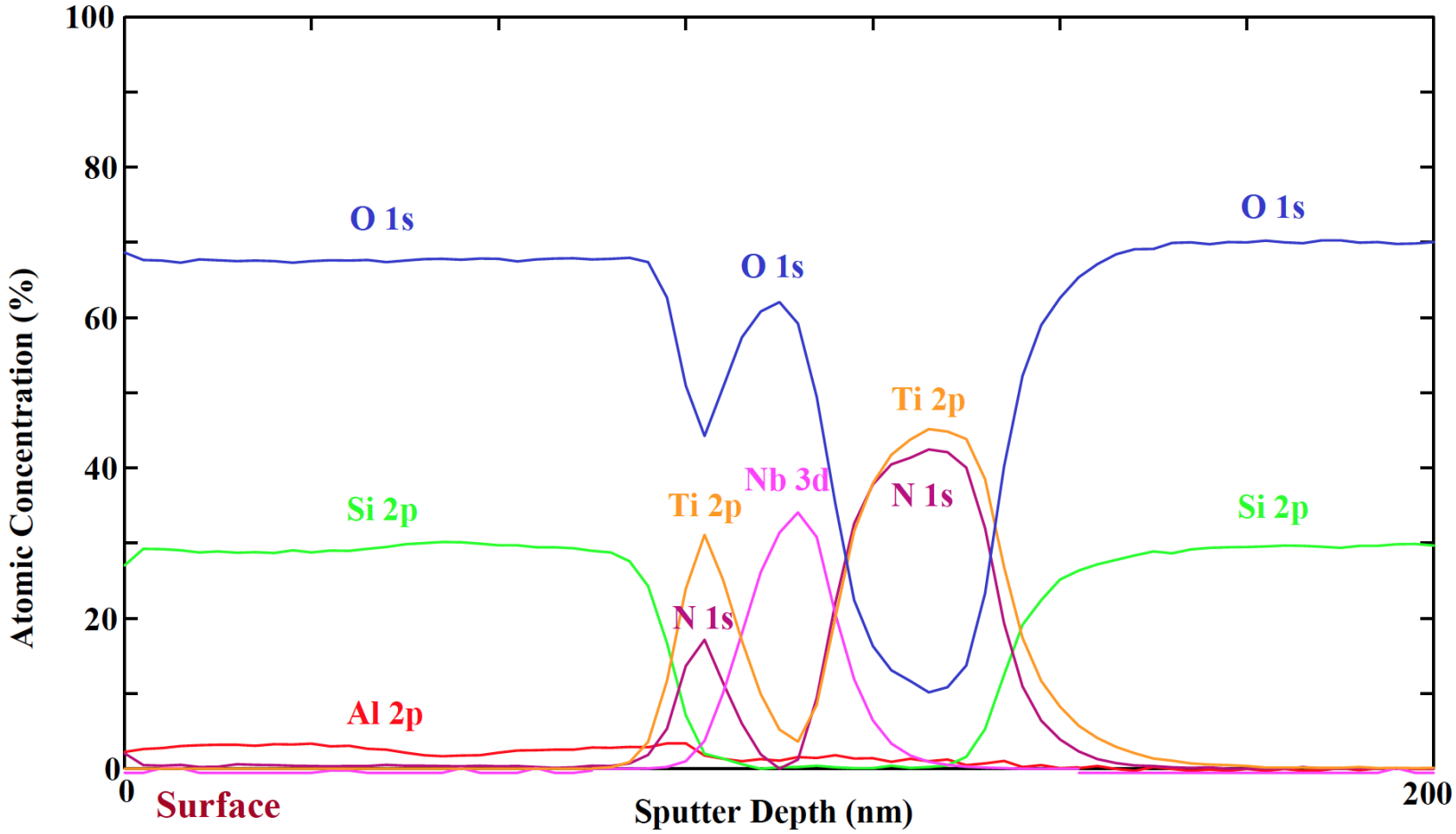


Depth profiling

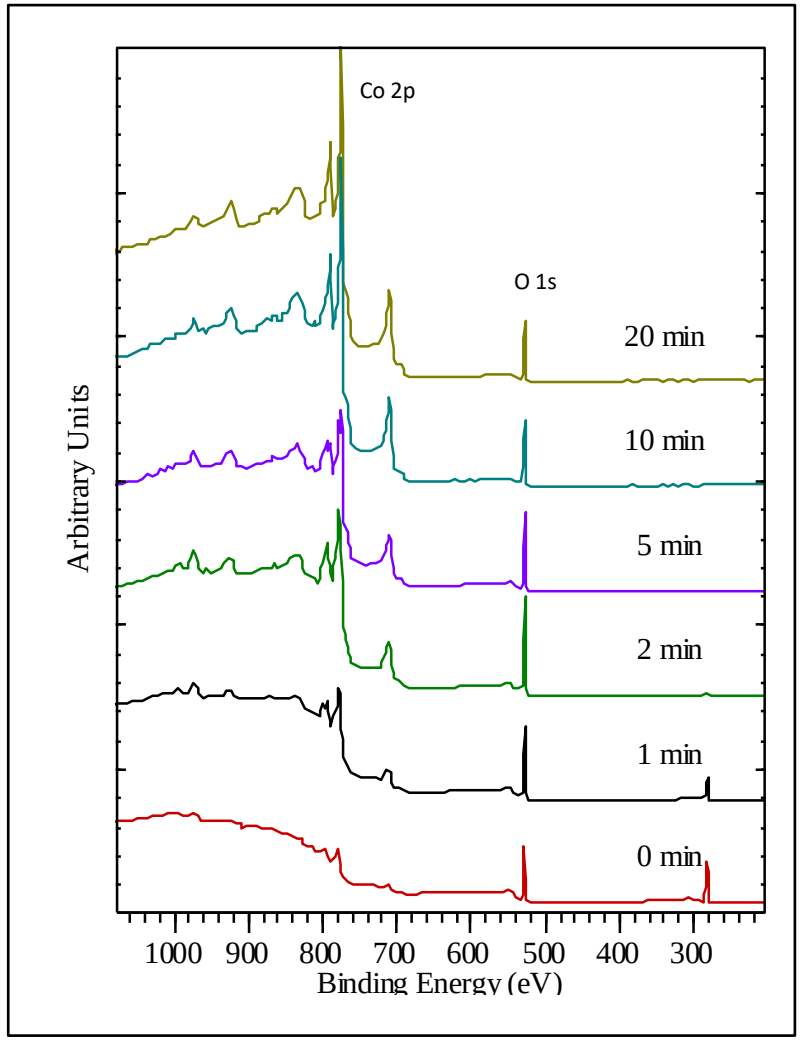
Depth profiling with sputtering

- Consecutive sputter + xps cycles
- Sputtering rate can be determined from time to sputter through a layer of material with known thickness

