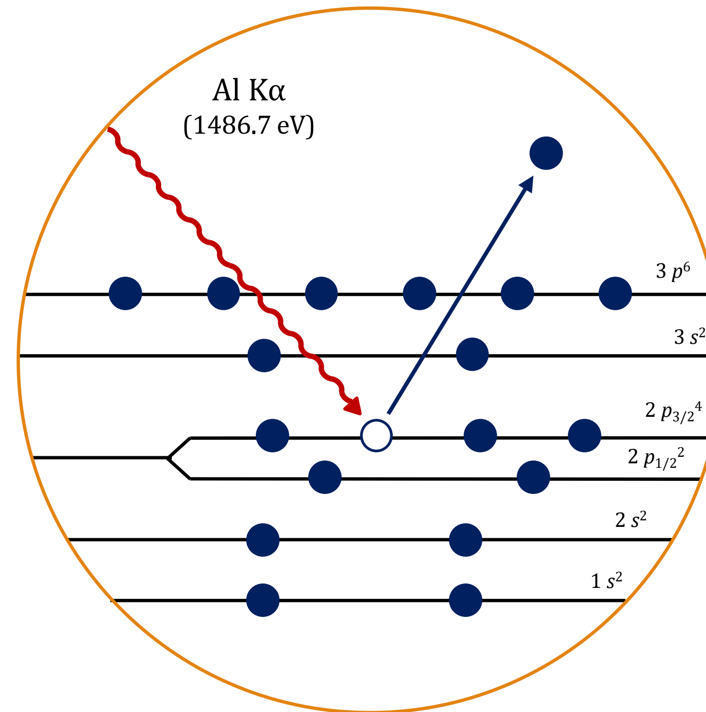
X-Ray Photoelectron Spectroscopy



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
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4. Technical issues & Auxiliary features
    1. Surface contamination & charging
    2. Ion beam sputtering & depth profiling
    3. Angle resolved XPS
    4. Small area analysis and imaging

The photoelectric effect

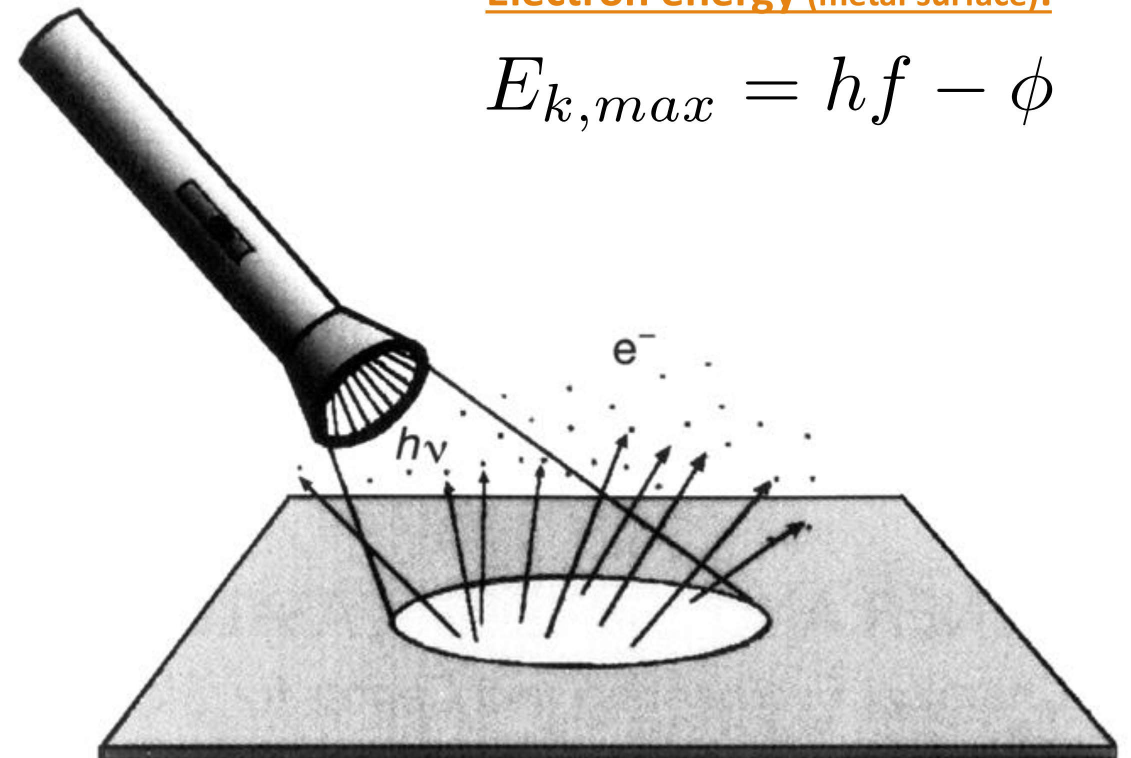
Emission of electrons when light is shone onto a material:

- 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

Electron energy (metal surface):

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



The electromagnetic spectrum

1–10 eV
Valence band

>1000 eV
Core electrons

Energy of one photon (electron volt)

10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10 100 1000 10^{4}

Frequency (Hz)

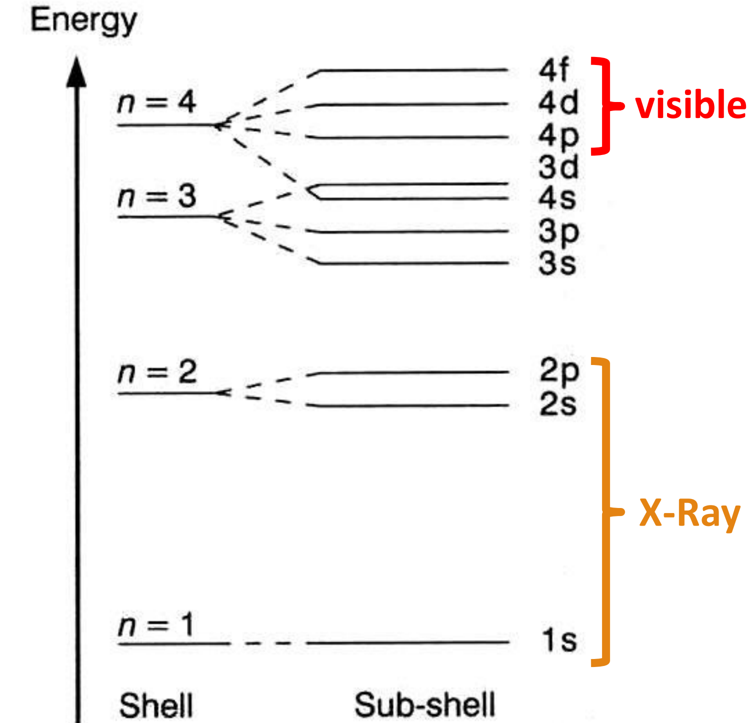
10^{6} 10^{7} 10^{8} 10^{9} 10^{10} 10^{11} 10^{12} 10^{13} 10^{14} 10^{15} 10^{16} 10^{17} 10^{18} 10^{19}

Wavelength

100 m 10 m 1 m 10 cm 1 cm 1 mm 100 μm 10 μm 1 μm 100 nm 10 nm 1 nm 0.1 nm

AM radio
VHF TV & FM radio
UHF TV
Mobile phones
Microwaves
Radar
Infra-red
Visible light
Ultra violet
X-rays
Gamma rays

Electron energy levels:



- Core levels have larger differences in energy!

Photoemission as an analytical tool

Electron Spectroscopy for Chemical Analysis (ESCA)

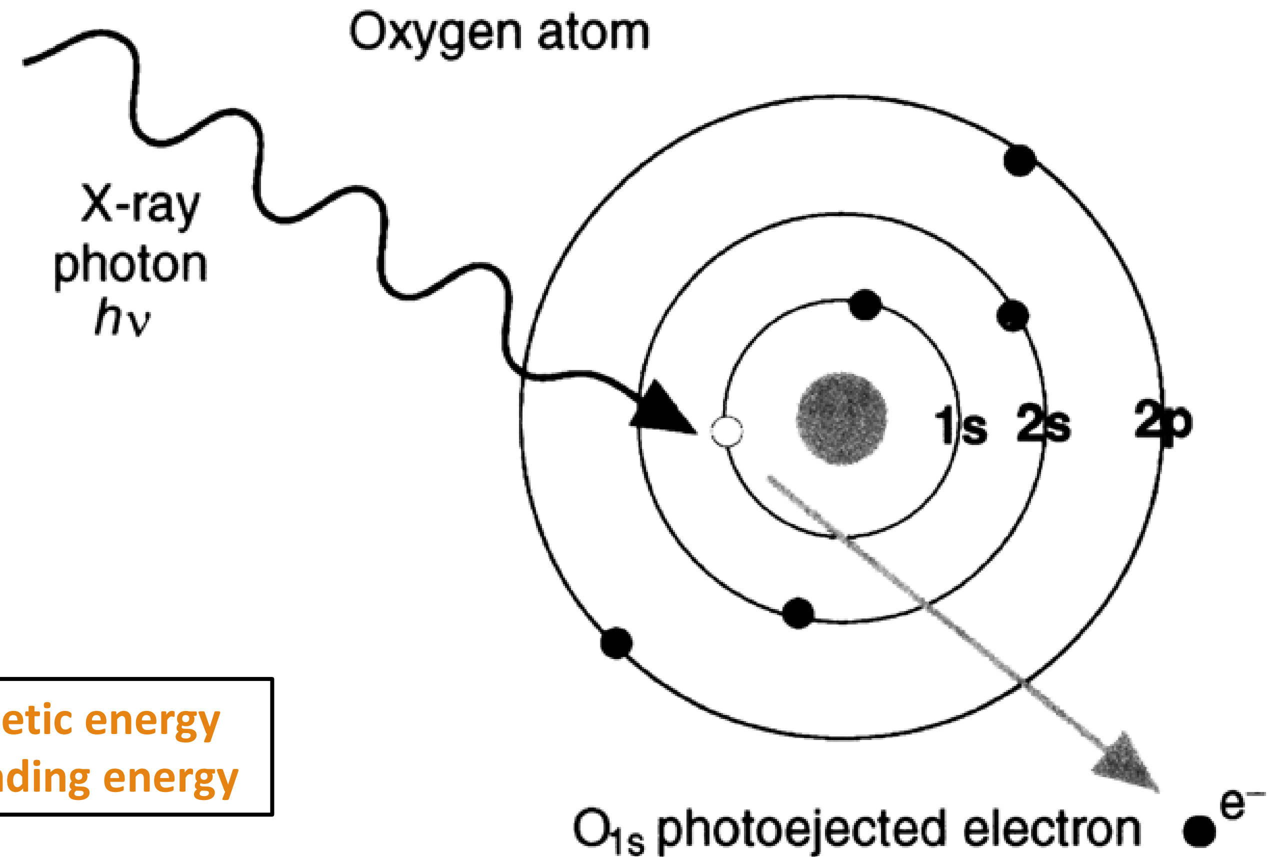
- Kai Siegbahn, 1957 (Nobel Prize 1981)

Widely used technique for surface analysis:

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

Requirement:

- Monochromatic & High energy photon source



Electron energy (any surface):

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

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

Instrumentation

Electron Analyser

electron
lenses
(variable V)

X-Ray Source

+20 kV

water cooling

cathode

Al

Mg

e⁻

hν

e⁻

electron
multiplier
detector

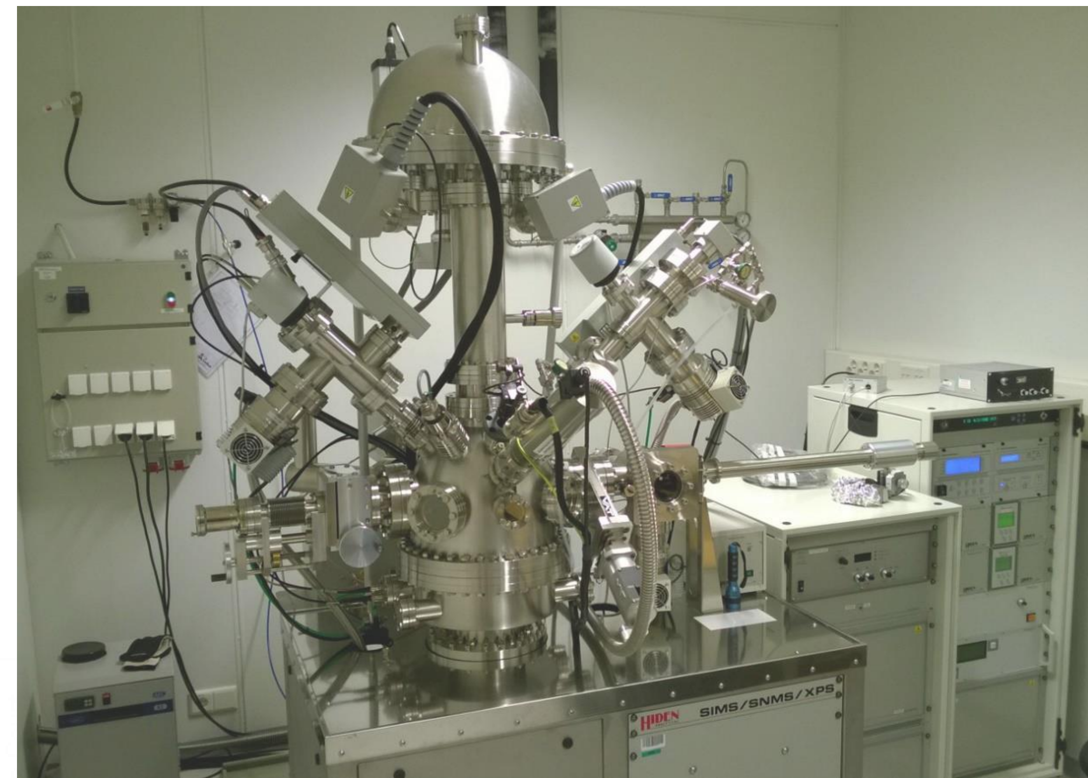
e⁻ count

Energy

switchable anodes
(thermonic emission
electron source)

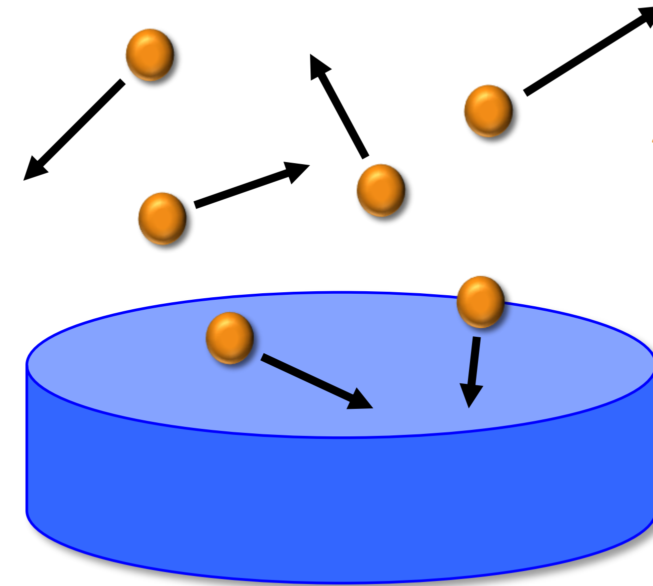
Sample
(grounded)

Computer Readout



- X-ray source (typically Mg or Al anode)
- Electron energy analyzer
- Electronics & computer system
- Vacuum system (ultra-high vacuum)
- Extras:
  - Ion gun for etching (argon ions)
  - Neutralizer (flood gun, non-conductive samples)
  - Cooling system (lots of heat from X-ray source)

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

Vacuum	Pressure
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
- $k = 1.381 \cdot 10^{-23}$ J/K

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

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

- Surface will be clean for about 1 second…

AXIS 165 / AXIS Ultra^{DLD}

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

- **Analysis on > 200 samples / year**

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
- Derivatives: TEMPO, click, CMC, silylation…
- Functional surfaces: bio-interfaces, biological surfaces, biomimetic materials
- Composites of cellulose and derivatives: polymers, clay, lignin, chitosan, graphene, CNTs
- Textiles: flax, cotton, MMC, synthetic fibers
- Carburized celluloses: e.g. catalysis

Other materials (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

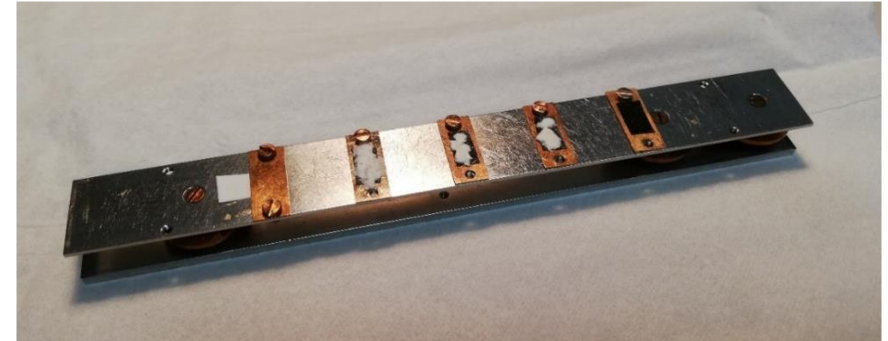
XPS in applied surface science

Quantification of elements at the surface of materials:

- Detection of all elements (except for hydrogen and helium)
- Chemical identification
- Surface distribution of elements (such as films vs islands)
- Easy sample preparation
- Non-destructive (no particle bombardment, only soft X-rays)

Limitations:

- XPS can only analyze the outermost surface layers (0-10 nm)
- It will not tell you the average bulk composition
- Surface contamination is a big issue
- Samples must tolerate Ultra High Vacuum ($<10^{-9}$ mbar)



Samples:

- Almost any type of solid sample : Wafers, powders, fibers, composites, organic/biological specimens, etc.
- Allows for insulating, conducting or heterogeneous materials.
- Sample preparation: **As little as possible.**
- Secured on holder with springs or UHV-tape.

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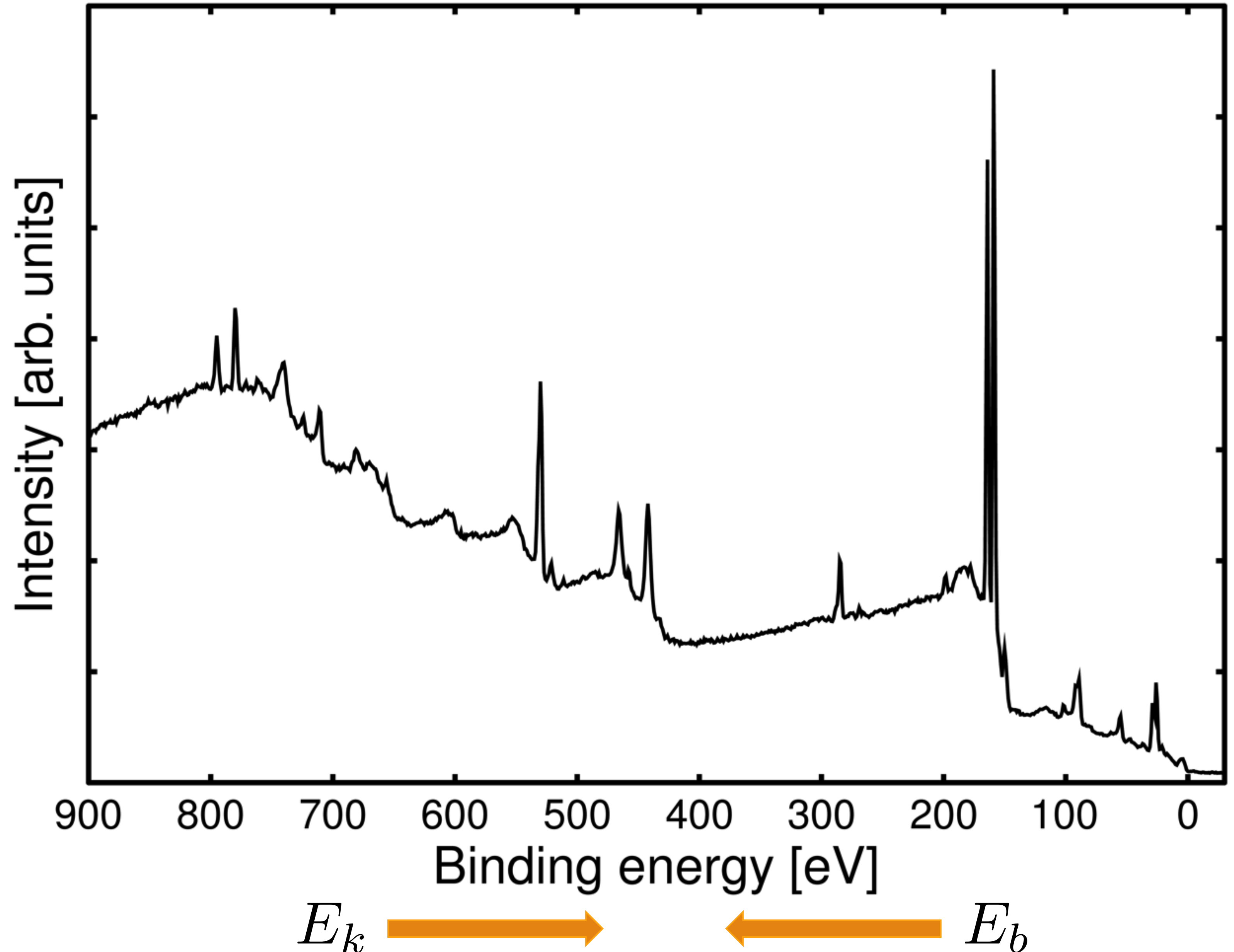
Experiment