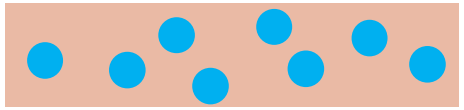




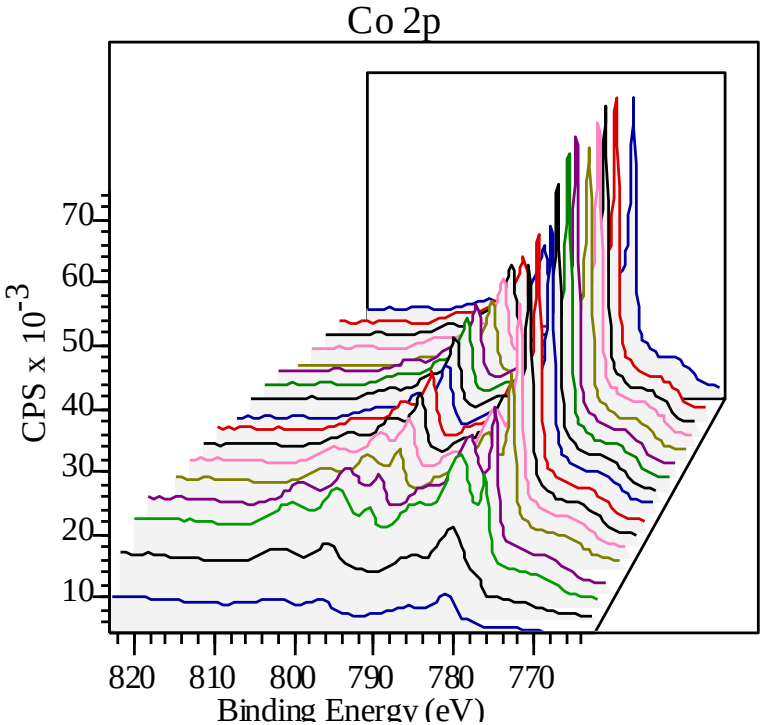
Example case

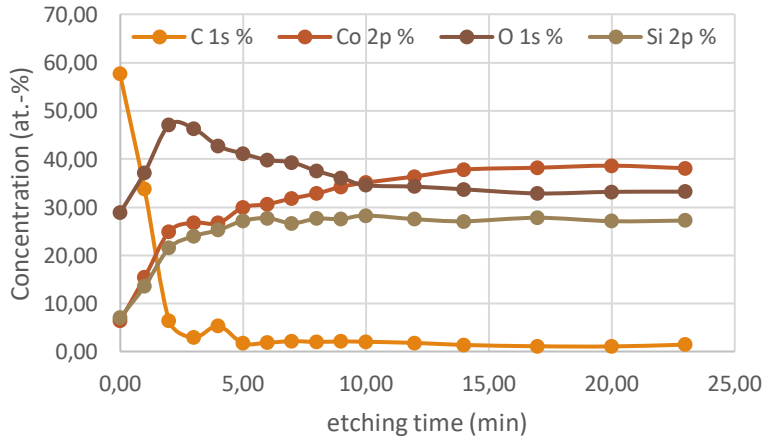


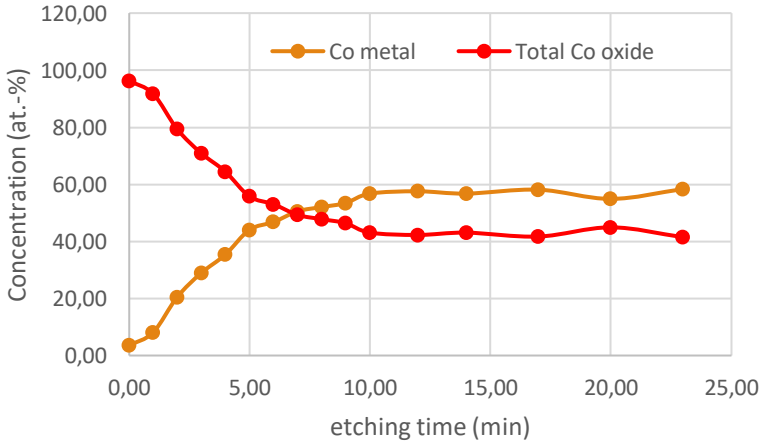
- Sample: SiO_x + embedded Co clusters



- Elemental depth profile
- Co 2p high-res shows dramatic changes!
  - Oxidation level changes at different depths!







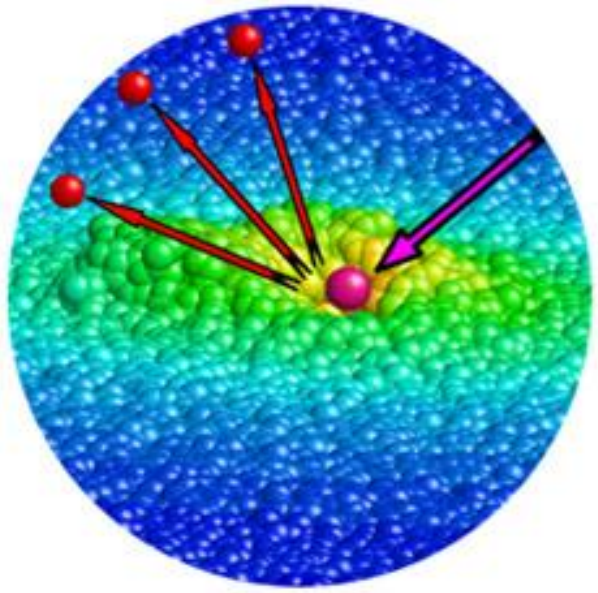
Radiation induced effects

Several factors affect accuracy and depth resolution when using ion beams:

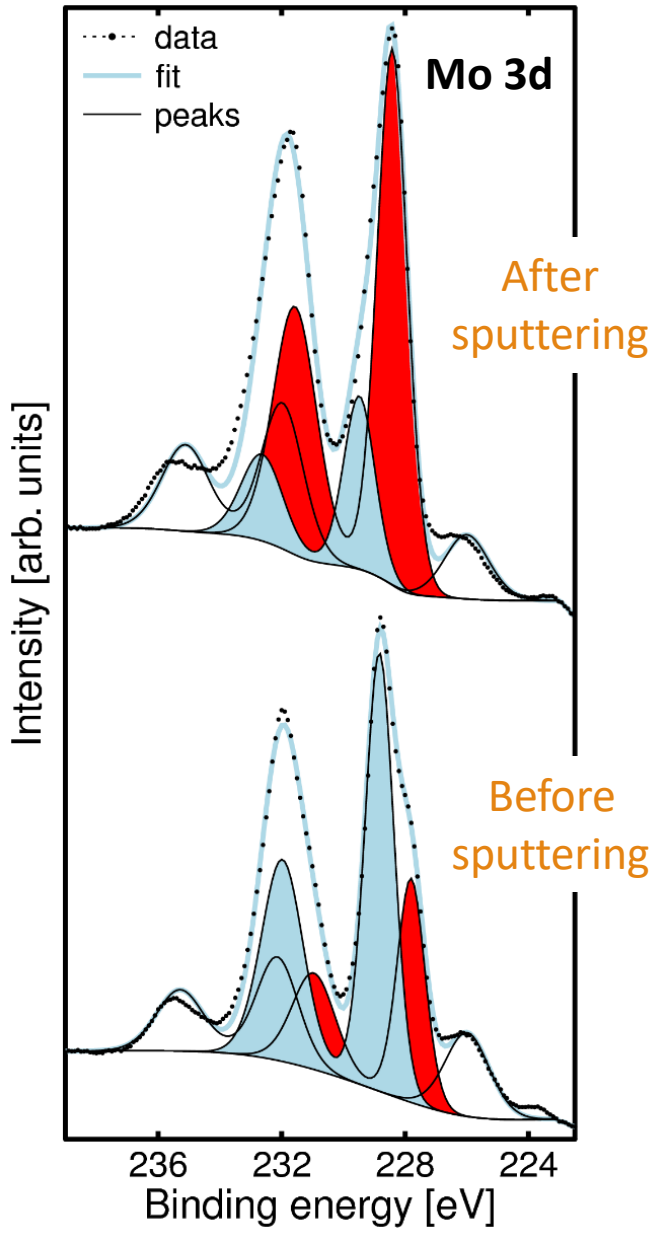
- Non-uniform ion beam intensity/impurity ions
- Re-deposition of sputtered species
- Adsorption of residual gases

- Surface roughness (original and ion-induced)
- Crystalline structure and defects

- Preferential sputtering
- Atomic mixing in layered materials
- Ion implantation
- Decomposition of compounds