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 specific for each element:

- 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

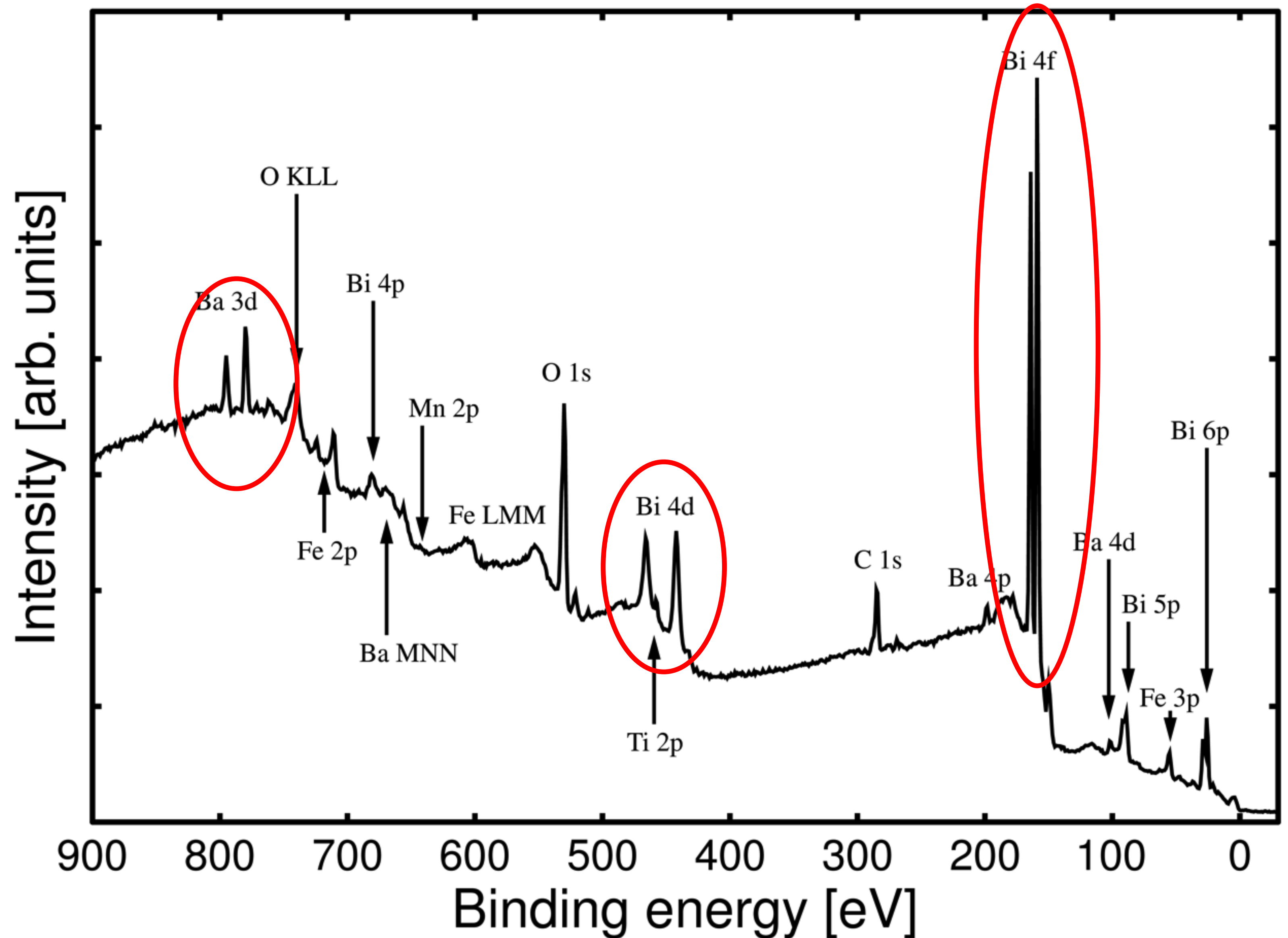
Z	El	$1s_{1/2}$ K	$2s_{1/2}$ L_1	$2p_{1/2}$ L_2	$2p_{3/2}$ L_3	$3s_{1/2}$ M_1	$3p_{1/2}$ M_2	$3p_{3/2}$ M_3	$3d_{3/2}$ M_4	$3d_{5/2}$ M_5
1	H	14								
2	He	25								
3	Li	55								
4	Be	111								
5	B	188		5						
6	C	284		6						
7	N	399		9						
8	O	532	24	7						
9	F	686	31	9						
10	Ne	867	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…

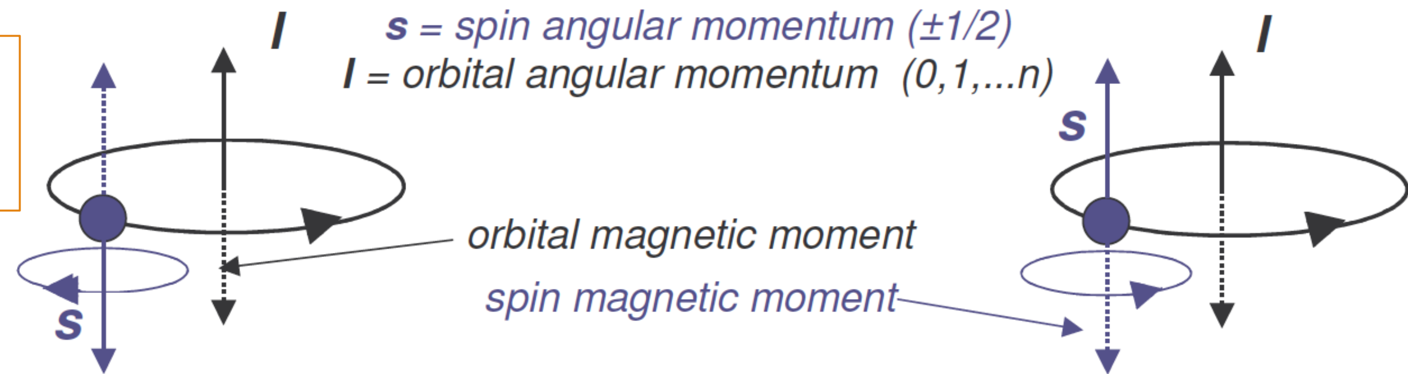


Spin-orbit splitting

Parallel spins
$j = l + s$
Lower E_b

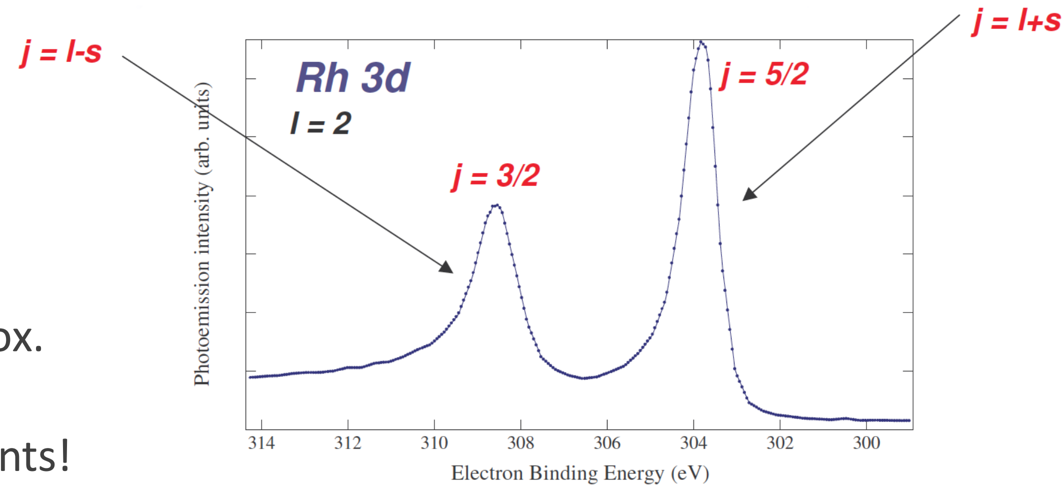
Before ionization
- Inner shells are filled
- No spin-orbit interactions

Antiparallel spins
$j = l - s$
Higher E_b

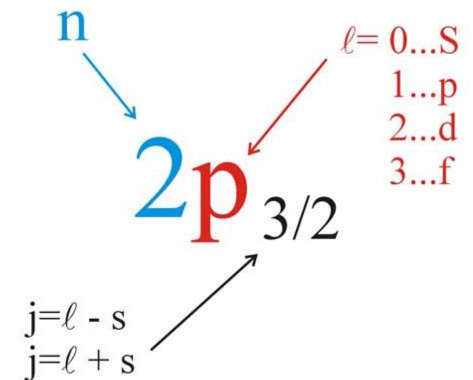


After ionization
- Un-paired electrons in inner shells
- Spin-orbit coupling
  - Interaction between magnetic moments from electron spin and orbit affects final energies

Spin-orbit splitting results in the formation of **doublets**:
- Fixed **intensity ratios** between peaks
- For the same element **ΔE_b** will be approx. constant in different compounds
- Can be used for identification of elements!

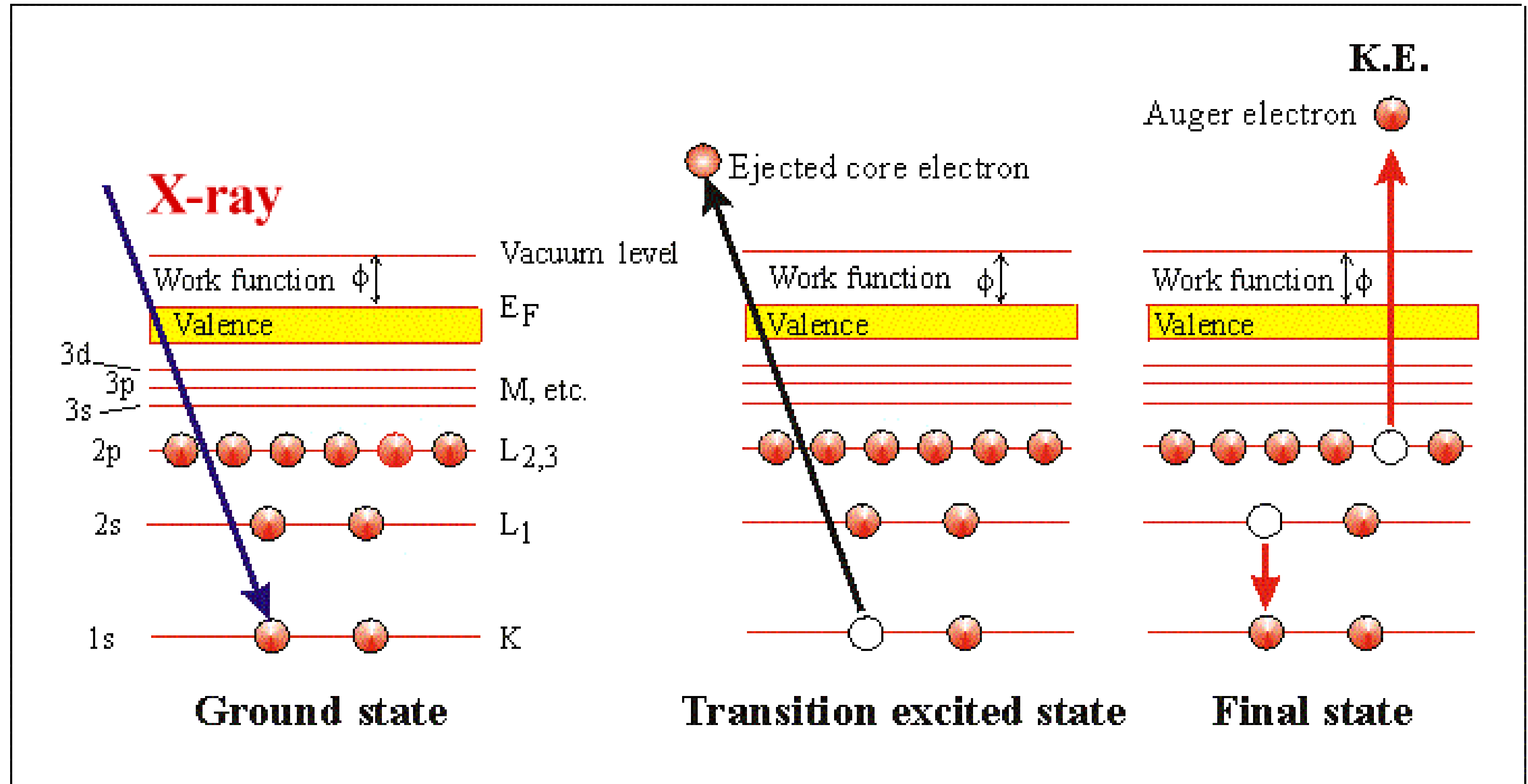


Peak labeling:



Auger electrons

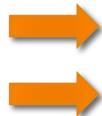
- Atoms are in transitional excited states after core electrons are ejected
- Auger electrons can be emitted when excited states are relaxed
- E_k is independent of X-ray photon energy
- Position in E_b scale will depend on X-ray source



Characteristic X-rays

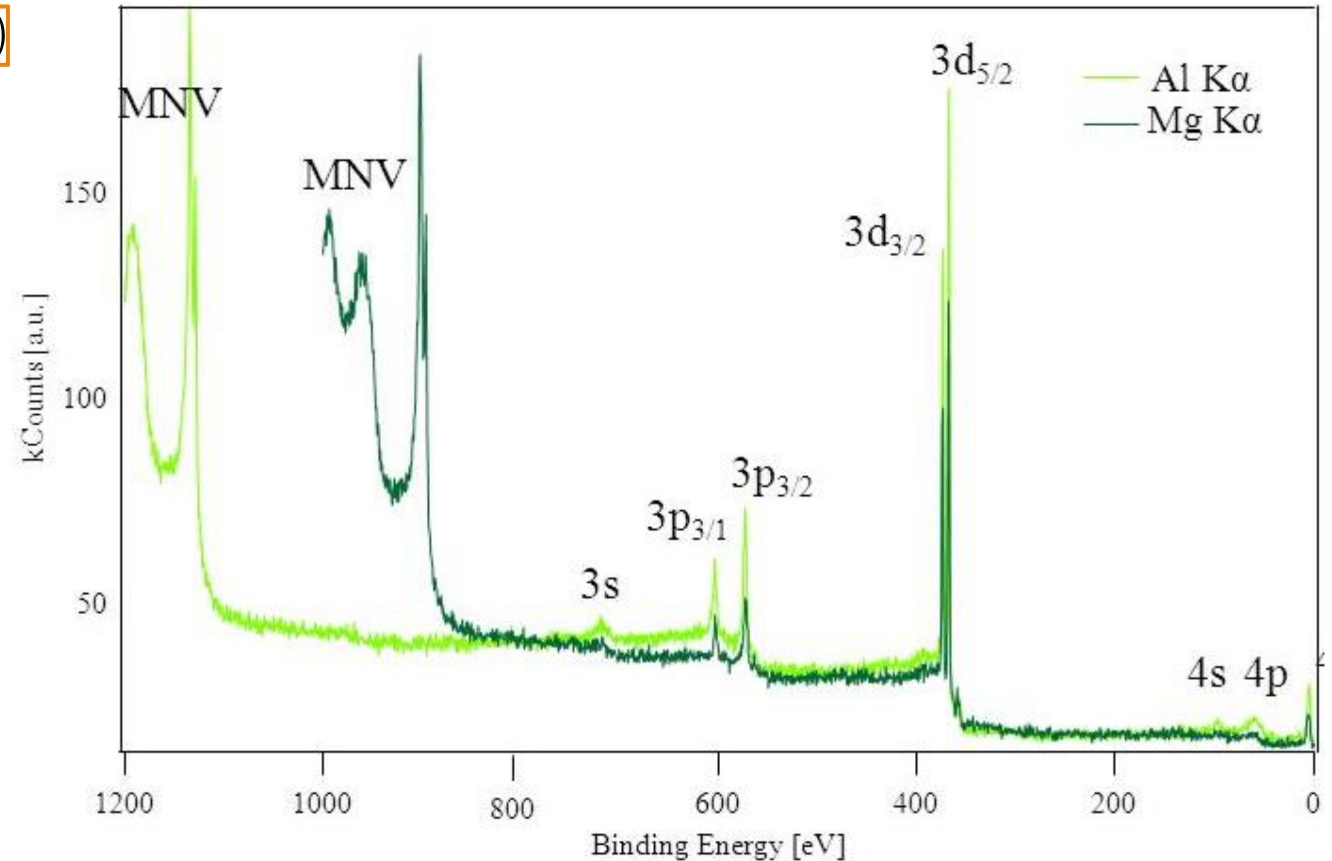
Different X-rays:

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

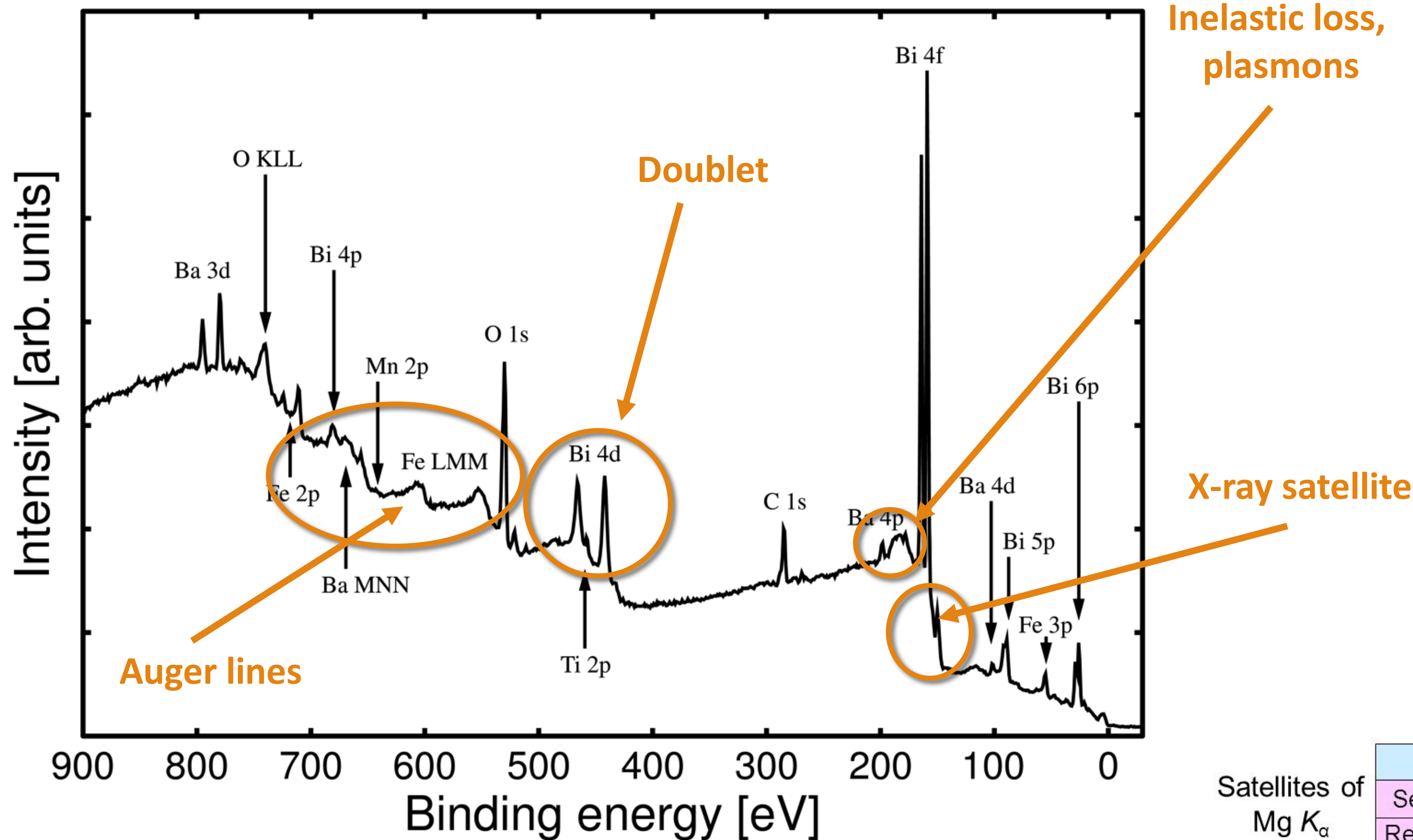


Line	Energy (eV)	Width (eV)
Y M_ζ	132.3	0.47
Zr M_ζ	151.4	0.77
Cr L_α	572.8	3.0
Cu L_α	929.7	3.8
Mg K_α	1253.6	0.7
Al K_α	1486.6	0.85
Si K_α	1739.5	1.0
Cu K_α	8048.0	2.6