Energy from ion impacts can be distributed over a large volume in the sample

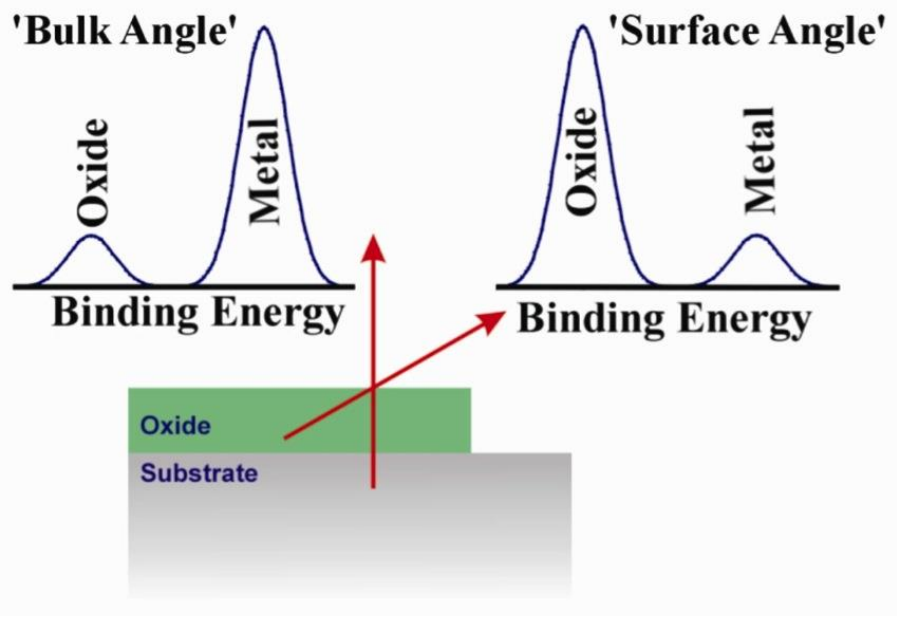


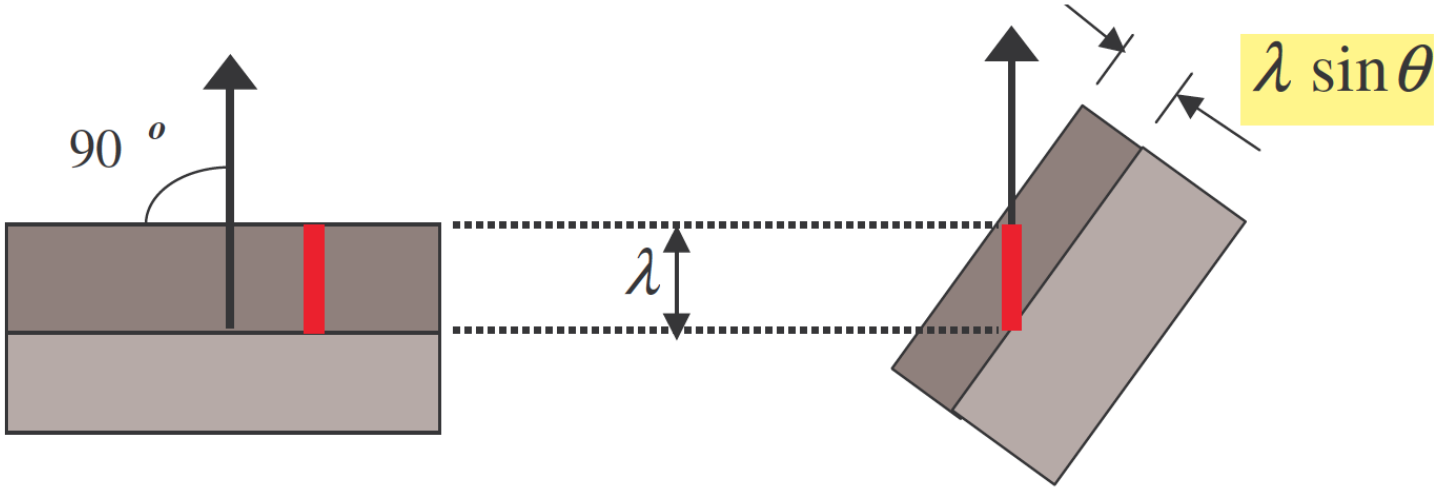
Angle resolved XPS

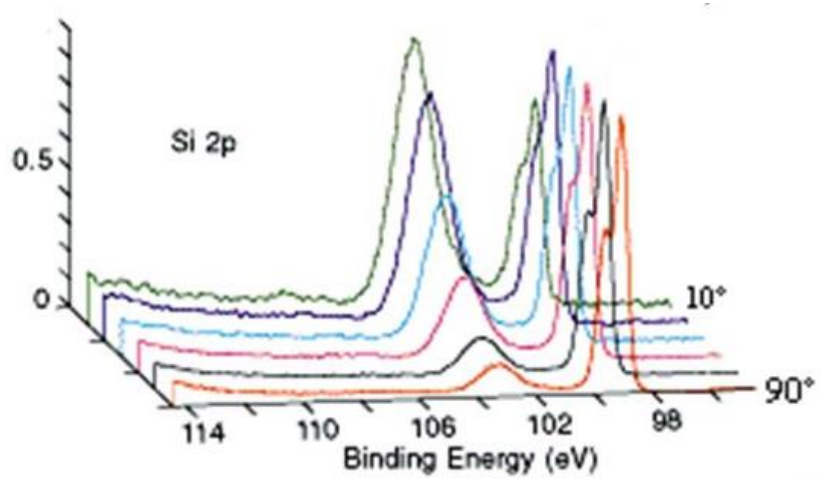
Alternative means for depth profiling:

- Consecutive XPS measurements are done while tilting the sample at increasing angles
- Escape depth for electrons decreases with increasing angle
- Higher surface sensitivity

- Reliable results only if surface is smooth enough!



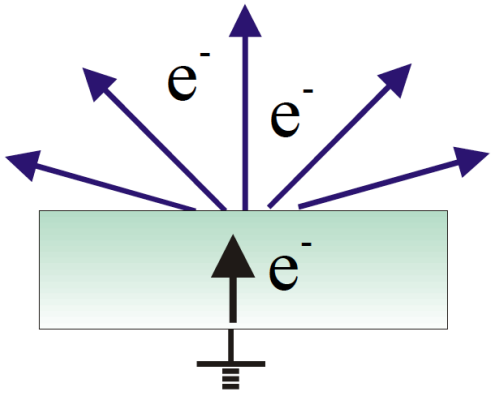




Surface charging

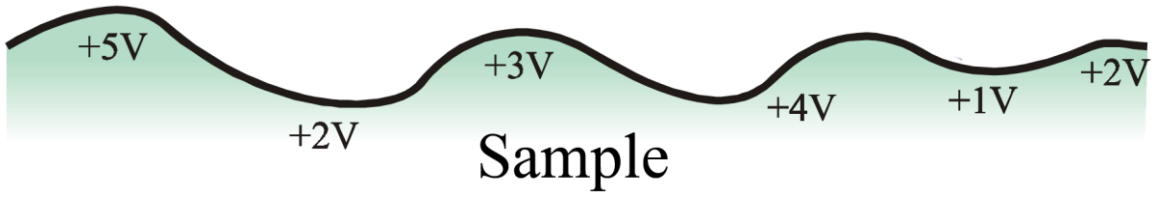
Electrons are continuously removed from the surface of the sample:

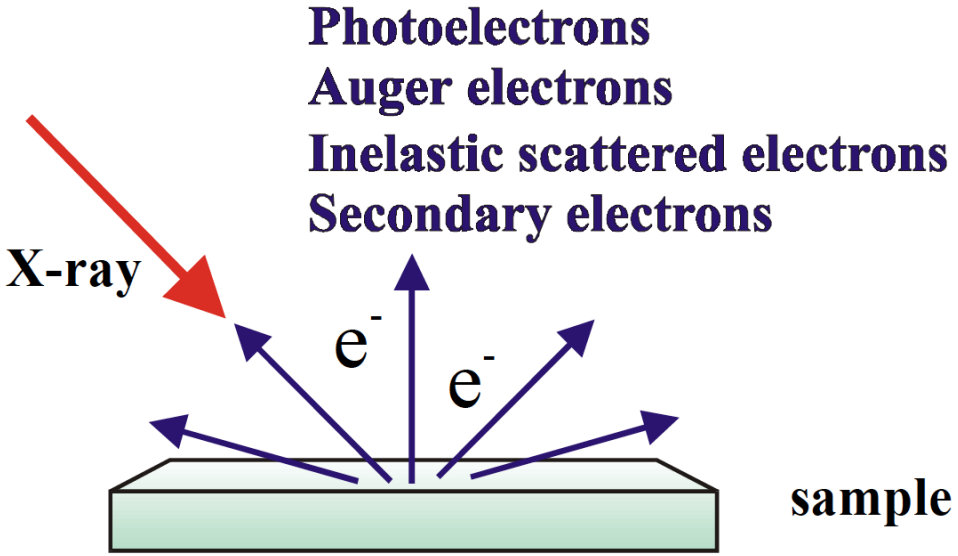
- Metals: electron loss is compensated
- Insulators: surface will collect (non-uniform) charge



Surface charging:

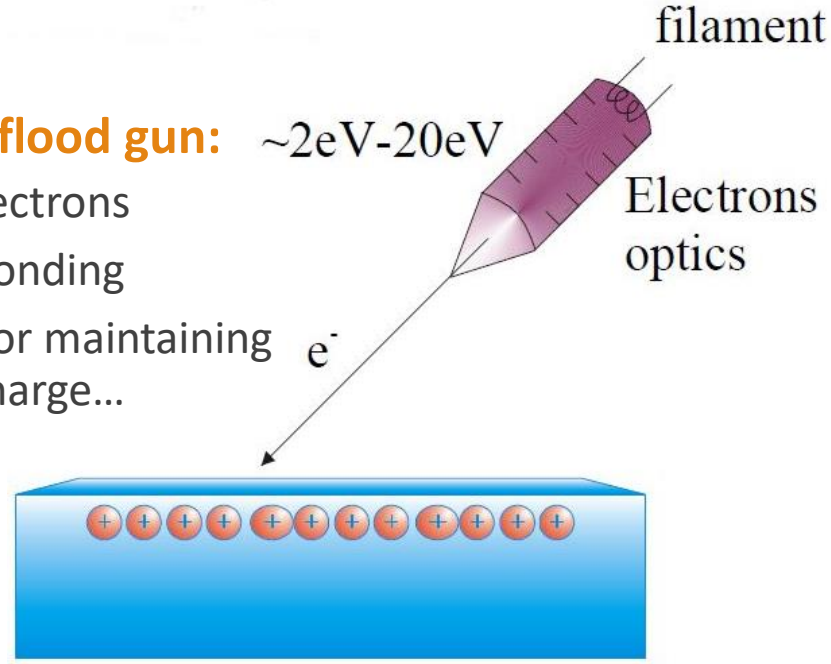
- Broadening of peaks
- Shift in peak energies





Low energy electron flood gun:

- Introduces excess electrons
- May affect surface bonding
- Not always reliable for maintaining a constant surface charge…



Energy calibration

Reference peaks can be used for calibration of peak positions on insulating samples

- All spectra can be shifted to align a certain peak with known binding energy

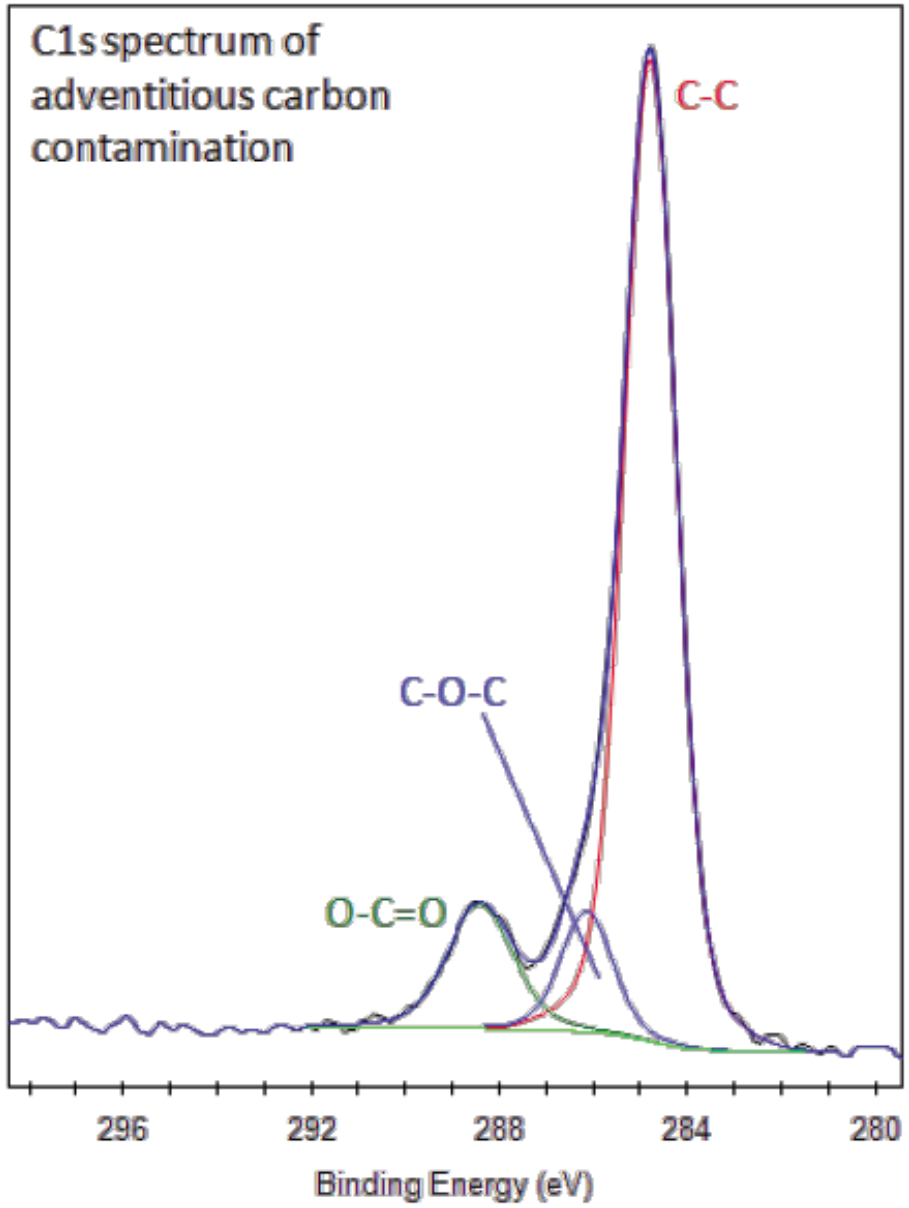
Adventitious carbon:

- C-C bonding in C 1s spectrum: 284.8 eV

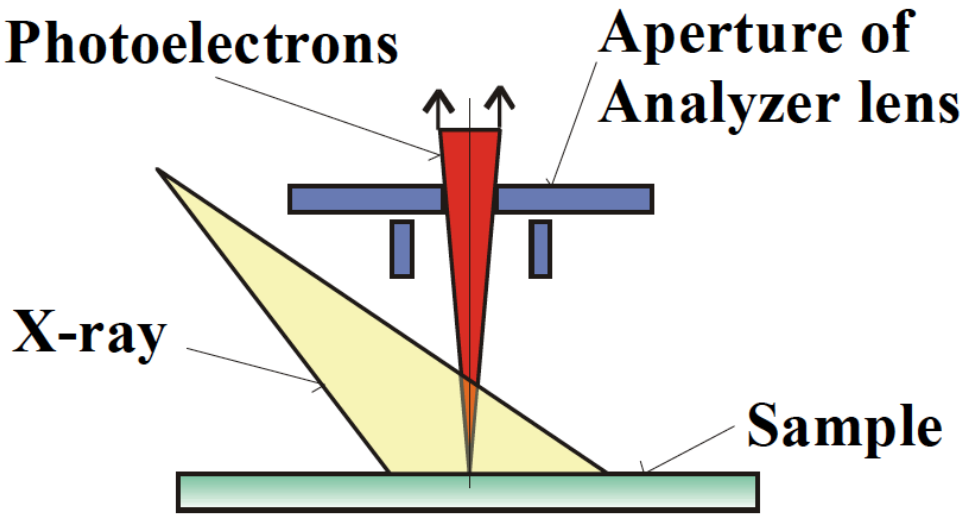
Gold surface:

- Au $4f_{7/2}$: 84.0 eV

Other peaks with known position in sample

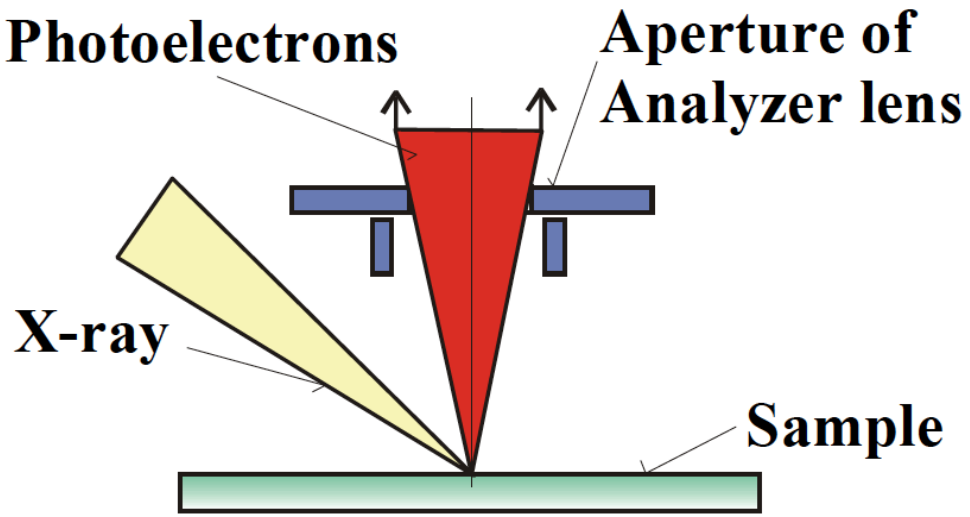


Small area analysis and imaging



Spot size determined by the analyser

Both monochromated and dual anode x-ray sources can be used



Spot size determined by the x-ray beam

Imaging methods

(1) Moving sample stage

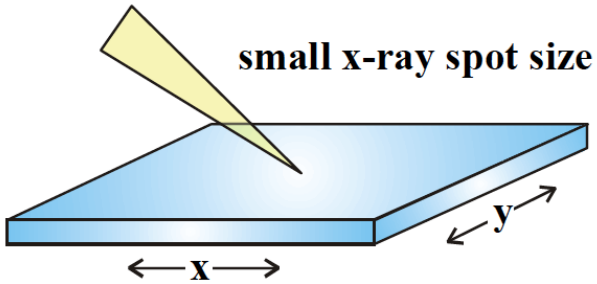


Image:

- x,y position vs photoelectron intensity
- Resolution: ~50 µm

(2) Use of scanning plates

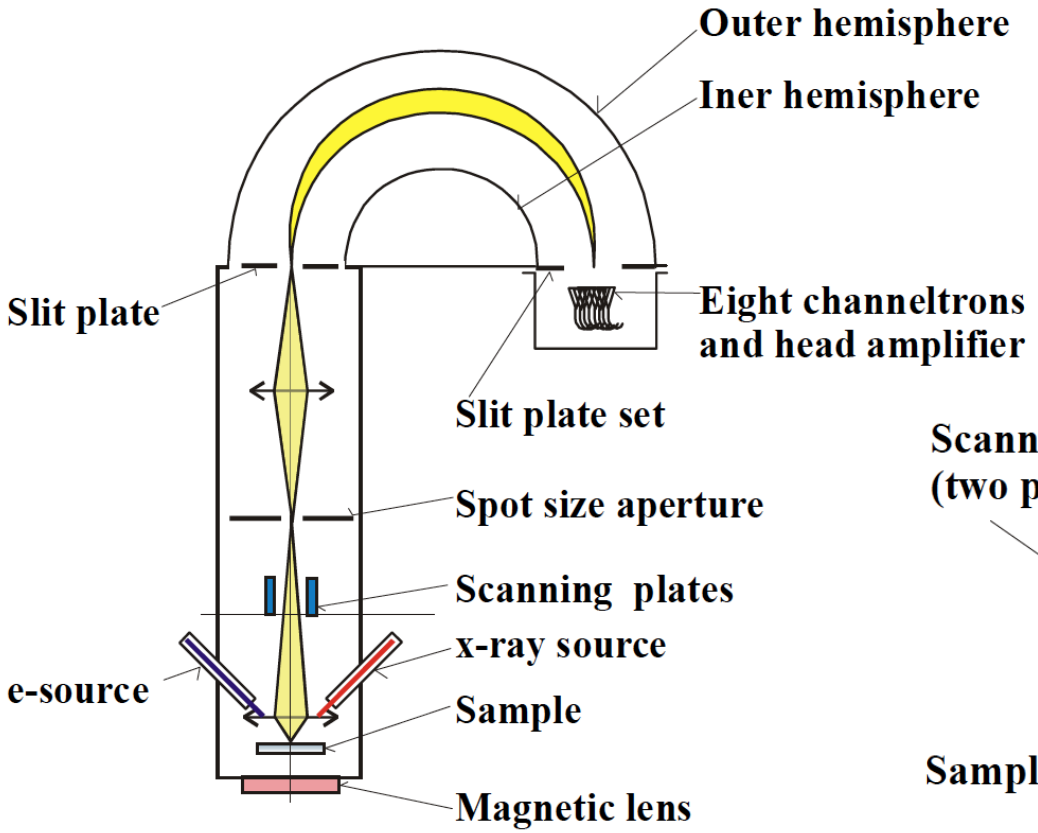
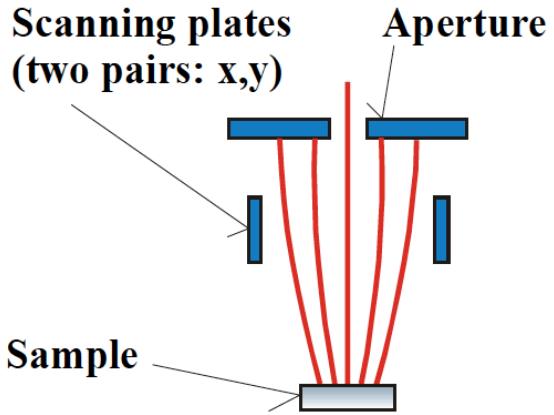
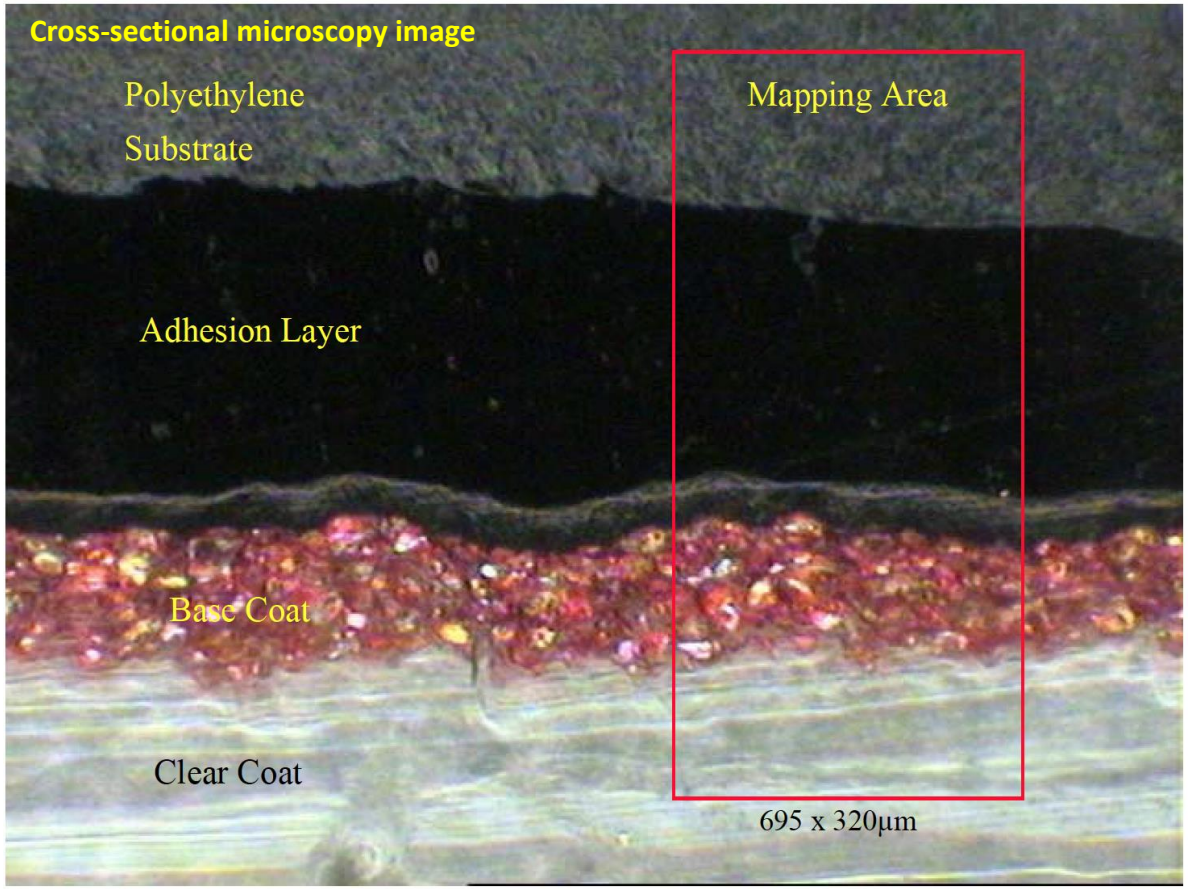