Typical Ag spectra:



Other features



Intrinsic loss features:

- **"Shake-up" satellites**
  - Finite probability that the ion formed in the photoemission process will be excited – lower E_k

Extrinsic loss features:

- **Plasmons**
  - 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 elements (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

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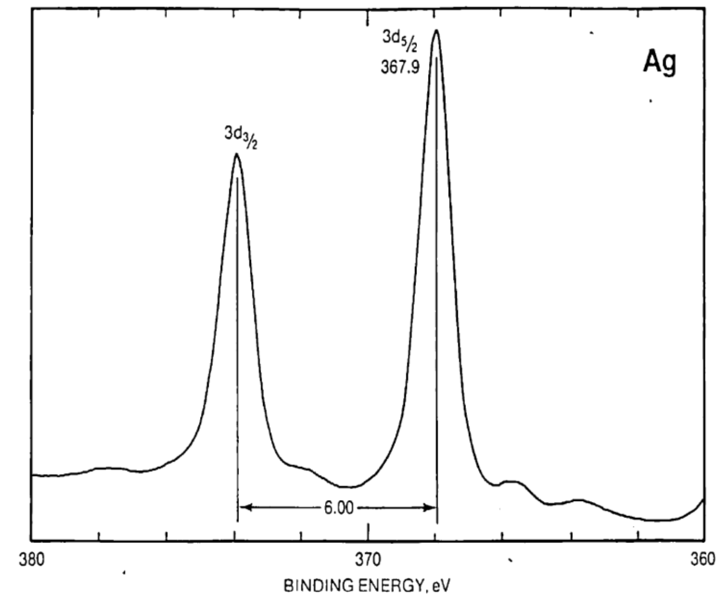
Reference spectra



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

Element	Atomic No.	Range (eV)	1s	2s	2p$_1$	2p$_3$	3s	3p$_1$	3p$_3$	3d$_3$	3d$_5$	4s	4p$_1$	4p$_3$	Range (eV)
Li	3		56												
Be	4	4	113												
B	5	8	191												
C	6	12	287												
N	7	9	402												12
O	8	4	531	23											10
F	9	6	686	30											8
Ne	10	0	863	41		14									0
Na	11	2	1072	64		31									4
Mg	12	2		90		51									
Al	13	4		119		74									
Si	14	6		153	103	102									
P	15	8		191	134	133	14								
S	16	8		229	166	165	17								6
Cl	17	11		270	201	199	17								4
Ar	18	0		319	243	241	22								0
K	19	1		378	296	293	33		17						
Ca	20	2		439	350	347	44		25						
Sc	21	6		501	407	402	53		31						8
Ti	22	8		565	464	458	62		37						10
V	23	6		630	523	515	69		40						6
Cr	24	6		698	586	577	77	46	45						
Mn	25	4		770	652	641	83	49	48						6
Fe	26	8		847	723	710	93	56	55						6
Co	27	6		927	796	781	103	63	61						7
Ni	28	6		1009	873	855	112	69	67						7
Cu	29	4		1098	954	934	124	79	77						5
Zn	30	2		1196	1045	1022	140	92	89		10				7
Ga	31	2			1144	1117	160	108	105		20				7
Ge	32	4					184	128	124	32	31				10
As	33	7					207	148	143	45	44				
Se	34	8					232	169	163	58	57				
Br	35	7					256	189	182	70	69				
Kr	36	0					287	216	208	89	88	22			
Rb	37	1					322	247	238	111	110	29		14	
Sr	38	[illegible]					358	280	269	135	133	37		20	
Y	39	[illegible]					395	313	301	160	158	45		25	
Zr	40	6					431	345	331	183	181	51		29	

Auger Lines

Element	KL$_1$L$_1$	KL$_1$L$_{23}$	KL$_{23}$L$_{23}$[c]
B			1082
C			993
N			875
O	779	764	743
F	645	626	599
Ne	491	468	435
Na	332	303	264

Element	L$_3$M$_{23}$M$_{23}$[f]	L$_2$M$_{23}$M$_{23}$[d]	L$_3$M$_{23}$M$_{45}$ ^{1}P	L$_3$M$_{23}$M$_{45}$ ^{3}P	L$_2$M$_{23}$M$_{45}$ ^{1}P	L$_3$M$_{45}$M$_{45}$[e]	L$_2$M$_{45}$M$_{45}$
S	1103						
Cl	1071						
Ar	1037	1035					
K	1005	1003					
Ca	964	961					
Sc	920		892				
Ti	873		839				
V	822		784				
Cr	767		729				
Mn	715		670			620	
Fe	659		608			553	
Co	604	597	546	541		483	468
Ni	548	542	482	476		410	393
Cu	486	479	416	408	396	337	317
Zn	429	422	352	343	329	265	242
Ga	368	361	284	275	257	189	162
Ge	305	297	215	205	184	113	82

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.

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

eV	Line	Splitting
17	Hf 4f$_7$	(2)
23	O 2s	
25	Ta 4f$_7$	(2)
30	F 2s	
31	Ge 3d$_5$	(1)
34	W 4f$_7$	(2)
40	V 3p	
41	Ne 2s	
43	Re 4f$_7$	(2)
44	As 3d$_5$	(1)
45	Cr 3p$_3$	(1)
48	Mn 3p$_3$	(1)
50	I 4d$_5$	(2)
51	Mg 2p	
52	Os 4f$_7$	(3)
55	Fe 3p$_3$	(1)
56	Li 1s	
57	Se 3d$_5$	(1)
61	Co 3p$_3$	(2)
62	Ir 4f$_7$	(3)
63	Xe 4d$_5$	(2)
64	Na 2s	
67	Ni 3p$_3$	(2)
69	Br 3d$_5$	(1)
73	Pt 4f$_7$	(3)
74	Al 2p	
75	Cs 4d$_5$	(2)
77	Cu 3p$_3$	(2)
85	Au 4f$_7$	(4)
87	Zn 3p$_3$	(3)
88	Kr 3d$_5$	(1)
90	Ba 4d$_5$	(2)
90	Mg 2s	
100	Hg 4f$_7$	(4)
101	La 4d$_5$	(3)
102	Si 2p$_3$	(1)
105	Ga 3p$_3$	(3)
108	Ce 4d$_5$	(4)
110	Rb 3d$_5$	(1)
113	Be 1s	
113	Ge (A)	
114	Pr 4d	
118	Tl 4f$_7$	(4)
119	Al 2s	
120	Nd 4d	
124	Ge 3p$_3$	(4)
132	Sm 4d	
133	P 2p$_3$	(1)
133	Sr 3d$_5$	(2)
136	Eu 4d	
138	Pb 4f$_7$	(5)
143	As 3p$_3$	(5)
150	Tb 4d	
153	Si 2s	
154	Dy 4d	
158	Y 3d$_5$	(2)
159	Bi 4f$_7$	(5)
161	Ho 4d	
163	Se 3p$_3$	(6)
165	S 2p$_3$	(1)
169	Er 4d	
180	Tm 4d	
181	Zr 3d$_5$	(2)
182	Br 3p$_3$	(7)
185	Yb 4d$_5$	(9)
189	Ga (A)	
191	B 1s	
191	P 2s	
197	Lu 4d$_5$	(10)
199	Cl 2p$_3$	(2)
206	Nb 3d$_5$	(3)
208	Kr 3p$_3$	(8)
213	Hf 4d$_5$	(11)
229	S 2s	
229	Ta 4d$_5$	(12)
230	Mo 3d$_5$	(3)
238	Rb 3p$_3$	(9)
241	Ar 2p$_3$	(2)
245	W 4d$_5$	(12)
263	Re 4d$_5$	(14)
264	Na (A)	
265	Zn (A)	
269	Sr 3p$_3$	(11)
270	Cl 2s	
279	Os 4d$_5$	(15)
282	Ru 3d$_5$	(4)
284	Tb 4p$_3$	(33)
287	C 1s	
293	Dy 4p$_3$	(36)
293	K 2p$_3$	(3)
297	Ir 4d$_5$	(16)
301	Y 3p$_3$	(12)
306	Ho 4p$_3$	(39)
309	Rh 3d$_5$	(5)
316	Pt 4d$_5$	(17)
319	Ar 2s	
320	Er 4p$_3$	(42)
331	Zr 3p$_3$	(14)
333	Tm 4p$_3$	(45)
335	Th 4f$_7$	(9)
336	Au 4d$_5$	(18)
337	Pd 3d$_5$	(5)
337	Cu (A)	
342	Yb 4p$_3$	(50)
347	Ca 2p$_3$	(3)
359	Lu 4p$_3$	(53)
359	Hg 4d$_5$	(20)
362	Gd (A)	
364	Nb 3p$_3$	(15)
368	Ag 3d$_5$	(6)
378	K 2s	
380	U 4f$_7$	(11)
385	Tl 4d$_5$	(21)
396	Mo 3p$_3$	(17)
402	N 1s	
402	Eu (A)	
402	Sc 2p$_3$	(5)
405	Cd 3d$_5$	(7)
410	Ni (A)	
413	Pb 4d$_5$	(22)
435	Ne (A)	
439	Ca 2s	
440	Sm (A)	
443	Bi 4d$_5$	(24)
445	In 3d$_5$	(8)
458	Ti 2p$_3$	(6)
463	Ru 3p$_3$	(22)
483	Co (A)	
486	Sn 3d$_5$	(8)
498	Rh 3p$_3$	(24)
501	Sc 2s	
515	V 2p$_3$	(8)
519	Nd (A)	
530	Sb 3d$_5$	(9)
531	O 1s	
534	Pd 3p$_3$	(27)
553	Fe (A)	
555	Pr (A)	
565	Ti 2s	
573	Ag 3p$_3$	(31)
575	Te 3d$_5$	(10)
577	Cr 2p$_3$	(9)
594	Ce (A)	
599	F (A)	
618	Cd 3p$_3$	(34)
619	I 3d$_5$	(11)
632	La (A)	
641	Mn 2p$_3$	(11)
657	Ba (A)	
666	In 3p$_3$	(38)
670	Mn (A)	
672	Xe 3d$_5$	(13)
677	Th 4d$_5$	(37)
684	Cs (A)	
686	F 1s	
710	Fe 2p$_3$	(13)
711	Xe (A)	
715	Sn 3p$_3$	(42)
724	Cs 3d$_5$	(14)
729	Cr (A)	
737	I (A)	
739	U 4d$_5$	(42)
743	O (A)	
765	Te (A)	
768	Sb 3p$_3$	(46)
780	Ba 3d$_5$	(15)
781	Co 2p$_3$	(15)
784	V (A)	
794	Sb (A)	
819	Sn (A)	
822	Te 3p$_3$	(51)
834	La 3d$_5$	(17)
839	Ti (A)	
846	In (A)	
855	Ni 2p$_3$	(18)
863	Ne 1s	
872	Cd (A)	
875	N (A)	
882	Ce 3d$_5$	(18)
897	Ag (A)	
920	Sc (A)	
928	Pd (A)	
930	Pr 3d$_5$	(20)
934	Cu 2p$_3$	(20)
954	Rh (A)	
961	Ca (A)	
970	U (A)	
980	Nd 3d$_5$	(21)
981	Ru (A)	
993	C (A)	
1003	K (A)	
1005	Th (A)	
1022	Zn 2p$_3$	(23)
1035	Ar (A)	
1071	Cl (A)	
1072	Na 1s	
1082	B (A)	
1083	Sm 3d$_5$	(27)
1088	Nb (A)	
1103	S (A)	
1117	Ga 2p$_3$	(27)
1136	Eu 3d$_5$	(30)
1155	Bi (A)	
1162	Pb (A)	
1169	Tl (A)	
1176	Hg (A)	
1184	Au (A)	
1186	Gd 3d$_5$	(33)
1192	Pt (A)	

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.

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Survey spectra: example 1

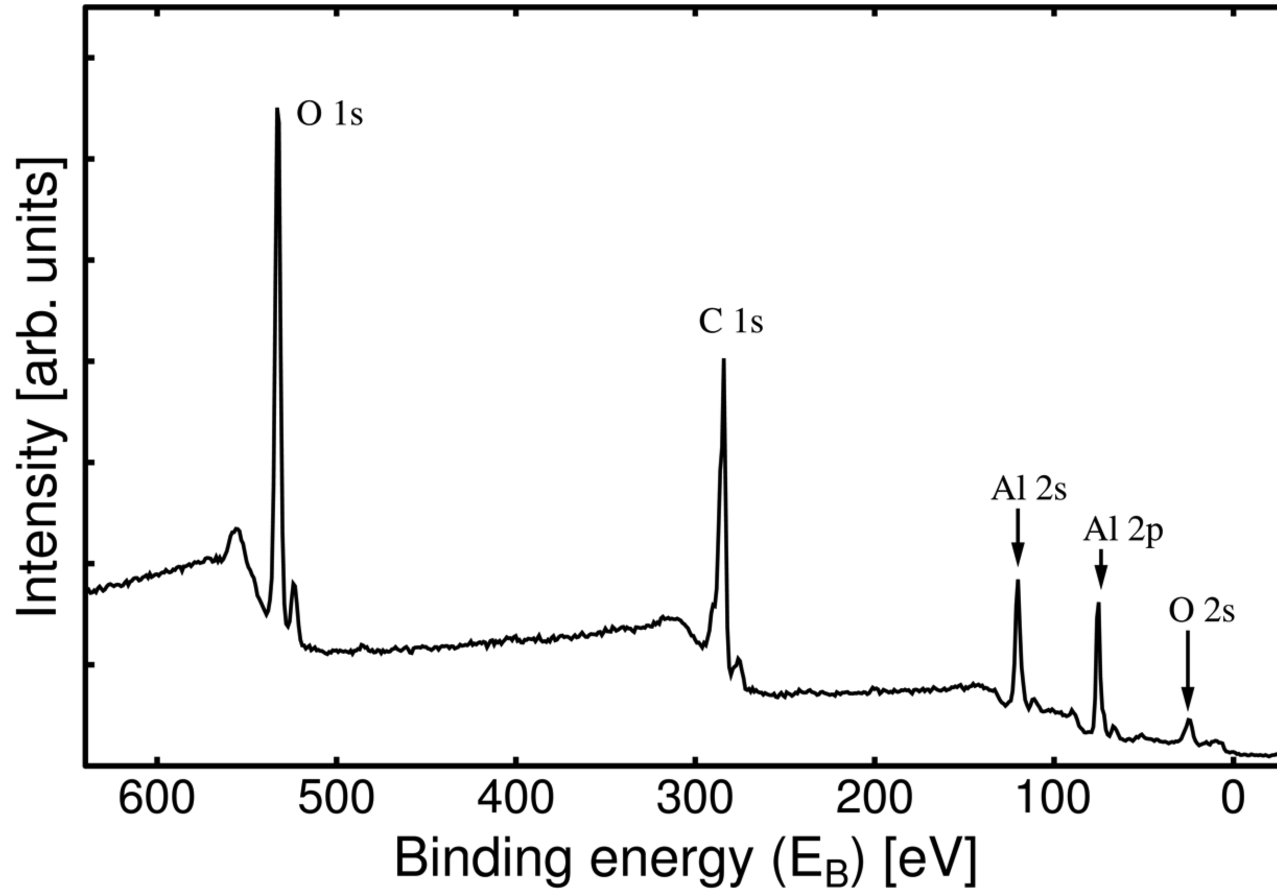

Table 3. Line Positions from Mg X-rays, in

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	F 2s		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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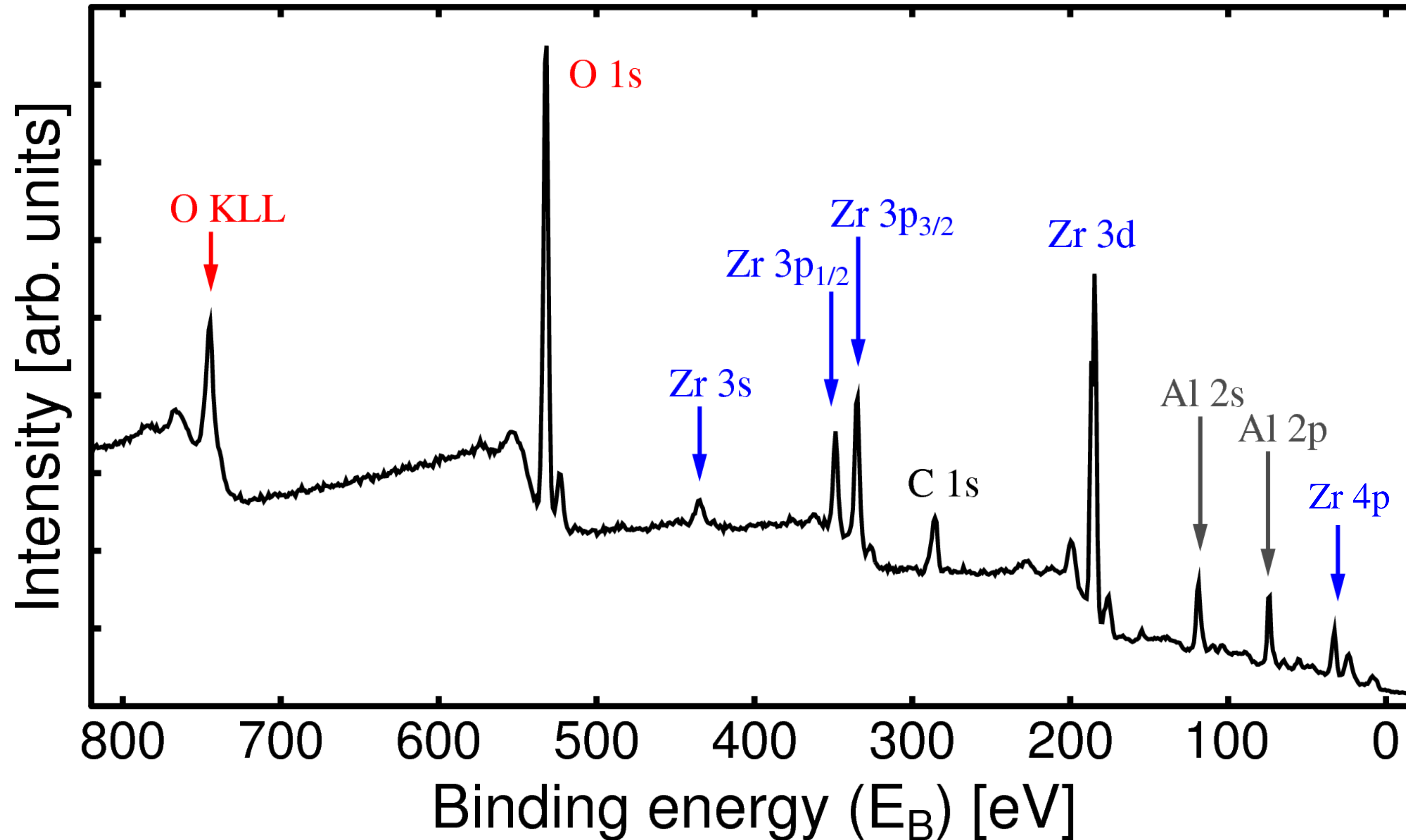
Example 2



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. Surface contamination & charging
   2. Ion beam sputtering & depth profiling
   3. Angle resolved XPS
   4. Small area analysis and imaging

Quantification

- Peak intensity proportional to surface concentration:

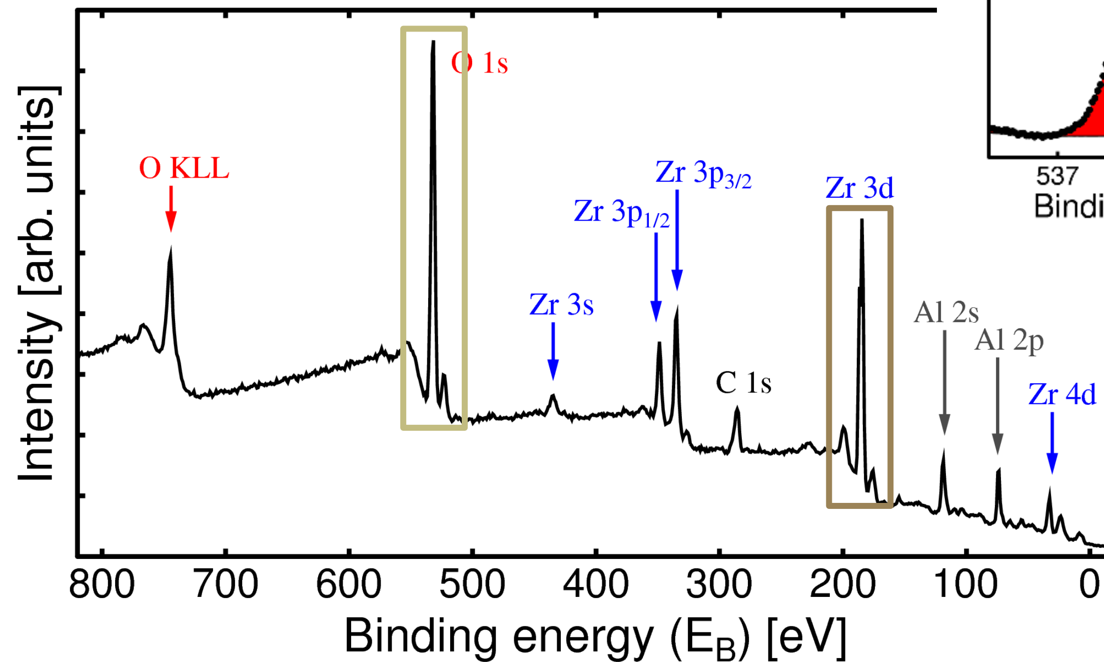
$$I_i \propto N_i a_i$$

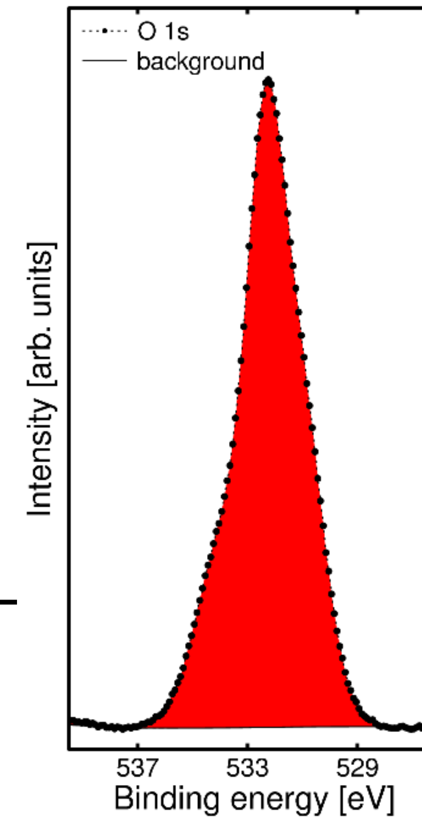
- I_i = peak intensity
- N_i = atomic concentration
- a_i = atomic sensitivity factor

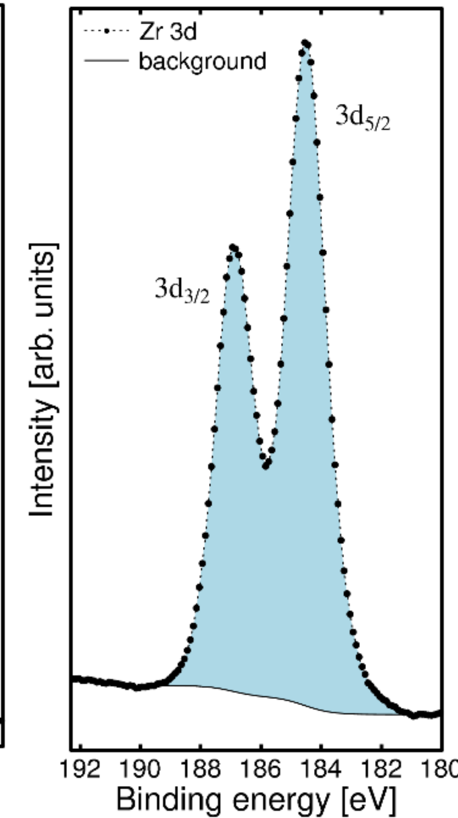
- Stoichiometry can be calculated using intensities and sensitivity factors
- Peak areas are best measure of intensity

For multi-element surface layer:

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







Stoichiometry:

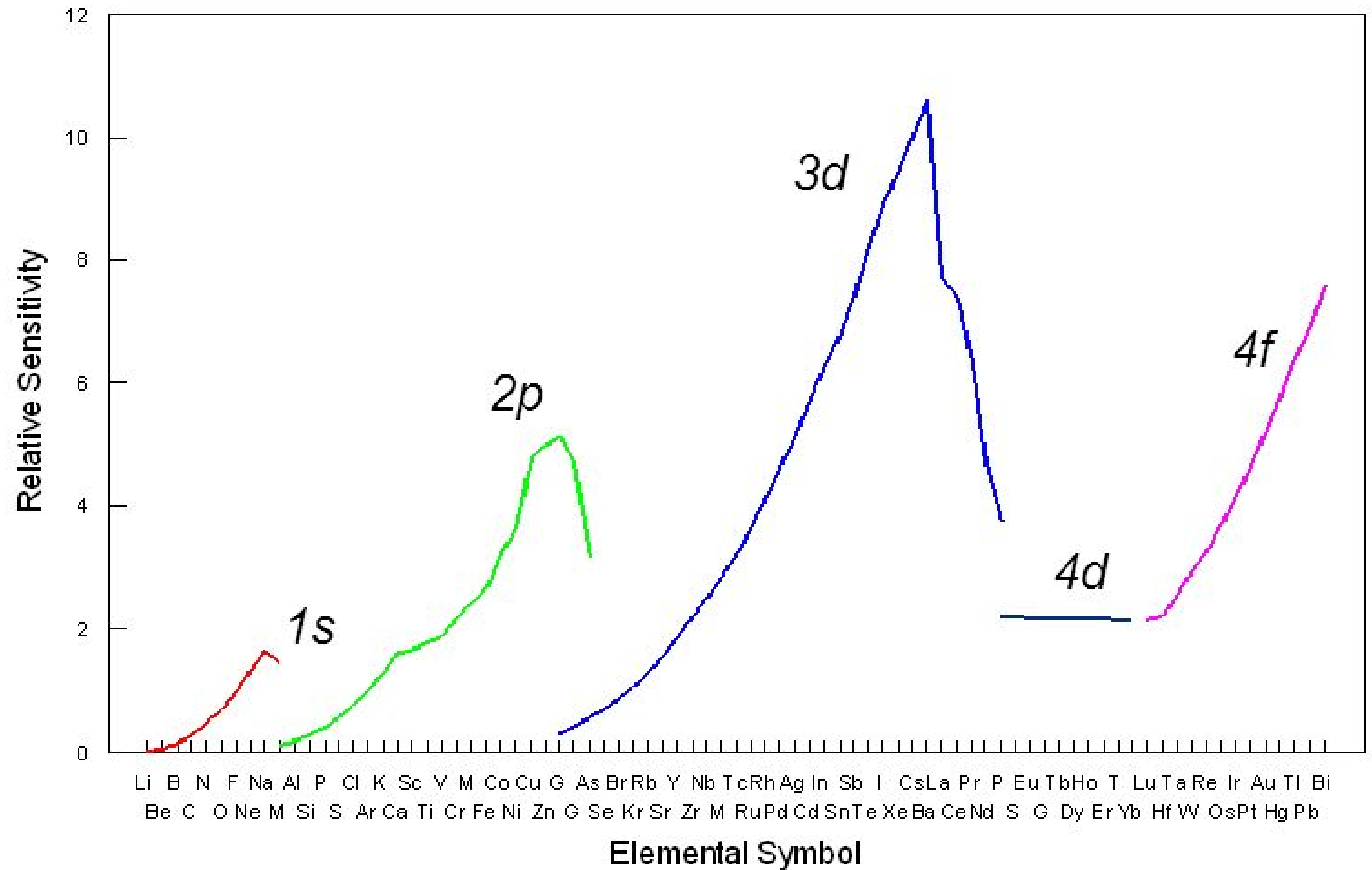
Zr:	12.56 %
Al:	28.10 %
O:	41.46 %
C:	17.77 %

Atomic sensitivity factors (ASF)

- Sensitivity will vary greatly for different elements
- Combination of several factors:

$$a_i = \sigma_i \lambda_i$$

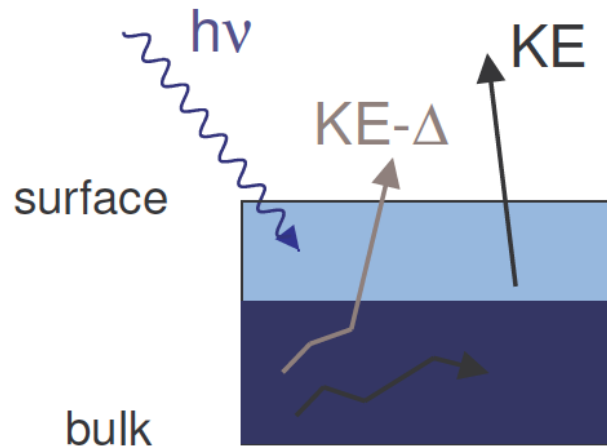
- $\boldsymbol{\sigma_i}$ – Scofield cross-section
  - Probability of X-ray producing photoelectron
- $\boldsymbol{\lambda_i}$ – Inelastic mean free path
  - Probability that the photoelectron will make it to the surface

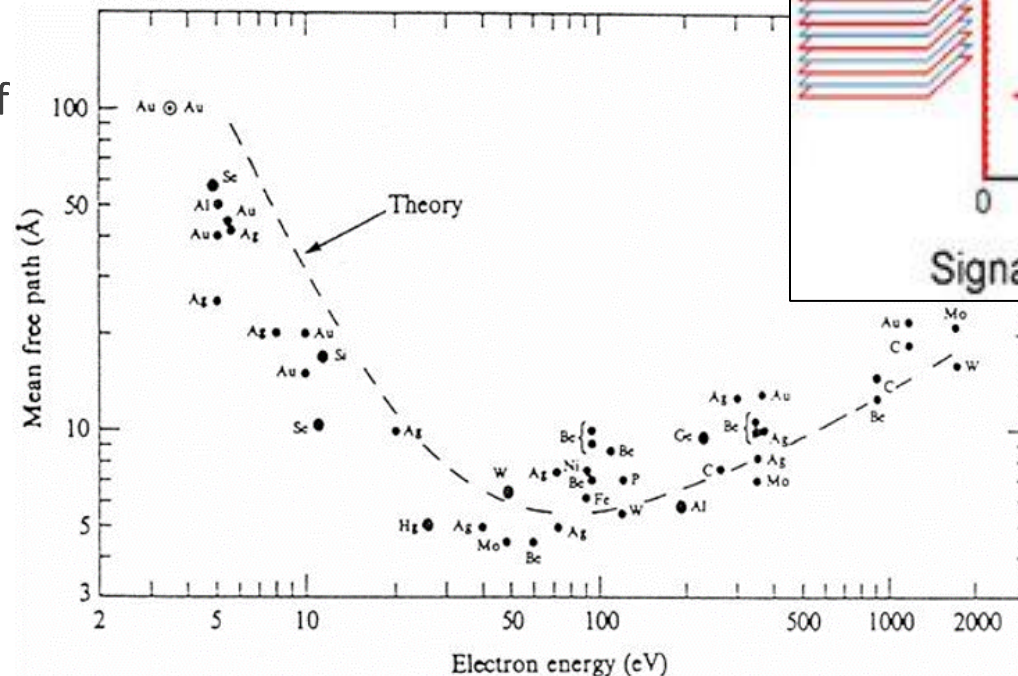


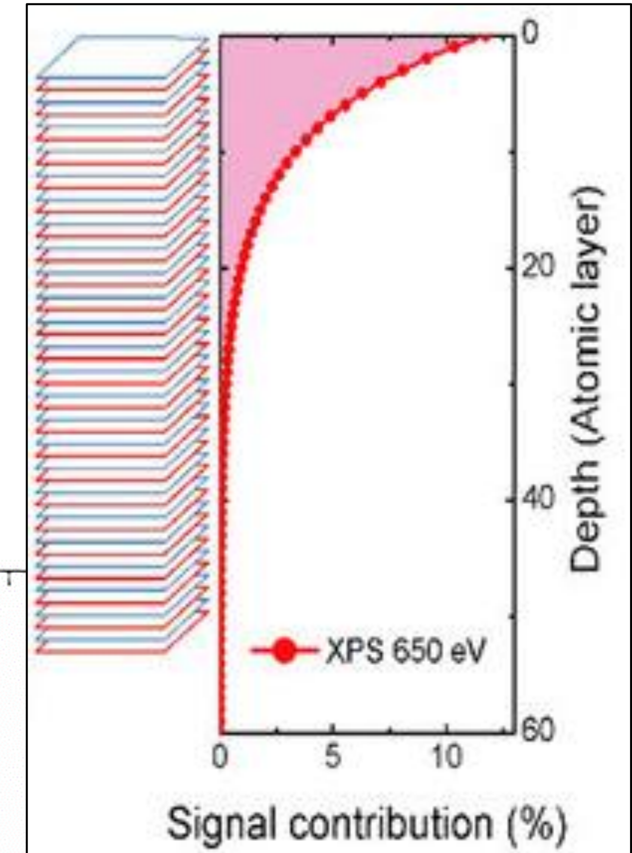
Inelastic mean free path – λ

- Core level peaks only account for a small part of all photoelectrons reaching the analyzer
  - **Number of electrons** (intensity) reaching surface with core level energy **decreases exponentially** with depth of photoionization
- Slight dependence on electron energy and elements in surface
- Most important reason for surface sensitivity of XPS analysis

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

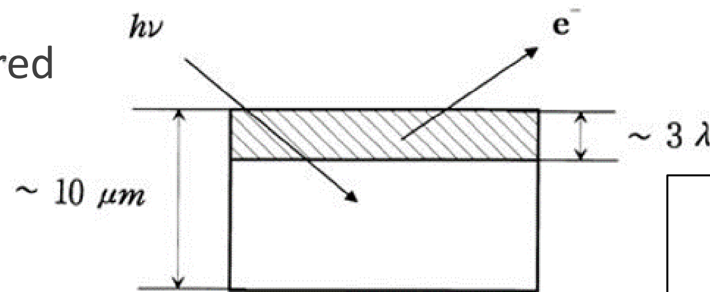


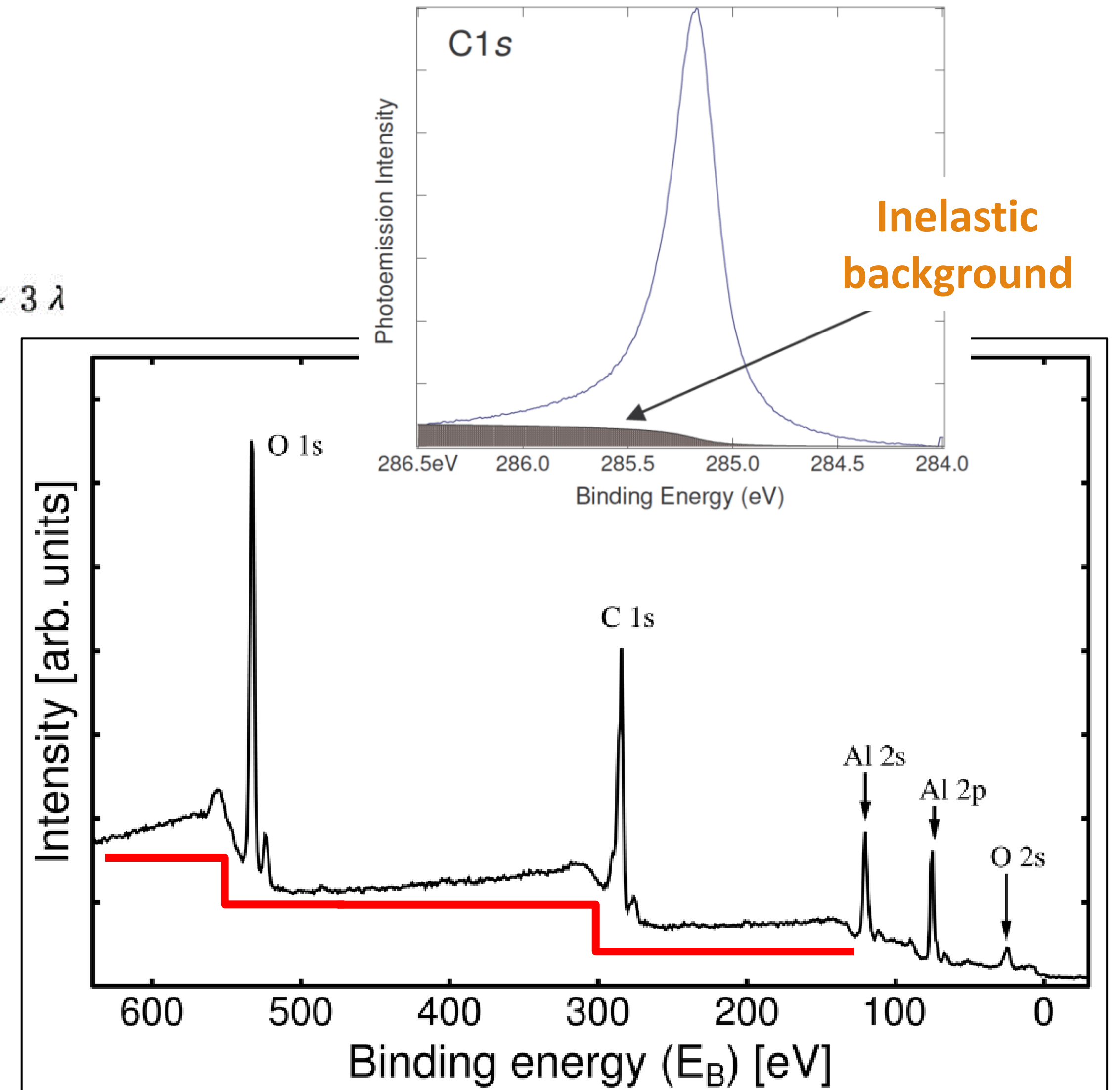




Inelastic background

- 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 –)

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

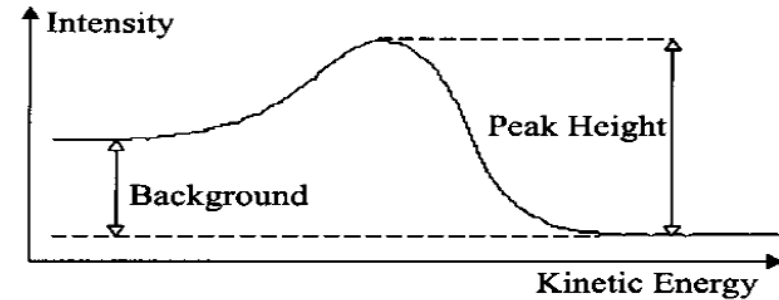
Background removal

How is peak intensity measured?

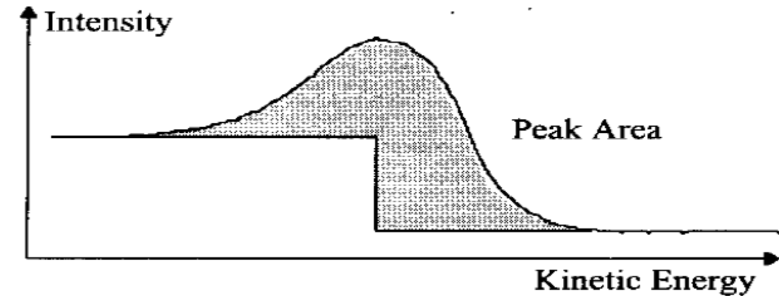
- Peak heights can sometimes be used
- Result not very good – shapes not always the same

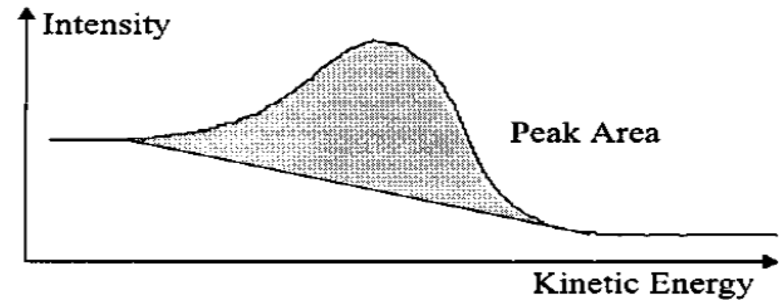
- **Area** is almost always used
- But background is not constant (nor linear) near peak
- **Shirley** background is most commonly used

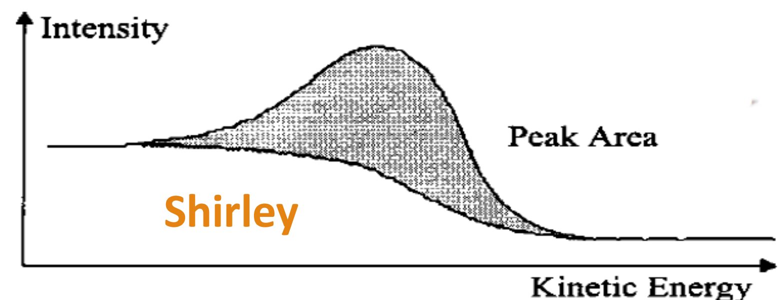
- With ASF’s: accuracy better than 15 %
- With standard samples on same instrument: ~5 %
- Reproducibility (precision) better than 2 %



Worst







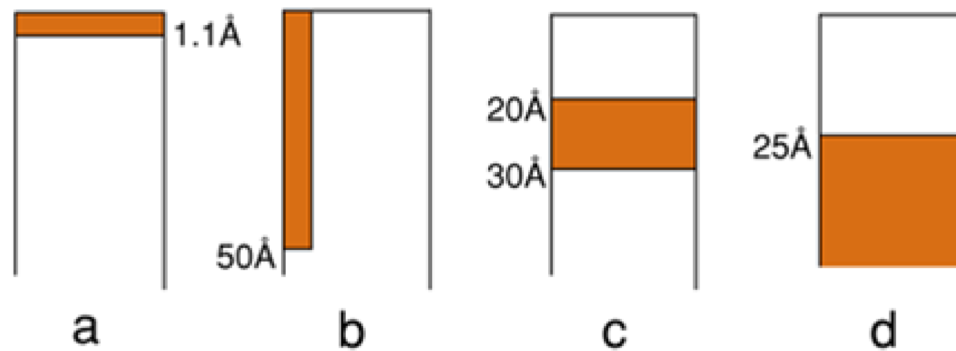
Best

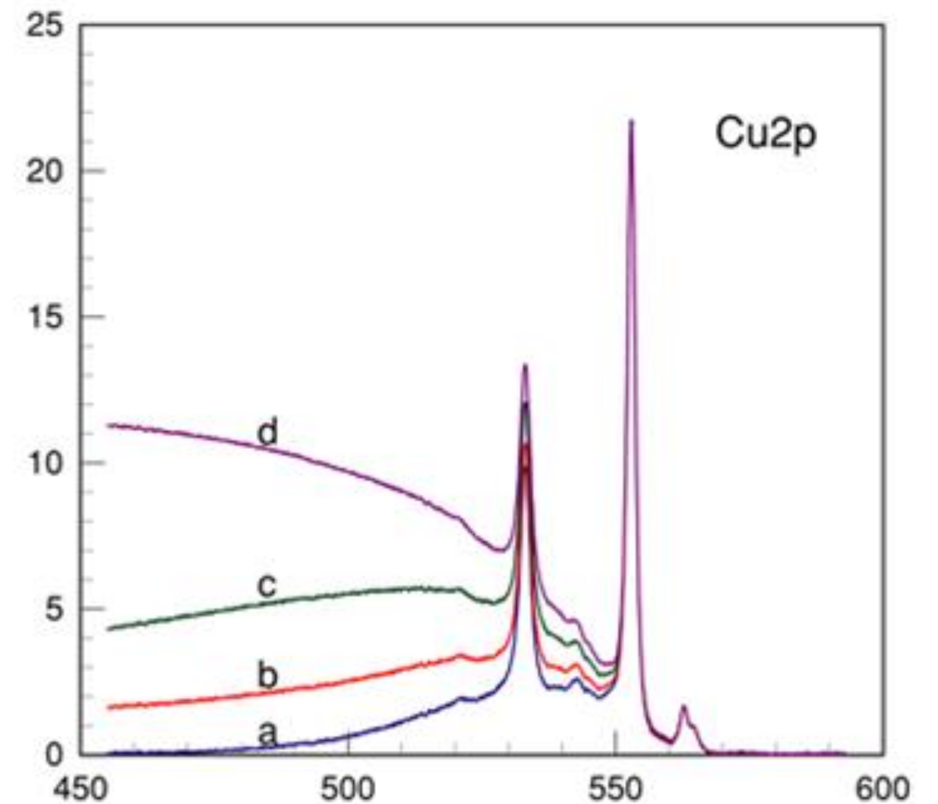
Surface morphologies

Traditional XPS quantification assumes:

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

- Depending on the depth and lateral distribution of emitting atoms the **background can change dramatically**





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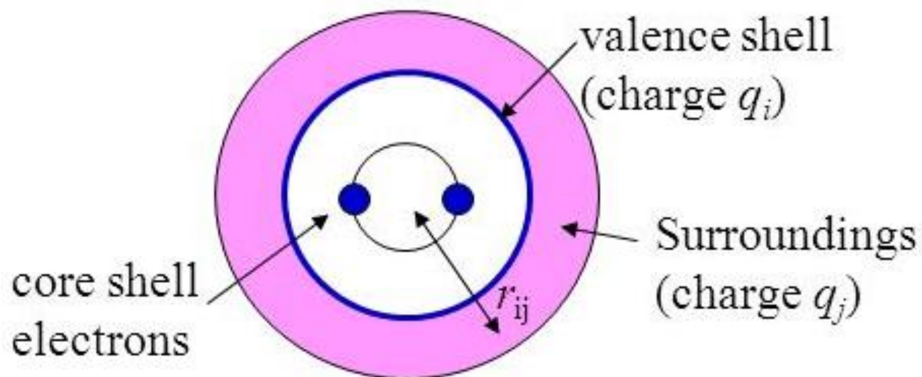
Chemical effect in XPS

Chemical shift:

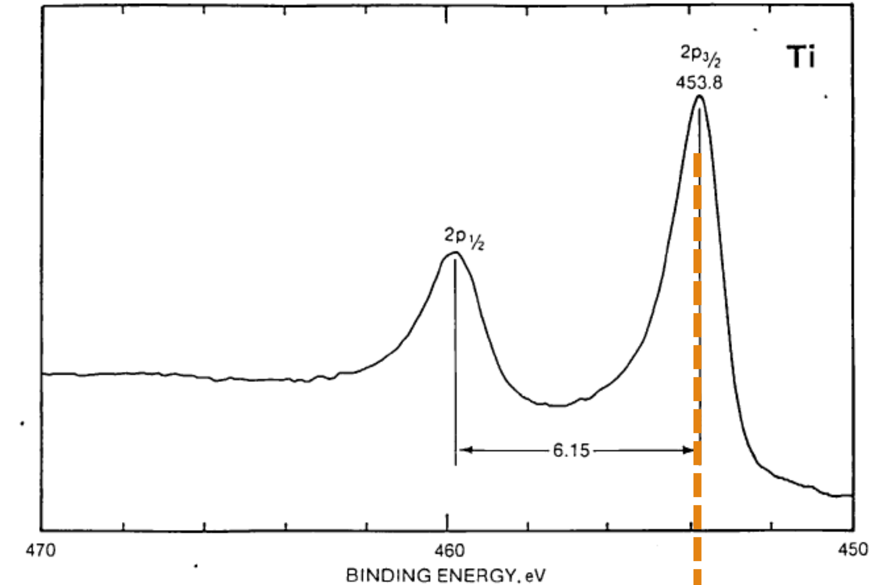
- Changes in the chemical bonding of an element will cause changes in the binding energy of core electrons

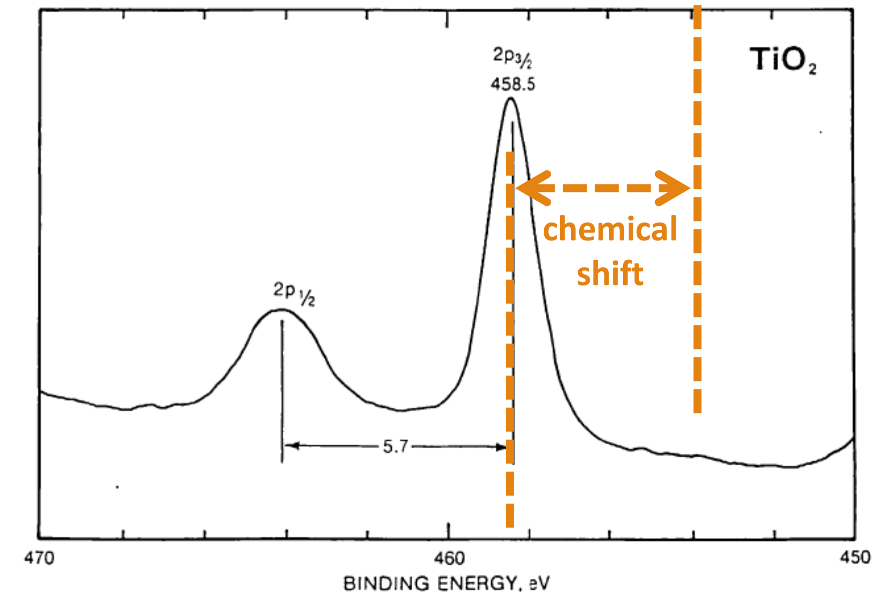
Core binding energies are determined by:

- 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

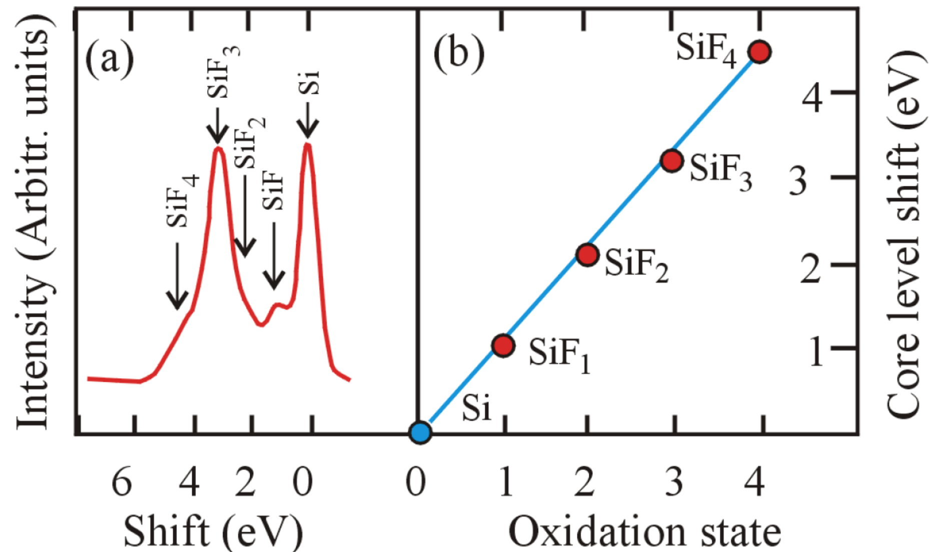


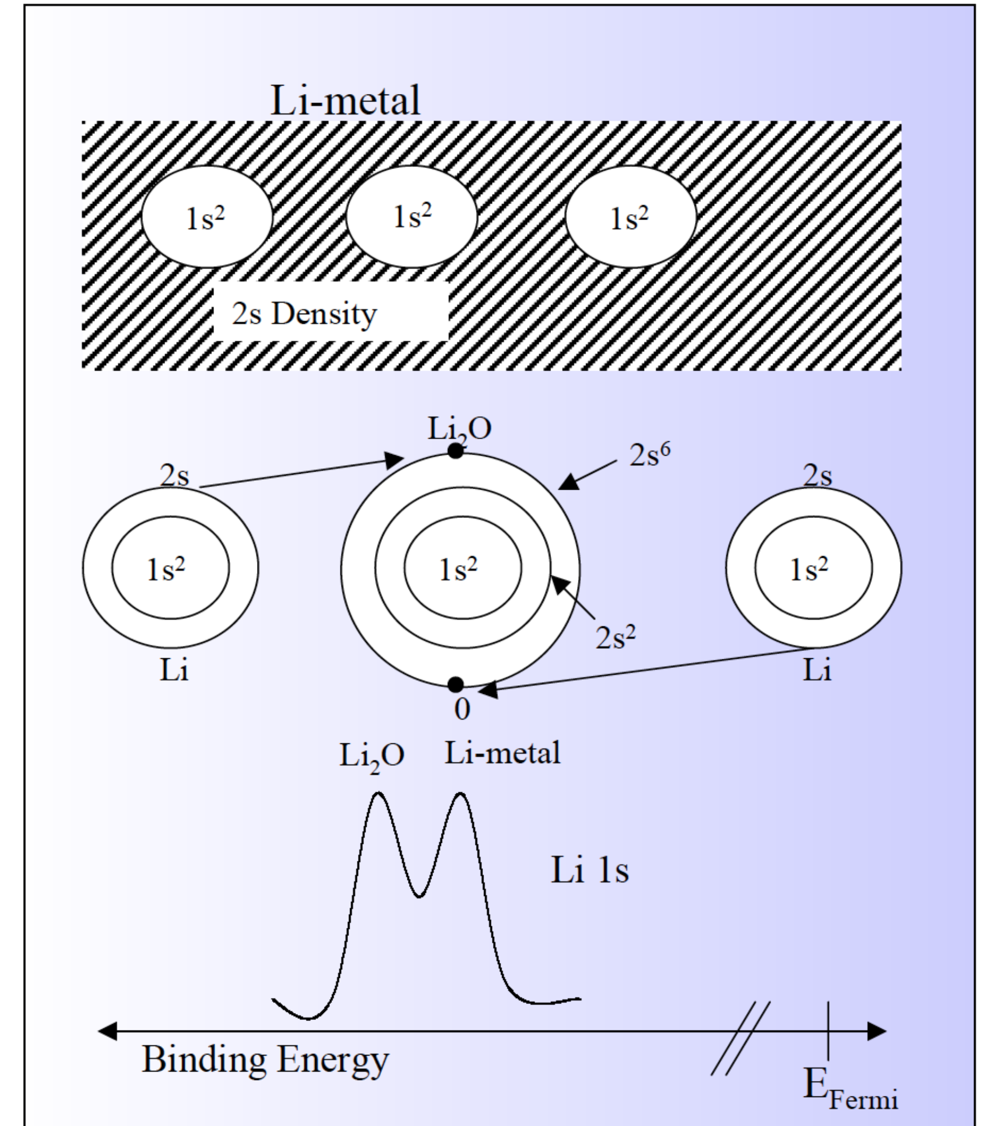


Chemical shift

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!





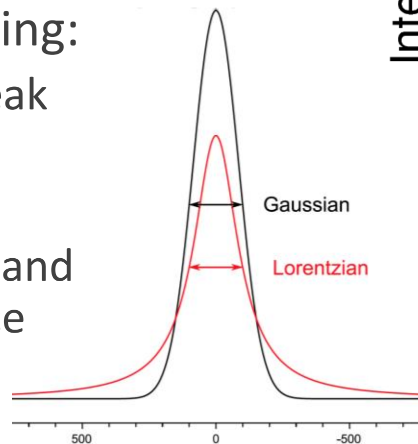
Peak fitting

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:

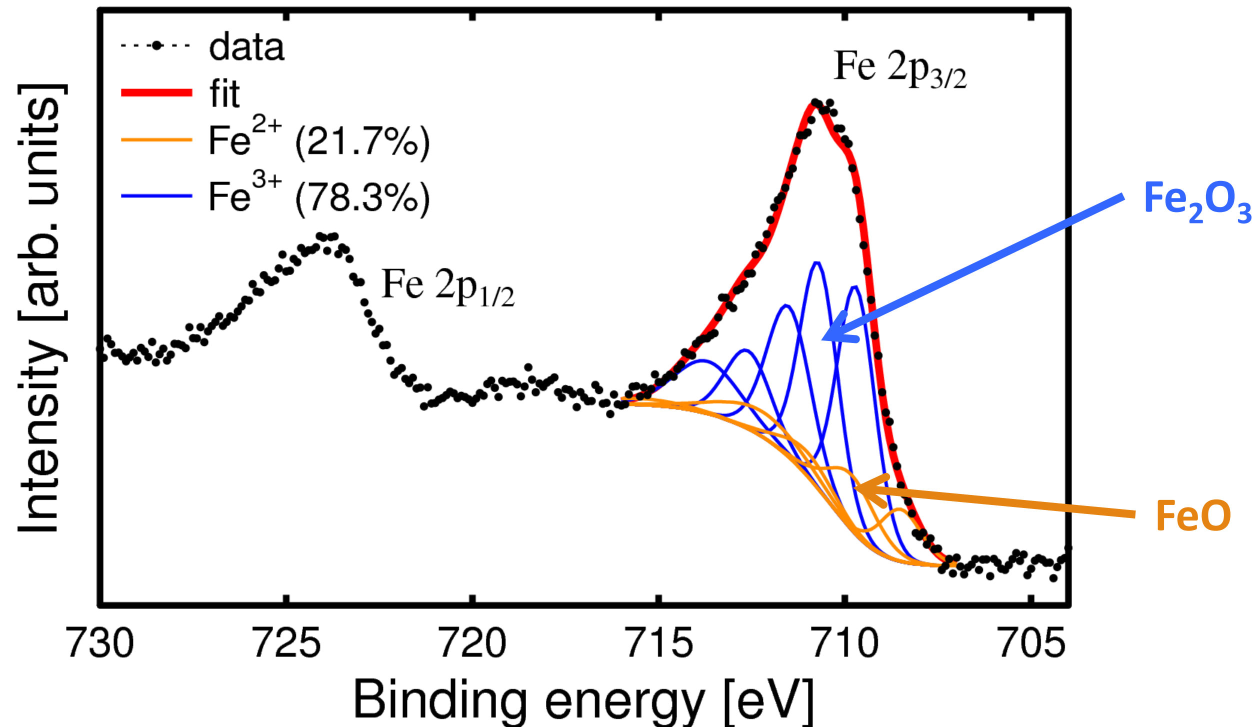
- Fixed ΔE_b and peak area ratios for doublets
- Known energies and FWHM (reference data)



Complex bonding

Complex bonding environments are typical for many materials

- A single compound will give an asymmetric peak shape
- Several GL peaks have to be fitted in order to get reproducibility



Iron, Fe Atomic Number 26

COMPOUND	$2p_{3/2}$ BINDING ENERGY, eV (705 – 710 – 715)	REF.
Fe		Φ
Fe_2B		MEC
FeB		MEC
FeS_2		B4
$Fe(C_5H_5)_2$		CDH
$Fe(C_5H_5)_2I_3$		CDH
$Zn_2Fe(CN)_6$		CSC
$K_4Fe(CN)_6$		CSC
$K_4Fe(CN)_6$		V
$Na_3Fe(CN)_5N_2$		YN2
$Na_2Fe(CN)_5NO$		YN2
$K_3Fe(CN)_6$		V
$Fe_2P_2S_6$		B4
$KFeS_2$		B4
FeS		CSC
$Fe(CO)_5$		BC1
$Fe(CO)_2(NO)_2$		BC1
$Fe(C_5H_5)(CO)_3BPh_4$		CDH
FeO		MZ
FeO		AC2
Fe_2O_3		Φ
Fe_2O_3		MZ
Fe_2O_3		AC2
FeOOH		AC2
FeOOH		MZ
Fe_3O_4		AC2
$NaFeO_2$		AC2
$NiFe_2O_4$		MZ
$FeBr_2$		CSC
$FeBr_3$		CSC
$FeCl_2$		CSC
$FeCl_3$		CSC
FeF_2		CSC
FeF_3		CSC
K_3FeF_6		CSC

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

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

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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

Step 2. Select an element for binding energy:

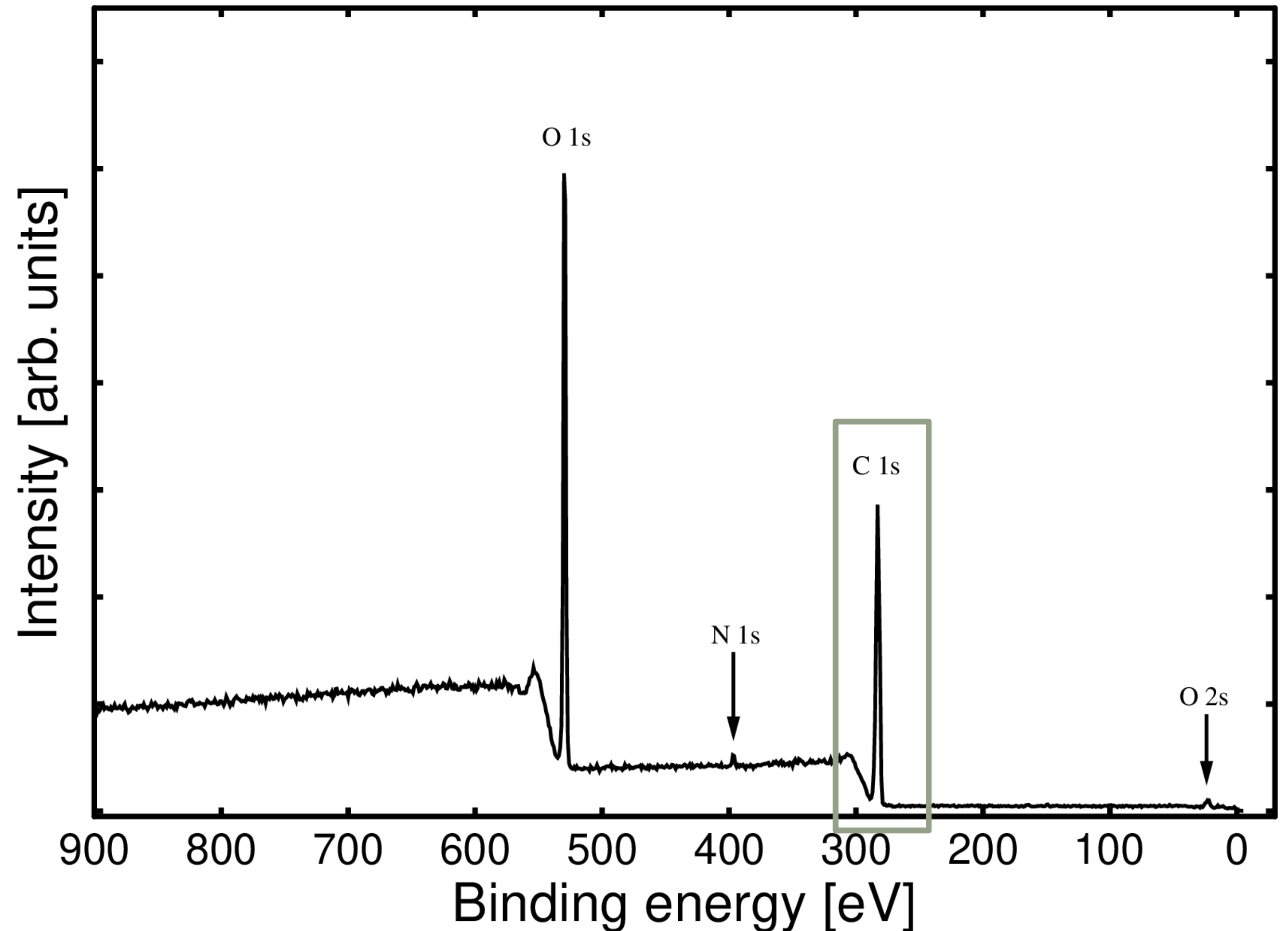
IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
^{1}H																	^{2}He
^{3}Li	^{4}Be				Metals / Transition metals / Metalloids / Nonmetals							^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
^{11}Na	^{12}Mg											^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
^{19}K	^{20}Ca	^{21}Sc	^{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	^{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

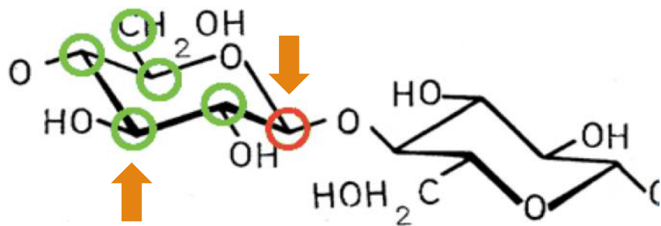
- Zooming in on individual peaks will give you a lot more information!