Image:

- Voltages V_x and V_y scanned
- Photointensity collected from different points in time sequence
- Resolution: ~10 µm

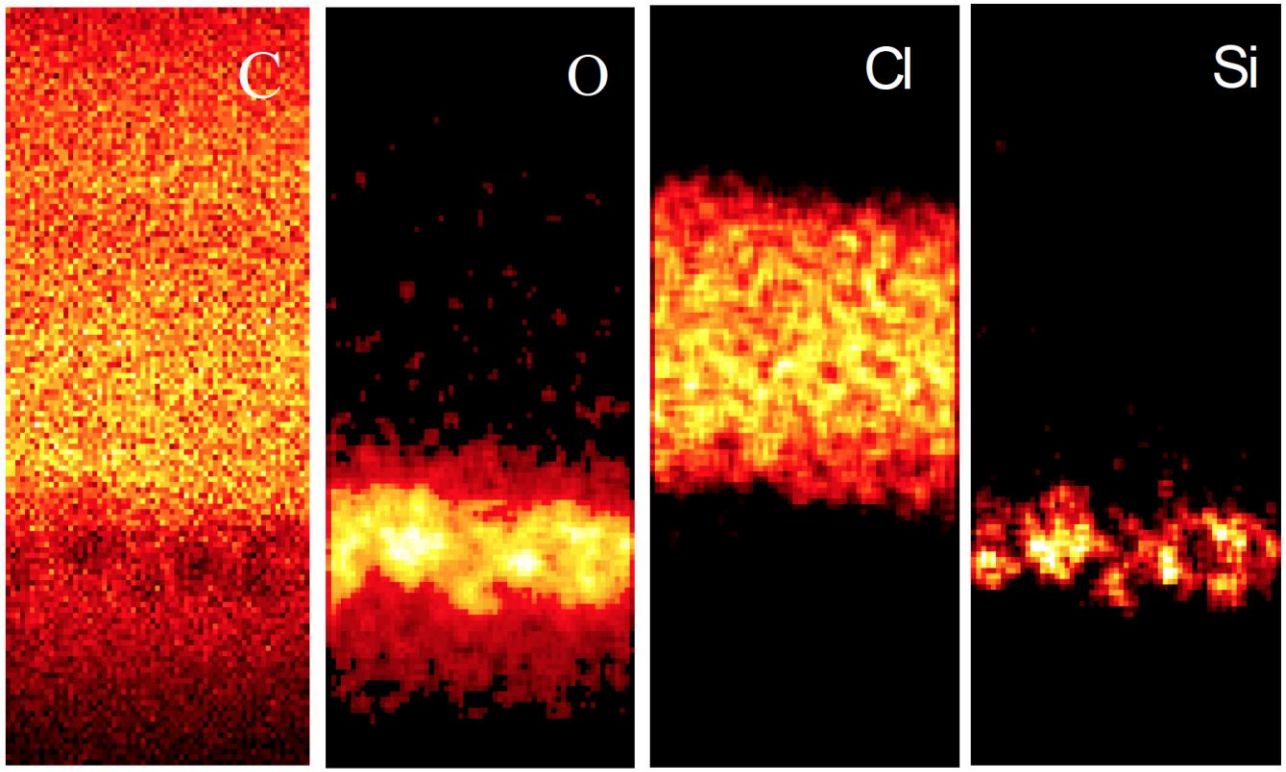


XPS study of paint



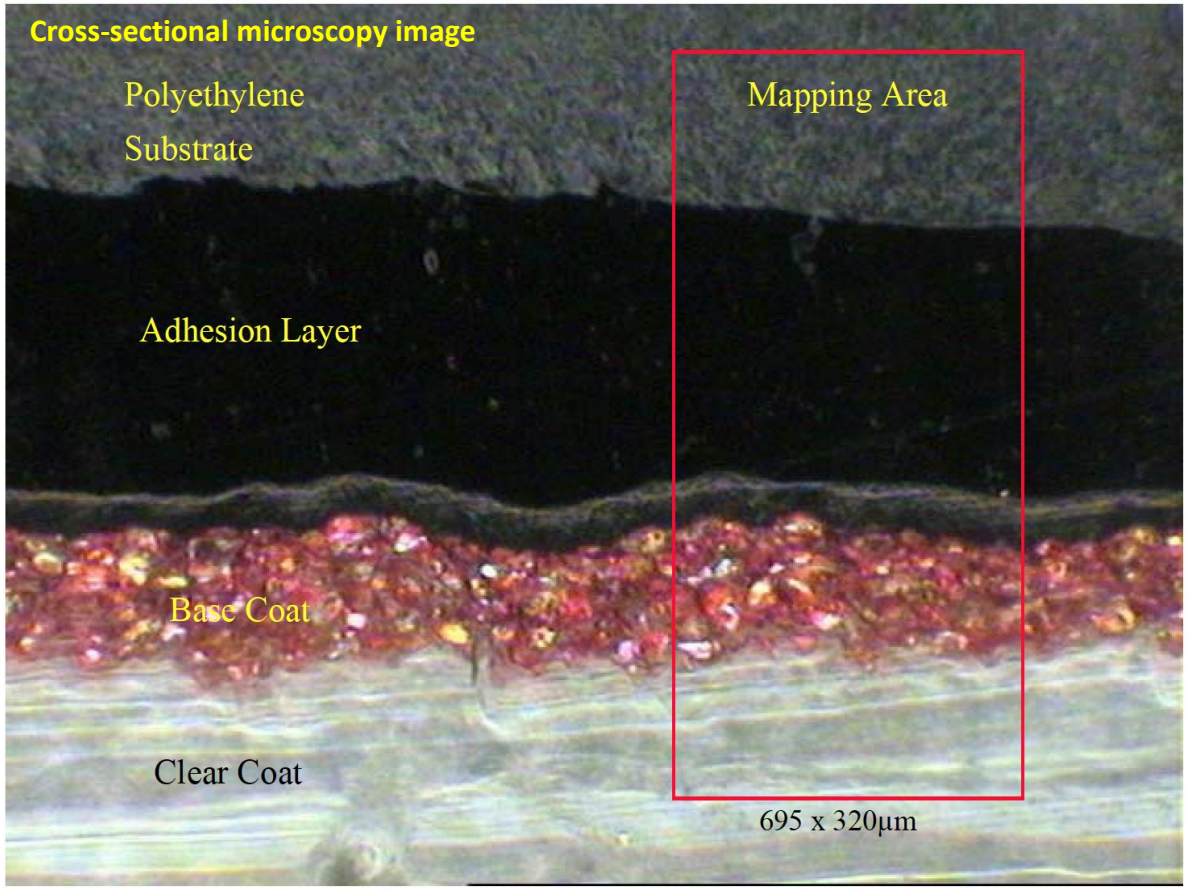
1072 x 812mm

Elemental maps using C 1s, O 1s, Cl 2p, and Si 2p signals.