Practical example – Cellulose

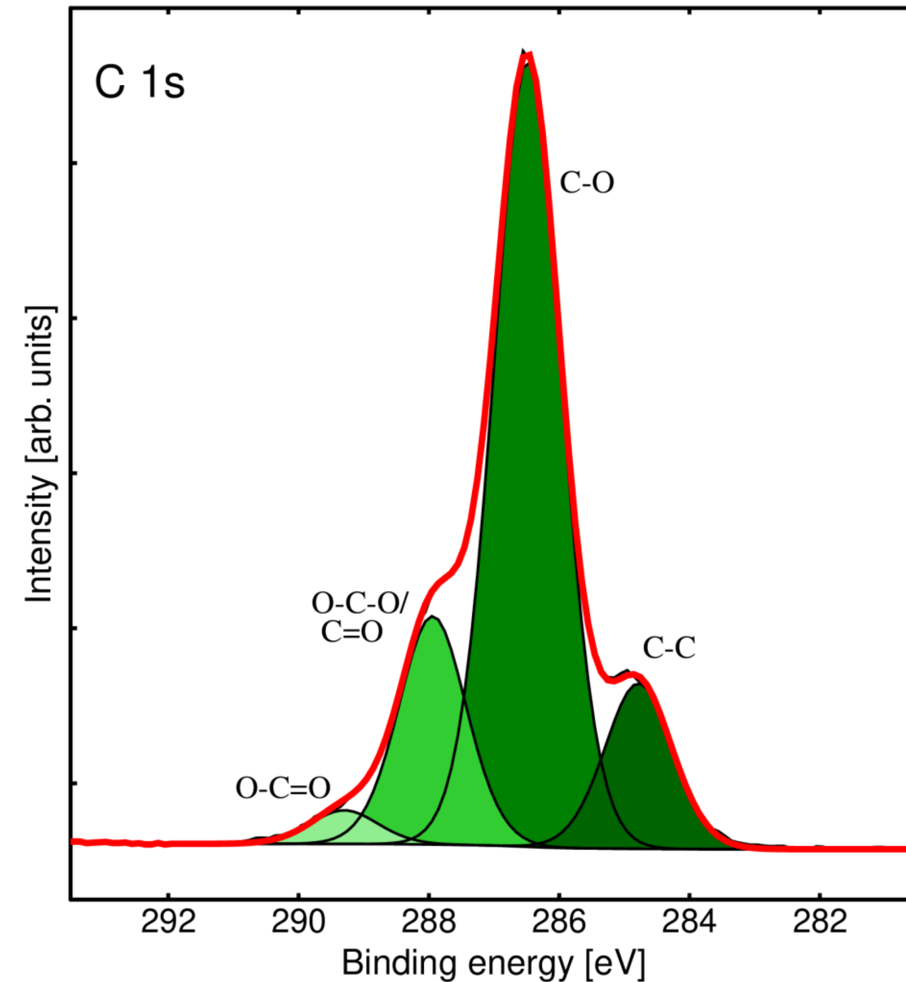
High resolution spectra:

- C 1s
- More components than a single Gaussian



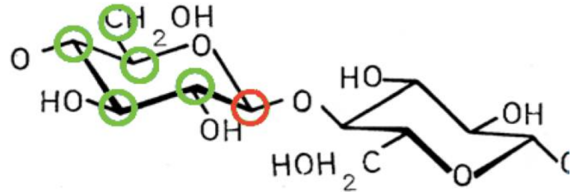
Understanding the material greatly improves the analysis

- Locating peaks
- Assigning peak energies



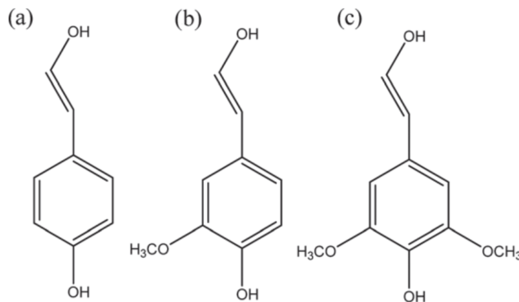
Cellulose vs lignin

Cellulose:

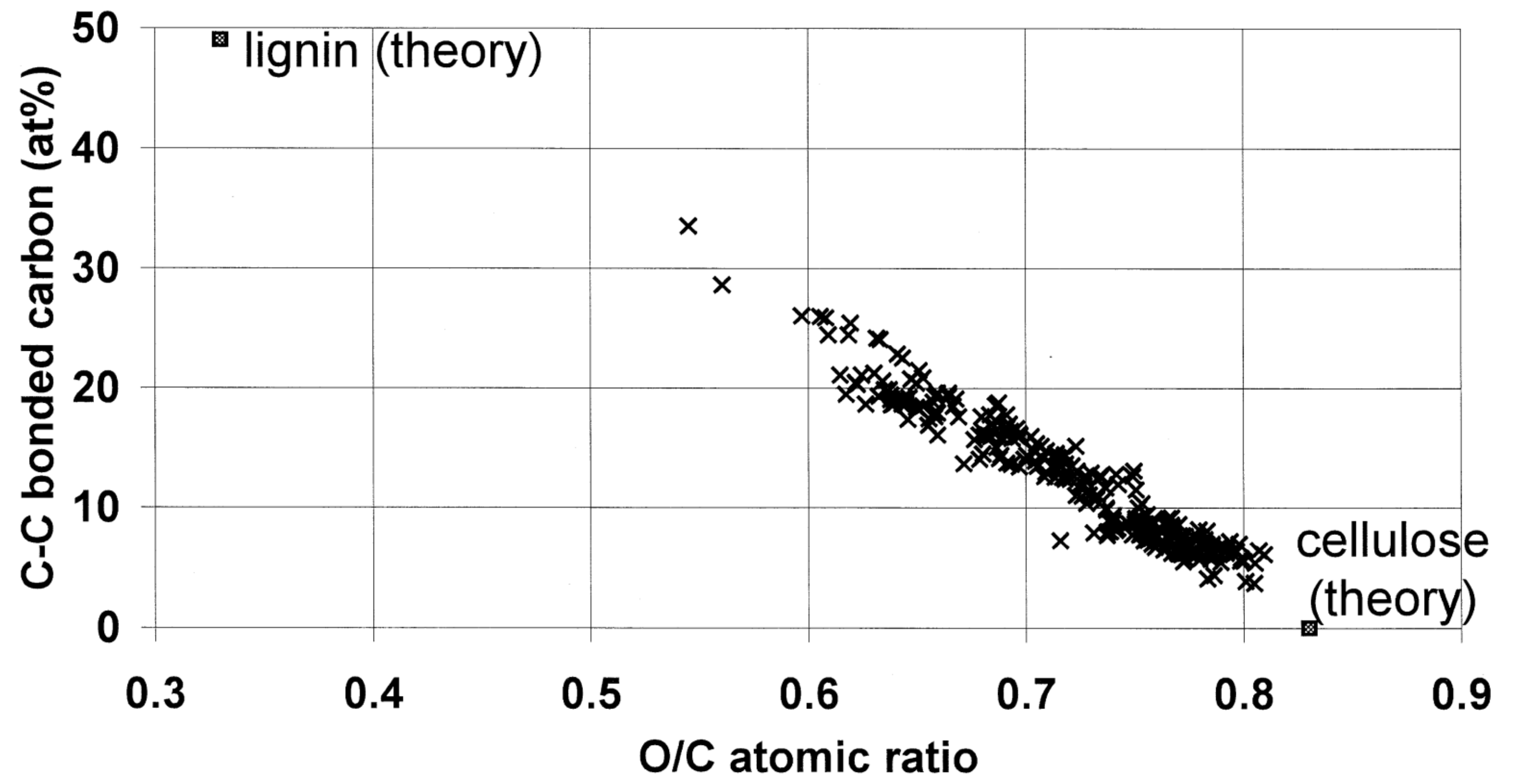


- O/C atomic ratio: 0.83
- C-C at.%: 0 %

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

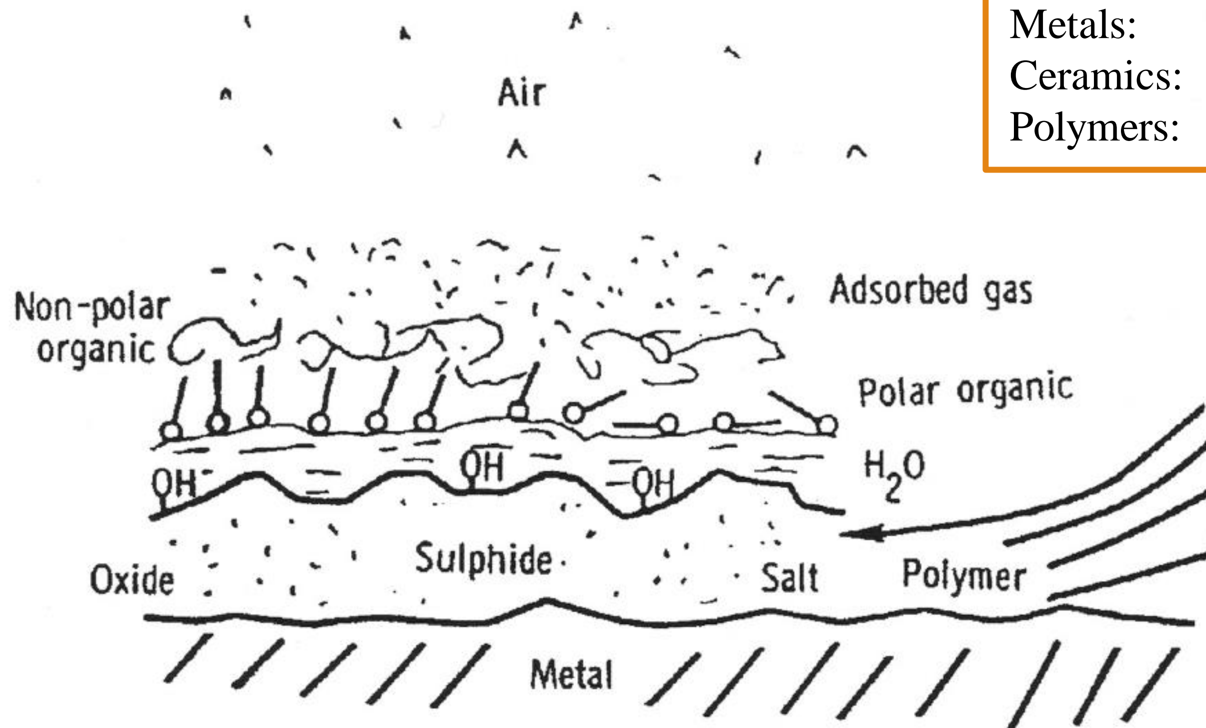
XPS

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. Surface contamination & charging
   2. Ion beam sputtering & depth profiling
   3. Angle resolved XPS
   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

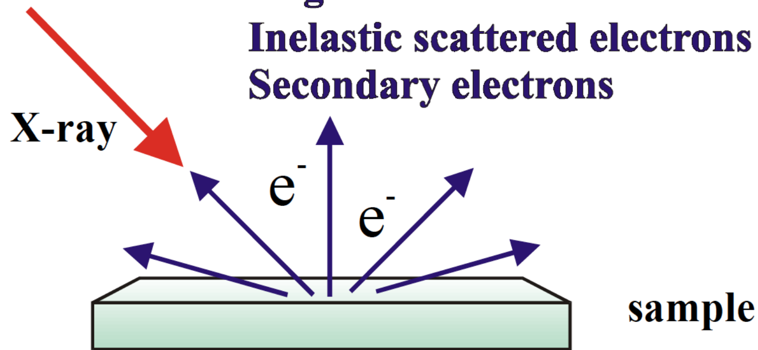
Carbon contamination
- Exists on all samples that have not been prepared in vacuum!

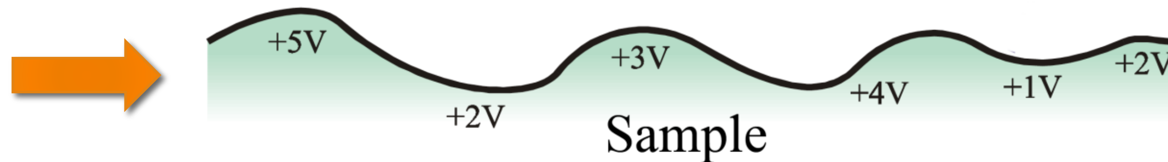
Sources:
- Organic molecules in air
- *In situ:*
  - Contamination due to pumping oil
  - Desorption from other samples in chamber

Surface charging

Electrons are continuously removed from the surface of the sample:

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



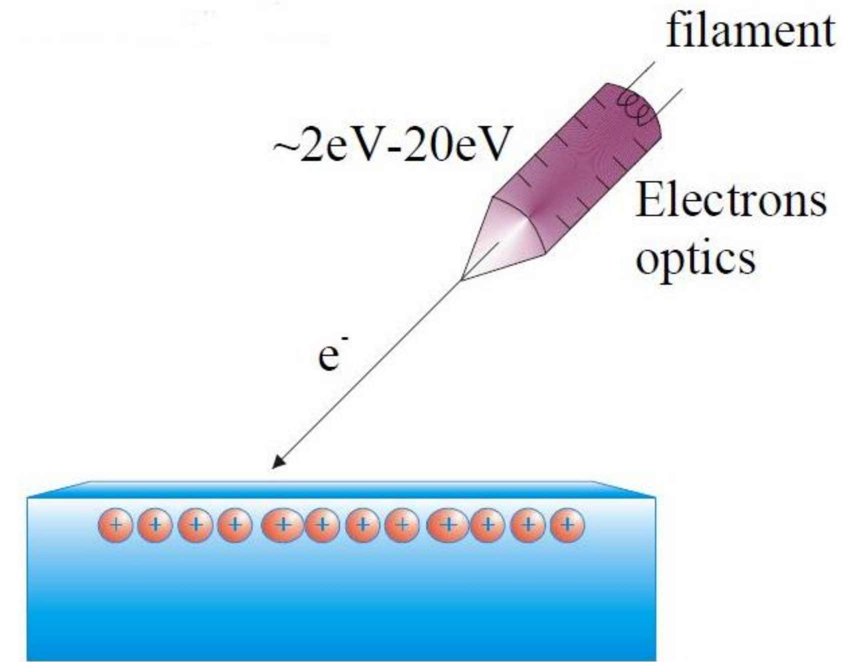


Non-uniform surface charging:

- 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

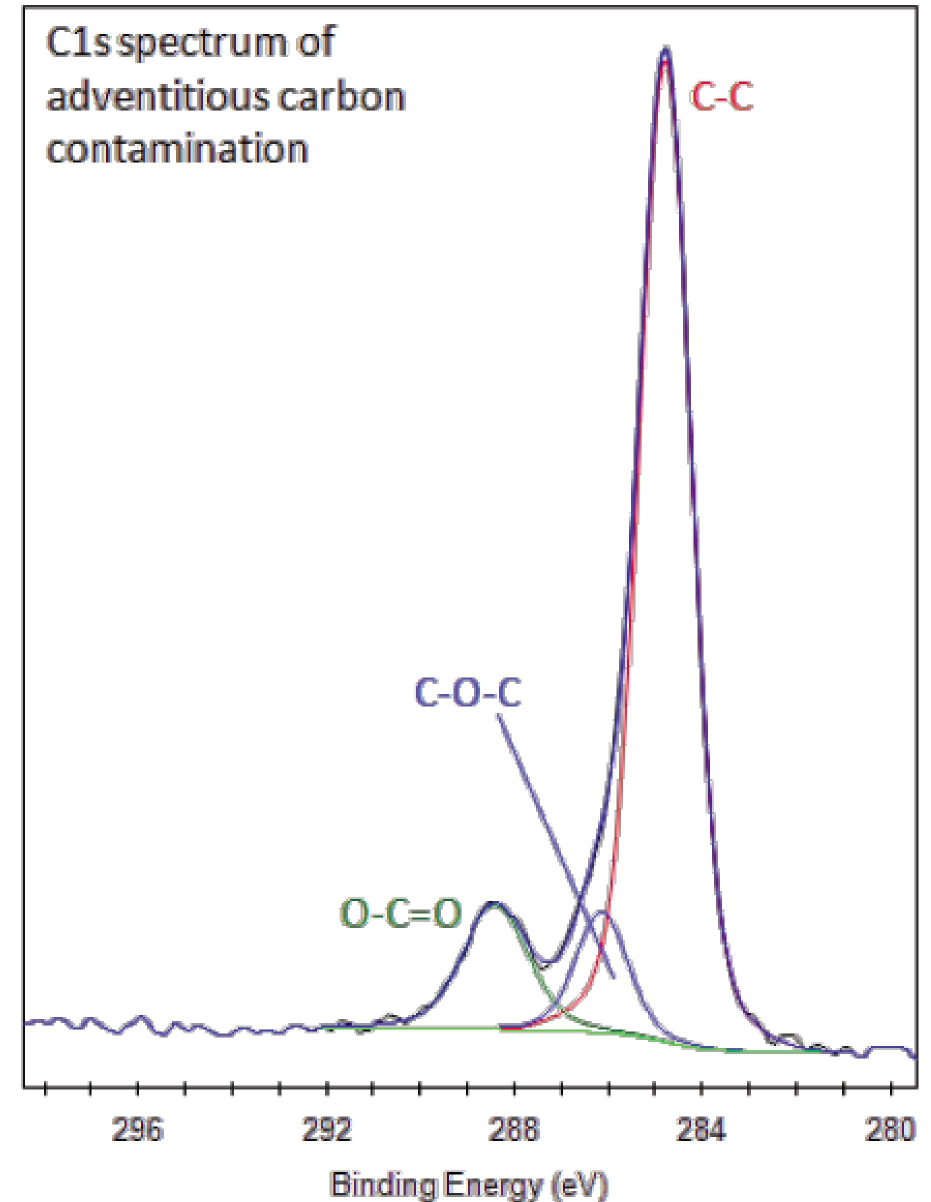
Adventitious carbon:

- C-C bonding in C 1s spectrum: 284.8 eV
- **NOTE:** Polymer scientist sometimes use 285.0 eV

Gold surface:

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

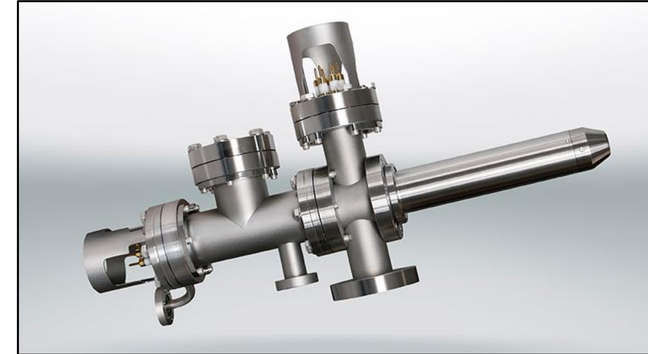
Other peaks with known position in sample