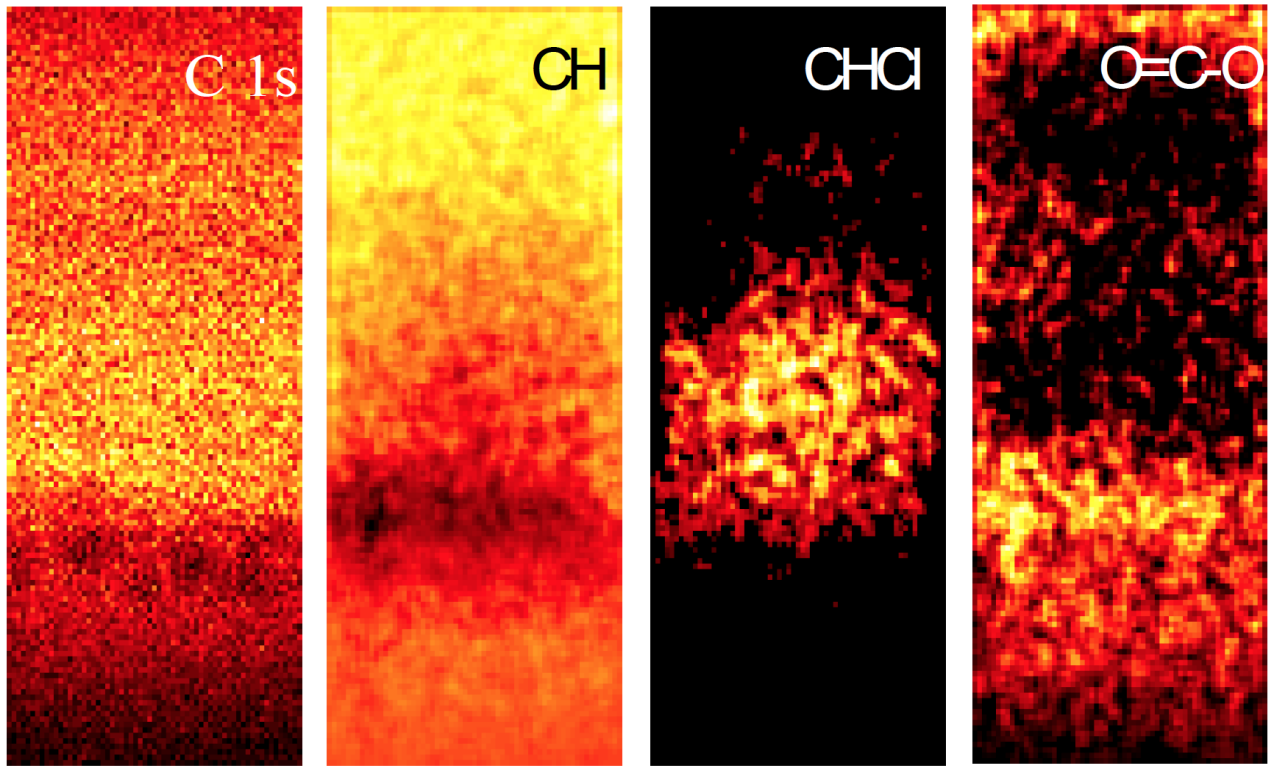
695 x 320mm

XPS study of paint – chemical state



1072 x 812mm

C 1s chemical state maps.



695 x 320mm

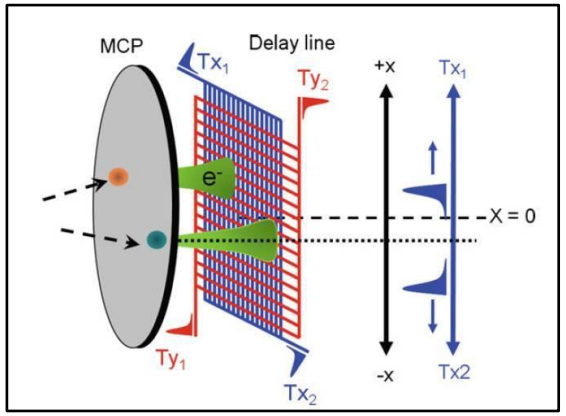
2D-detectors

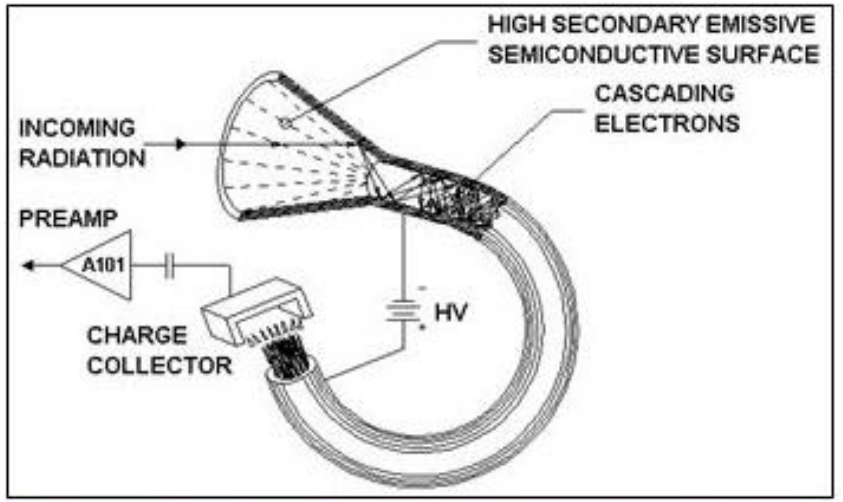
Types:

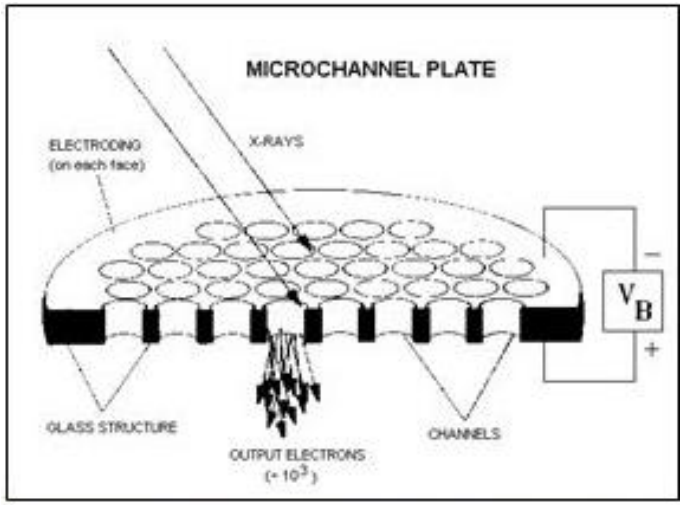
- Channeltron (CEM)
- Microchannel plate (MCP)

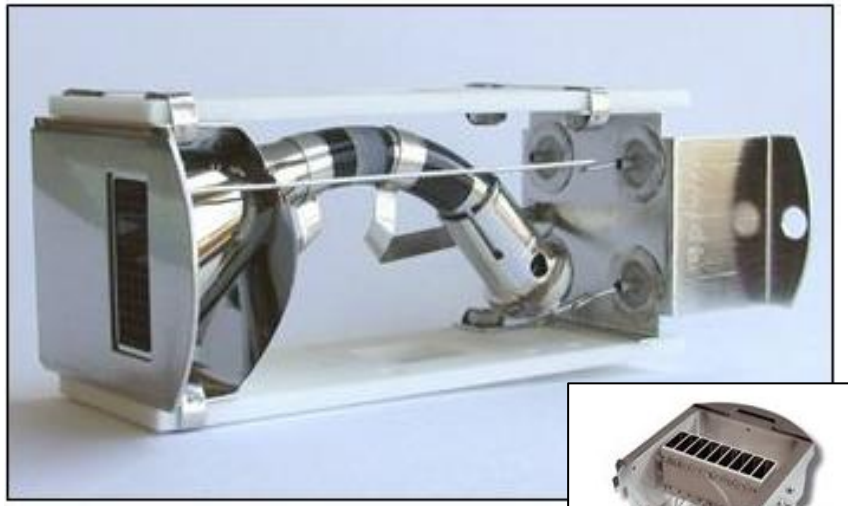
Position sensitivity:

- Channeltron array
- MCP+CCD (Charge-Coupled Device)
- DLD (Delay-Line Detector)









Imaging methods

(3) Use of multichannel plate

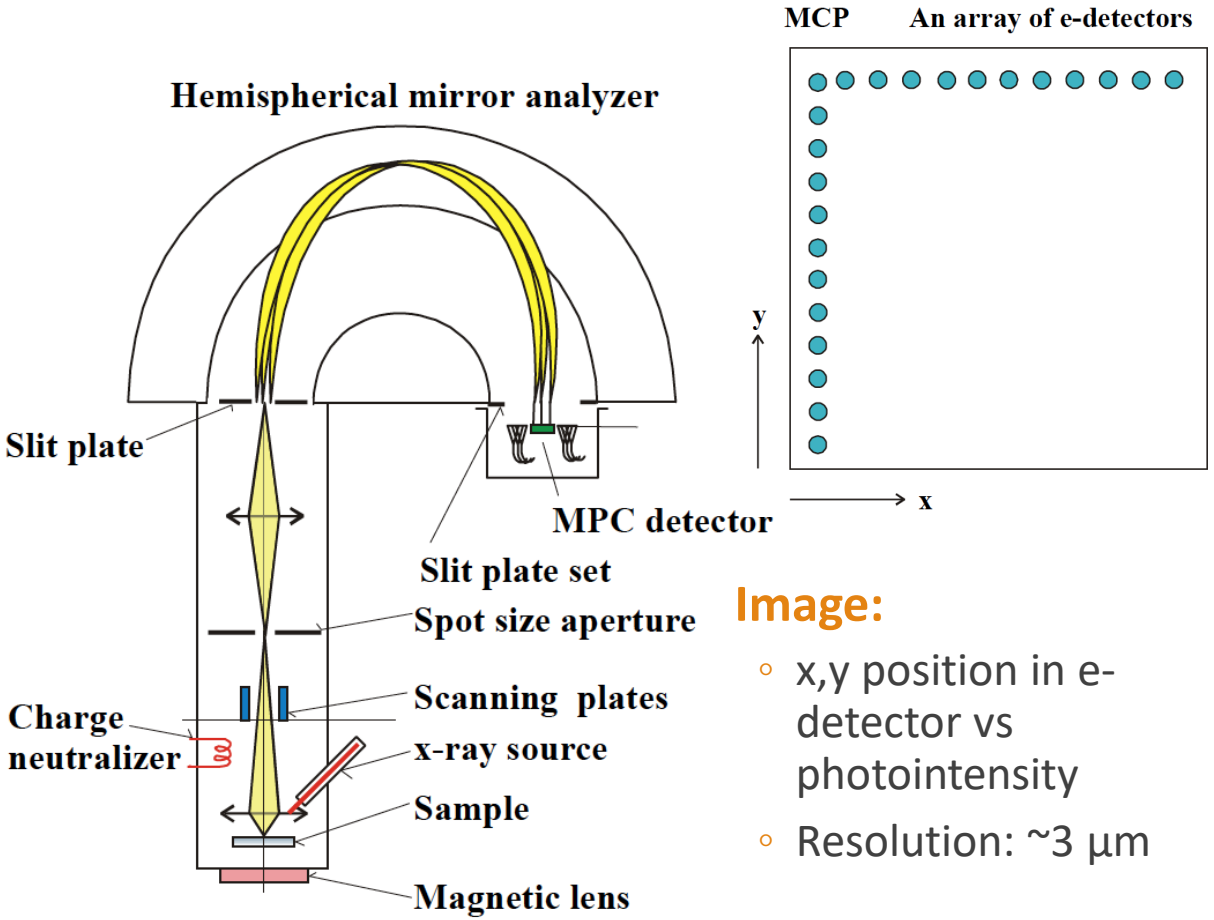
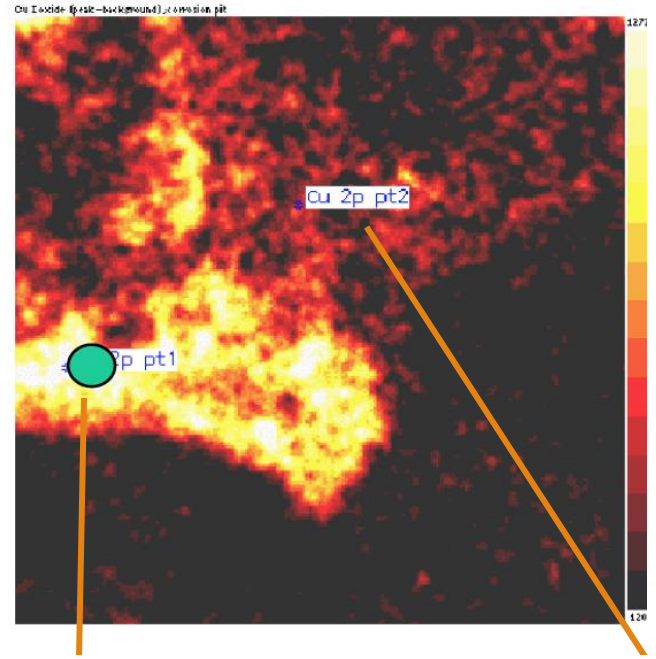


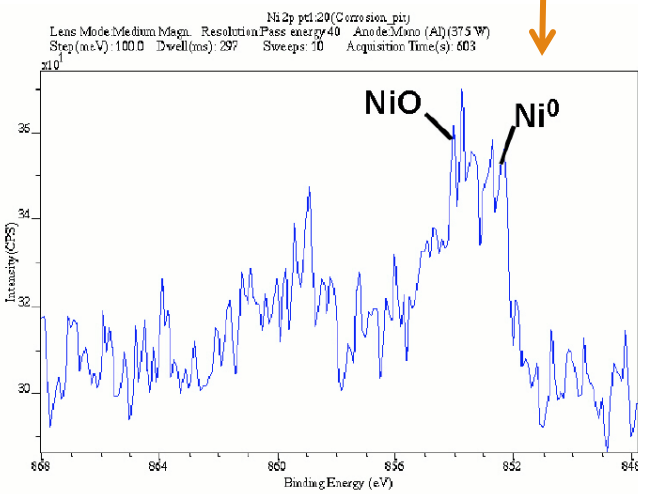
Image:

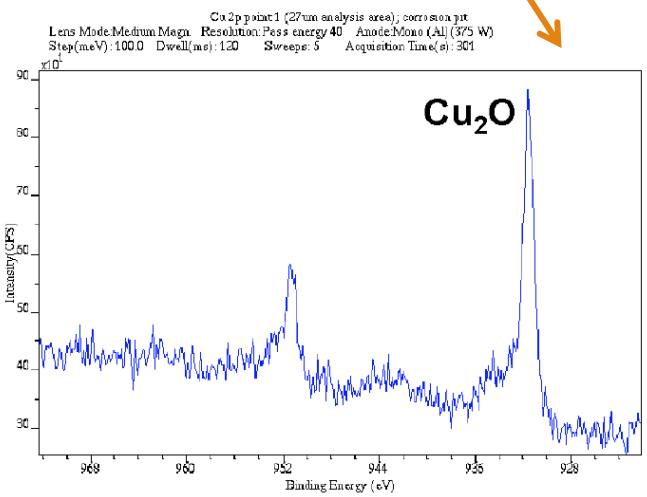
- x,y position in e-detector vs photointensity
- Resolution: ~3 µm

Cu_2O Map



- Chemical state can be identified for each "spot" in image





Synchrotron sources

- High intensity and resolution, energy tunability, polarization, pulsed beam, focused beam
- Big facilities: **high cost** – shared facilities