Ion beam sputtering

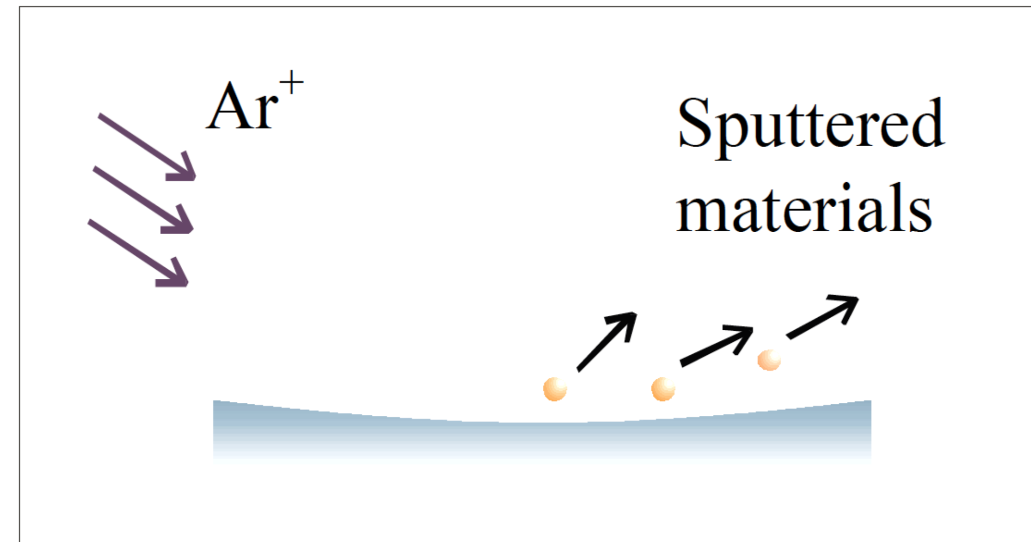
Ar-ion guns are often included in XPS-analysis chambers

- Ion energies usually 0-10 keV



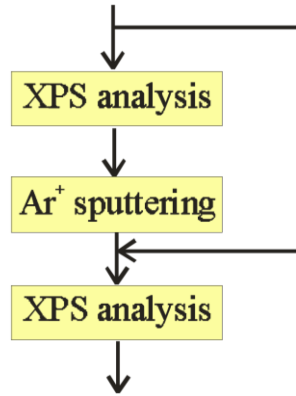
Removal of surface layers:

- Surface contamination
- Oxide removal
- Depth analysis



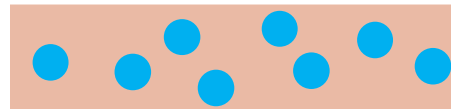
- NOTE: May affect surface chemistry and composition of materials
- Not always a good idea for XPS

Depth profiling

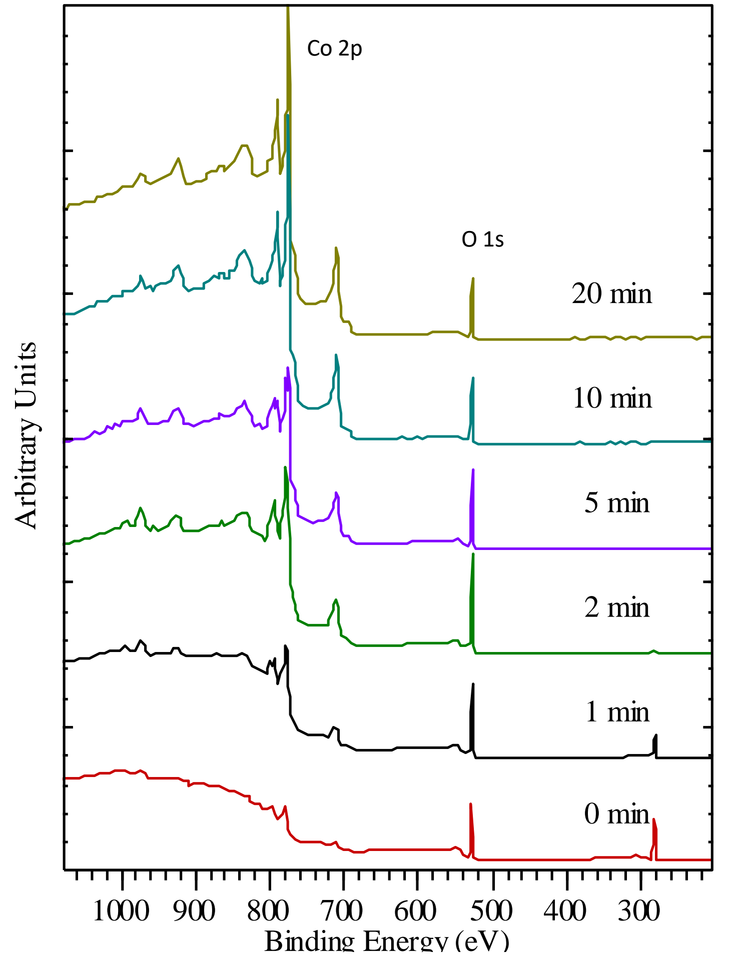


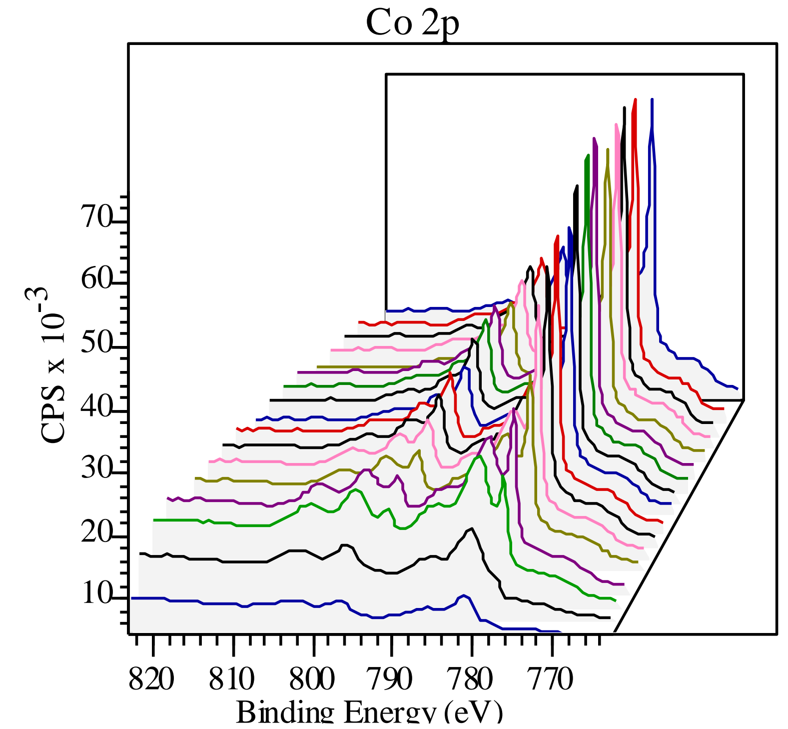
Example:

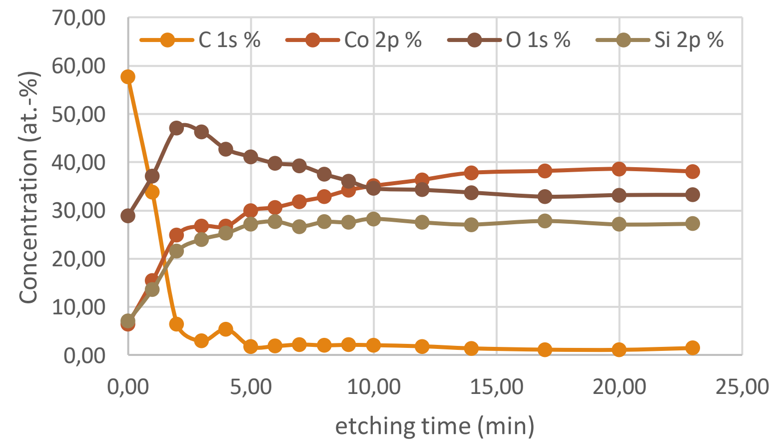
- SiO_x + embedded Co clusters

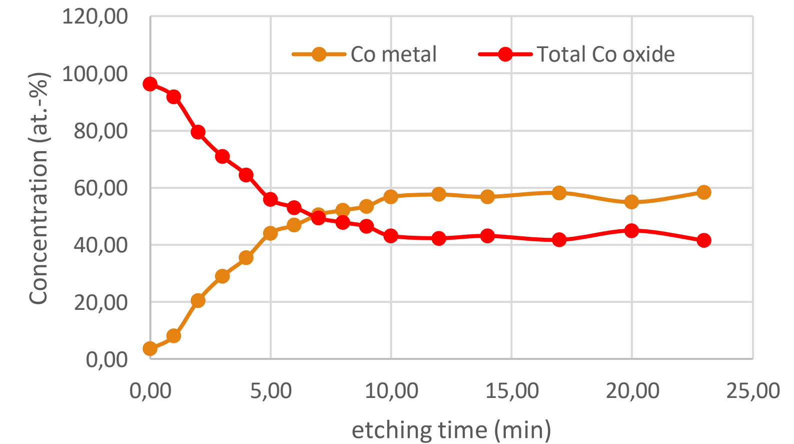


- Elemental depth profile
- Oxidation level vs depth!









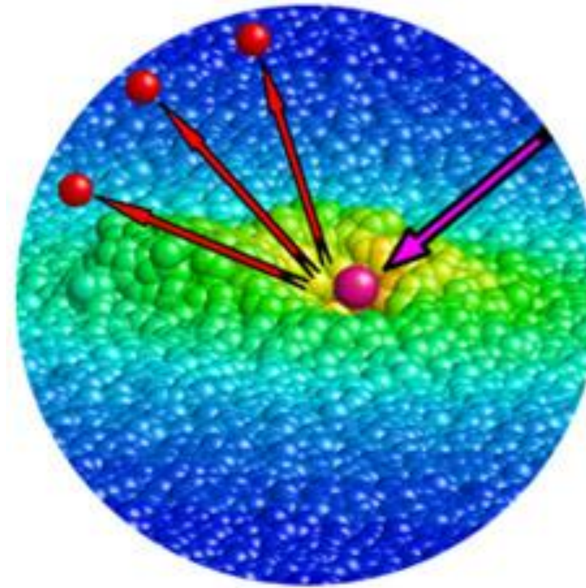
Radiation induced effects

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

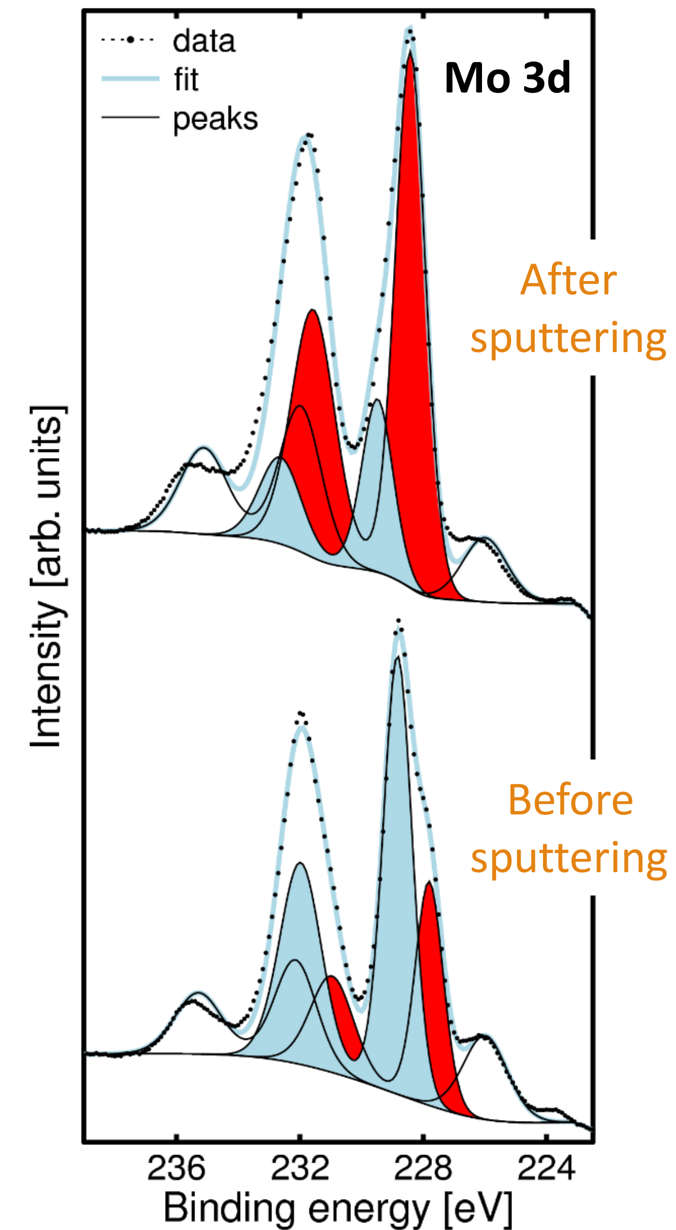
- Non-uniform ion beam intensity/impurity ions
- Re-deposition of sputtered species
- Adsorption of residual gases

- 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

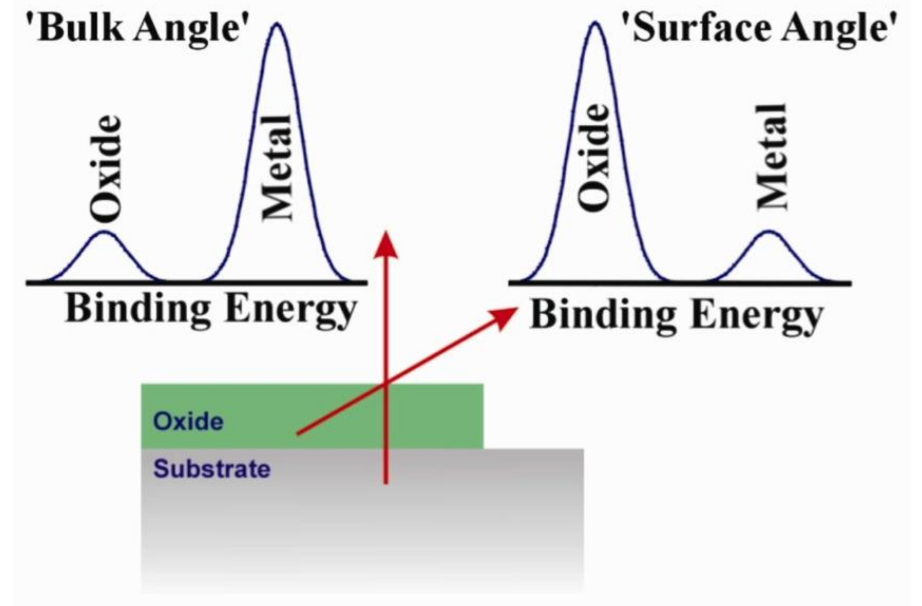


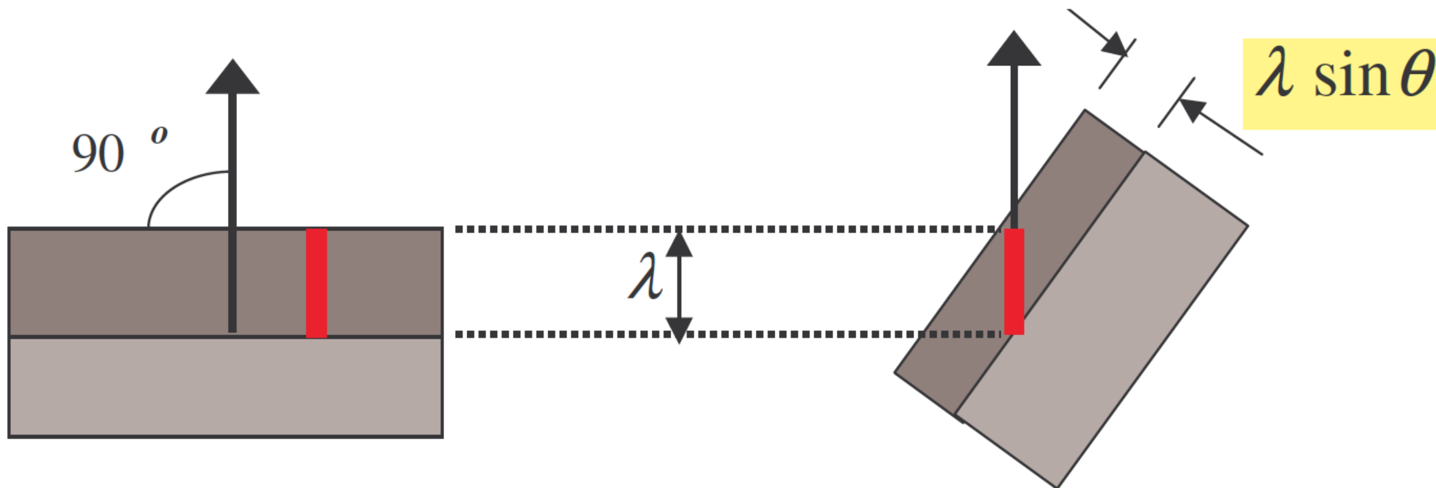
Angle resolved XPS

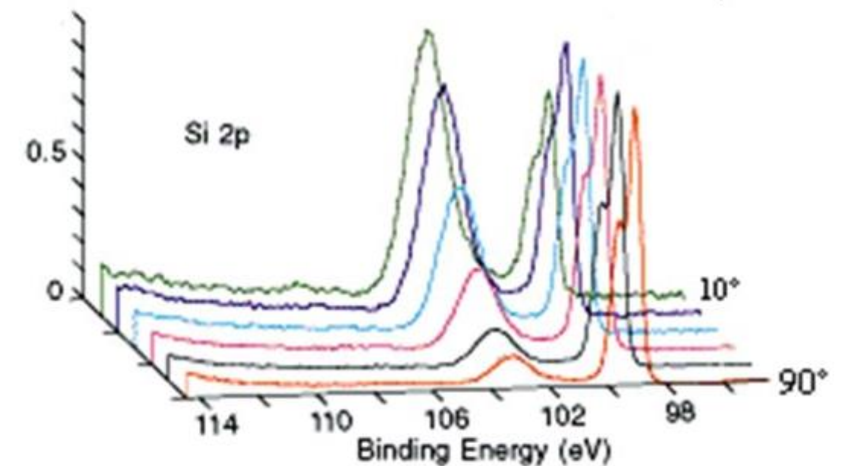
Alternative means for depth profiling:

- 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!







Imaging methods

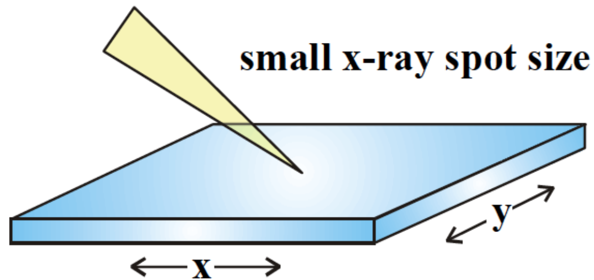


Image:

- Positions *x* and *y* scanned
- *x*,*y*-position vs photoelectron intensity
- Resolution: ~50 µm

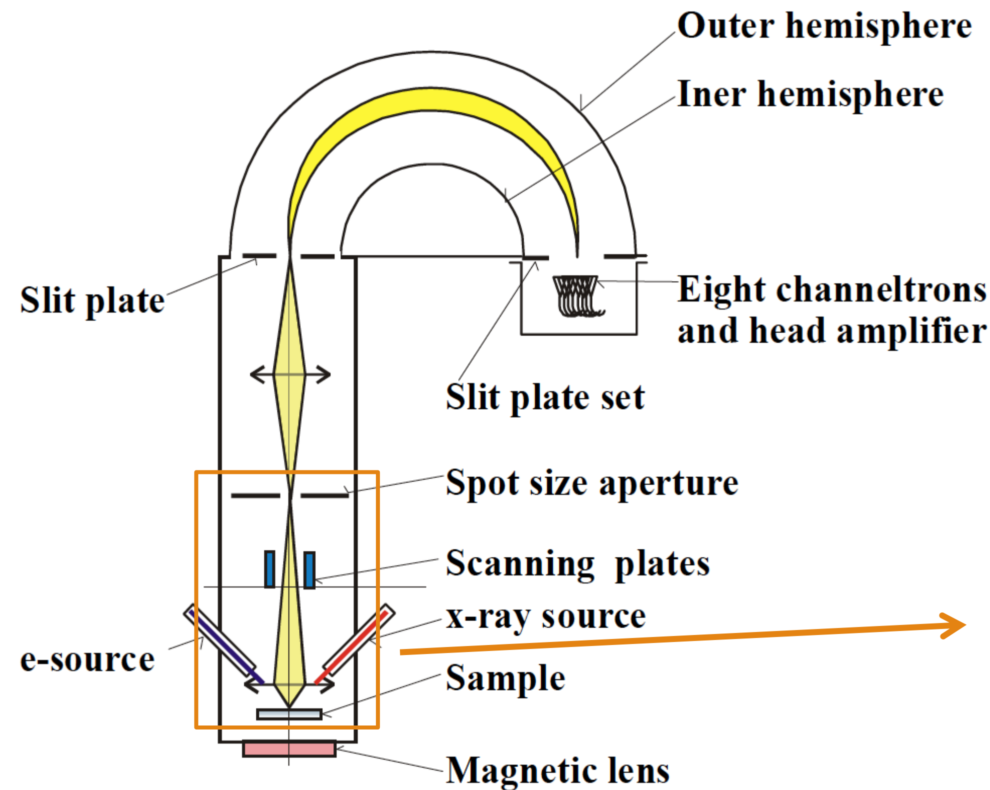
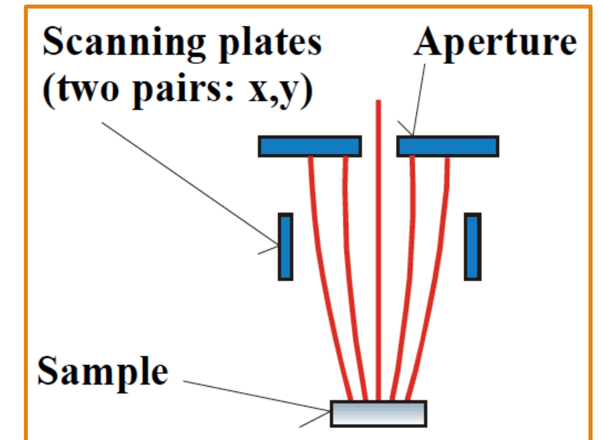


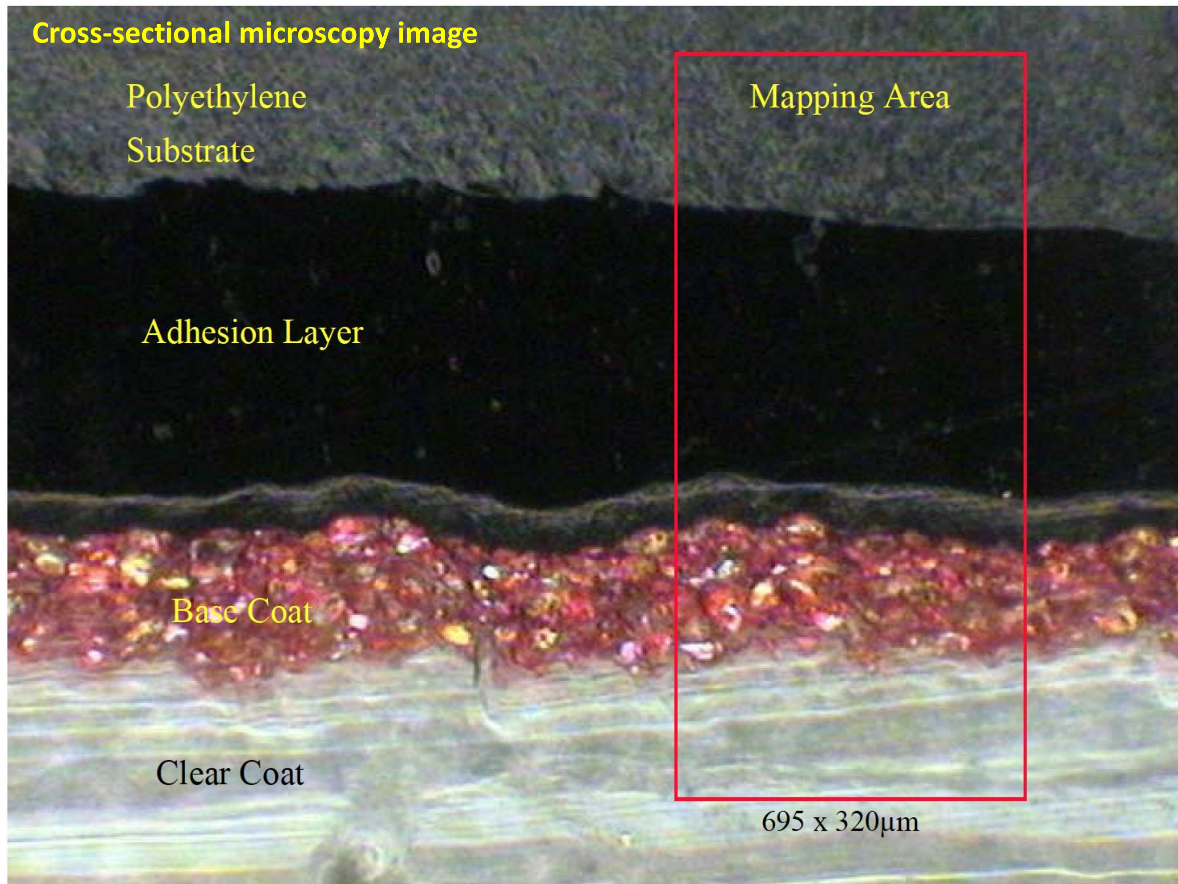
Image:

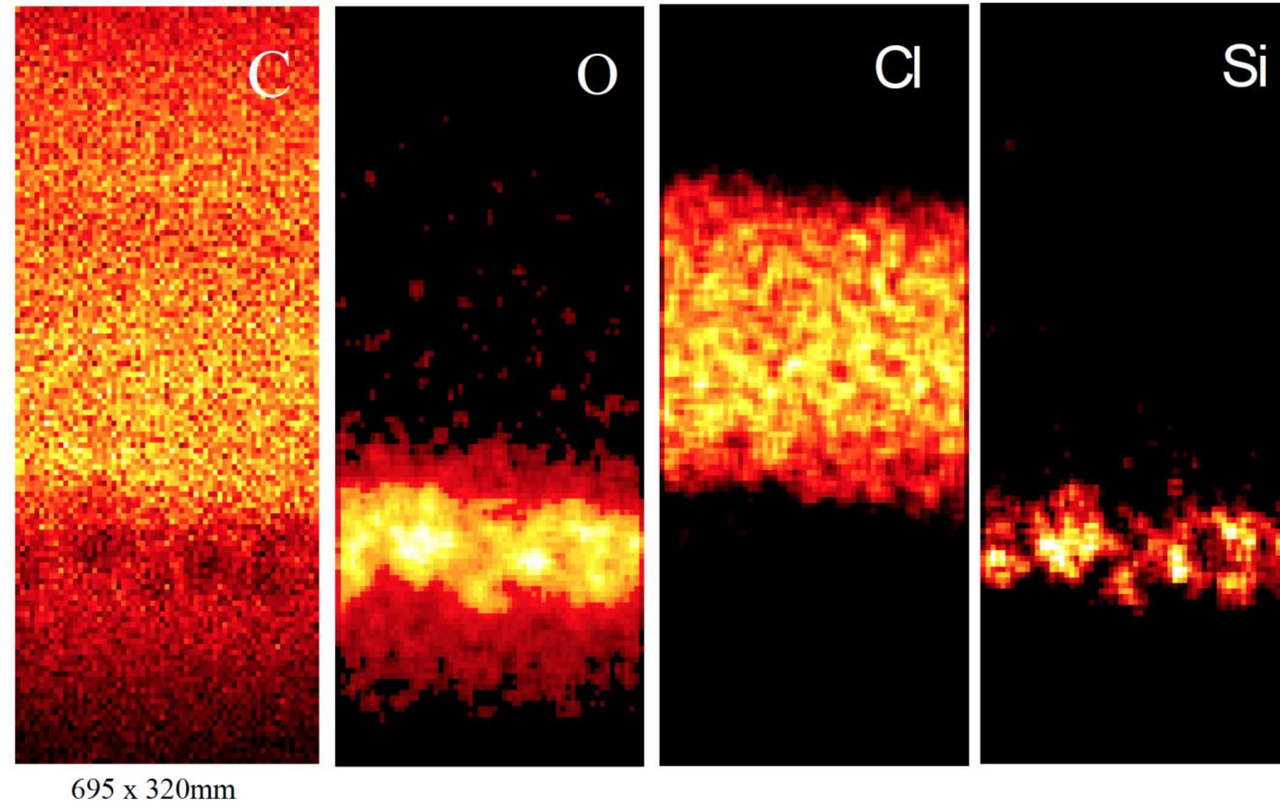
- Voltages V_x and V_y scanned
- Photoelectron intensity collected from different points in time sequence
- Resolution: ~10 µm



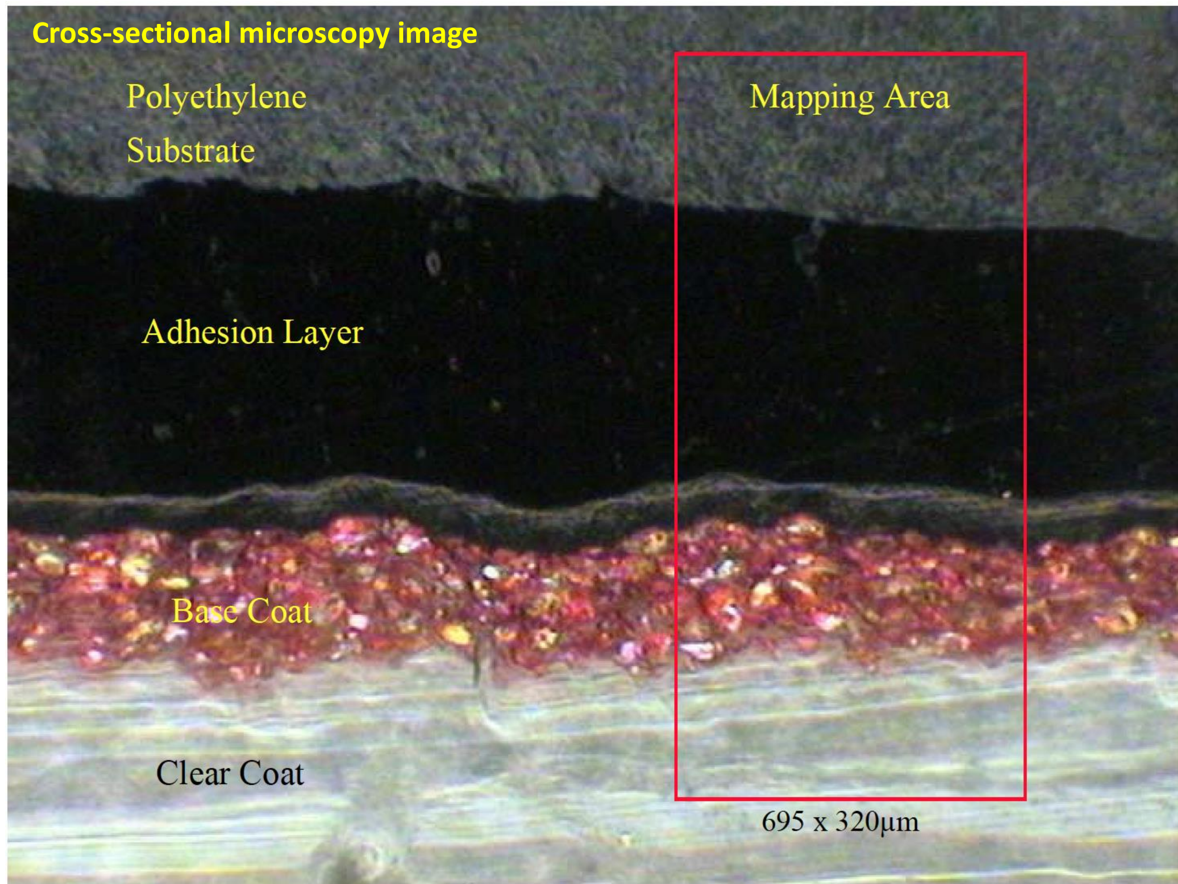
XPS study of paint

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

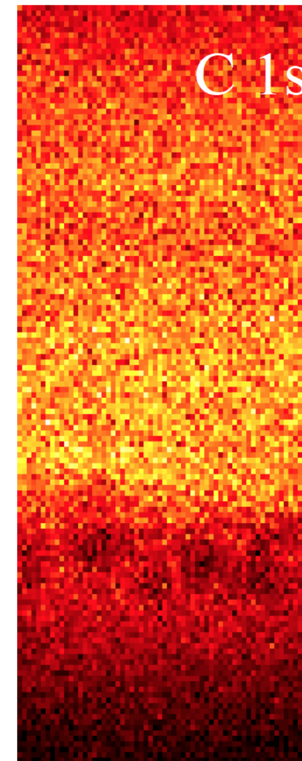


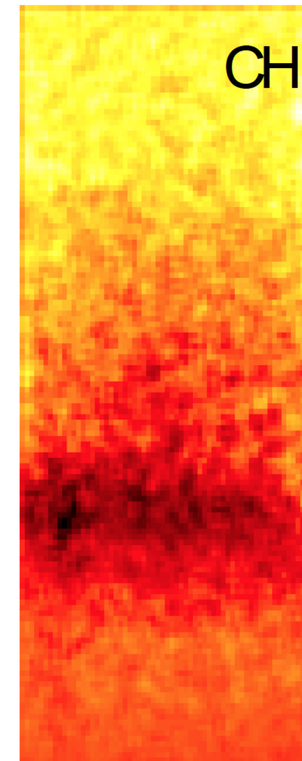


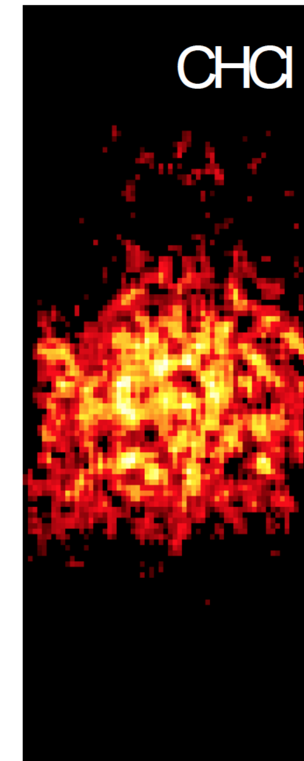
XPS study of paint – chemical state

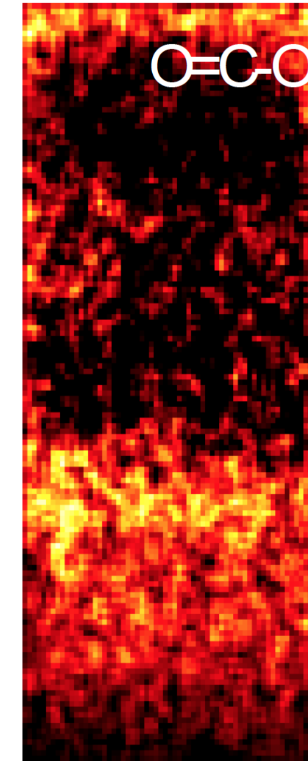


C 1s chemical state maps.









695 x 320mm

Imaging methods

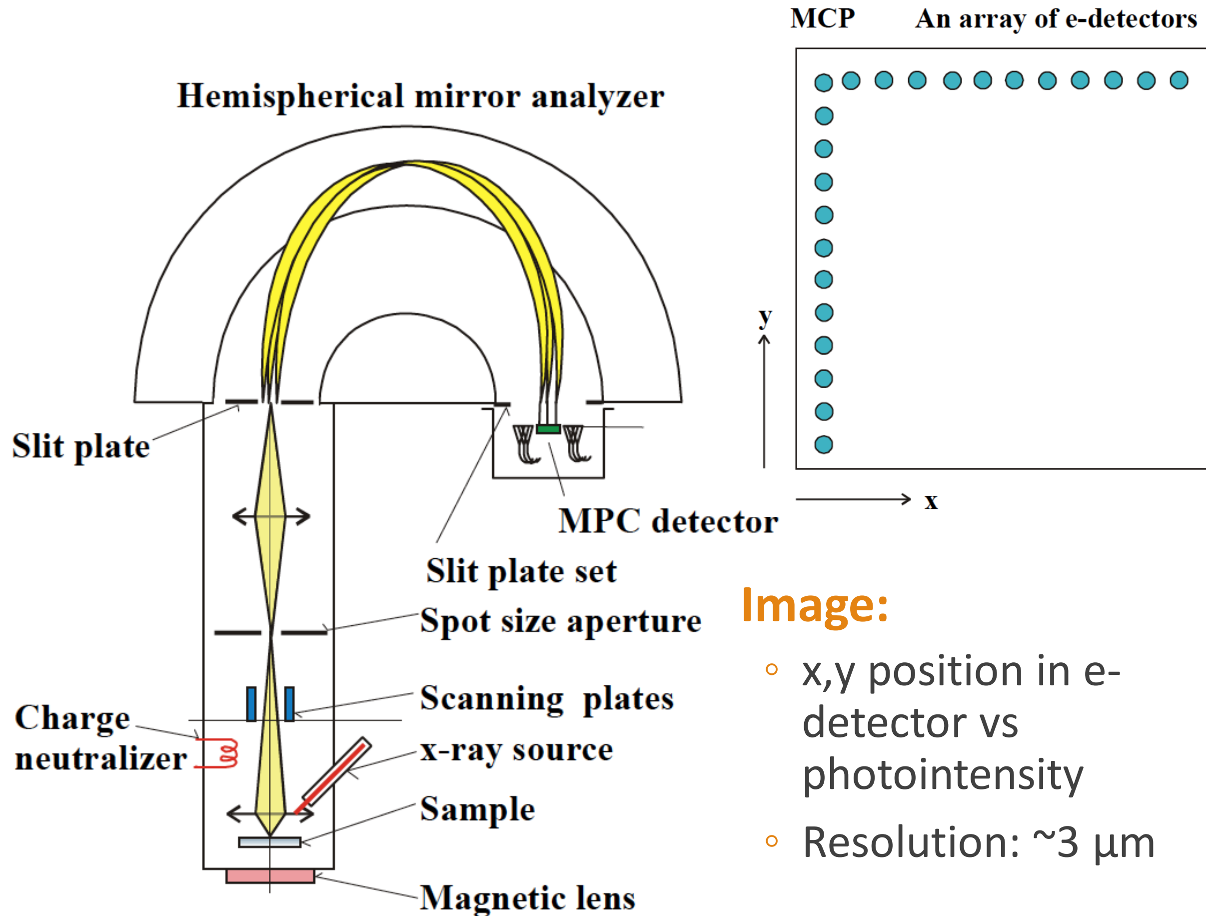
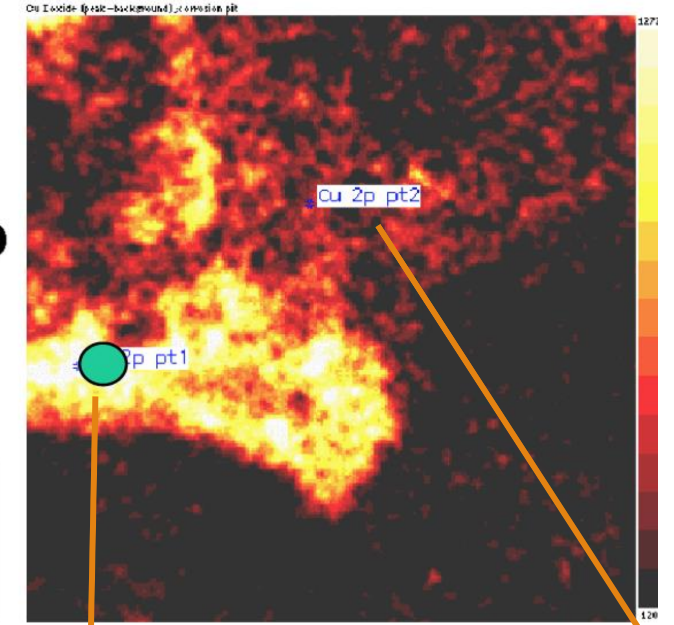
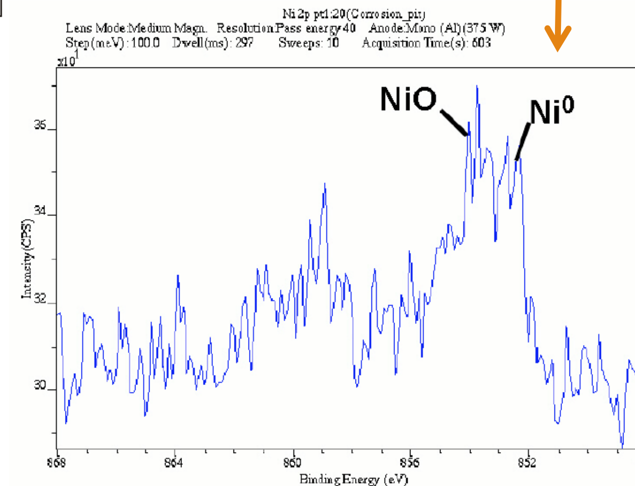


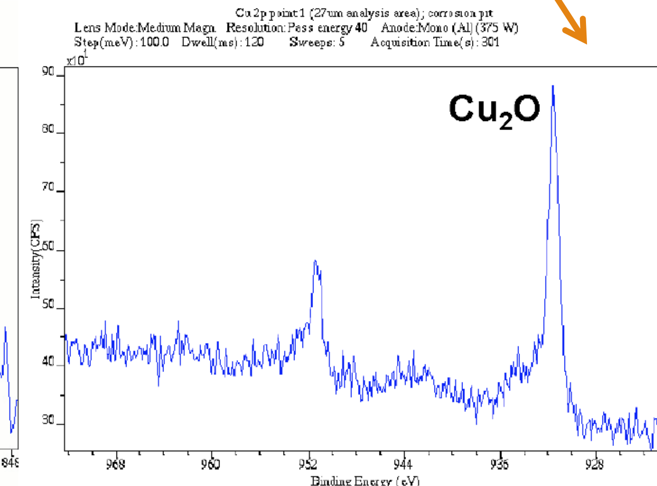
Image:

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

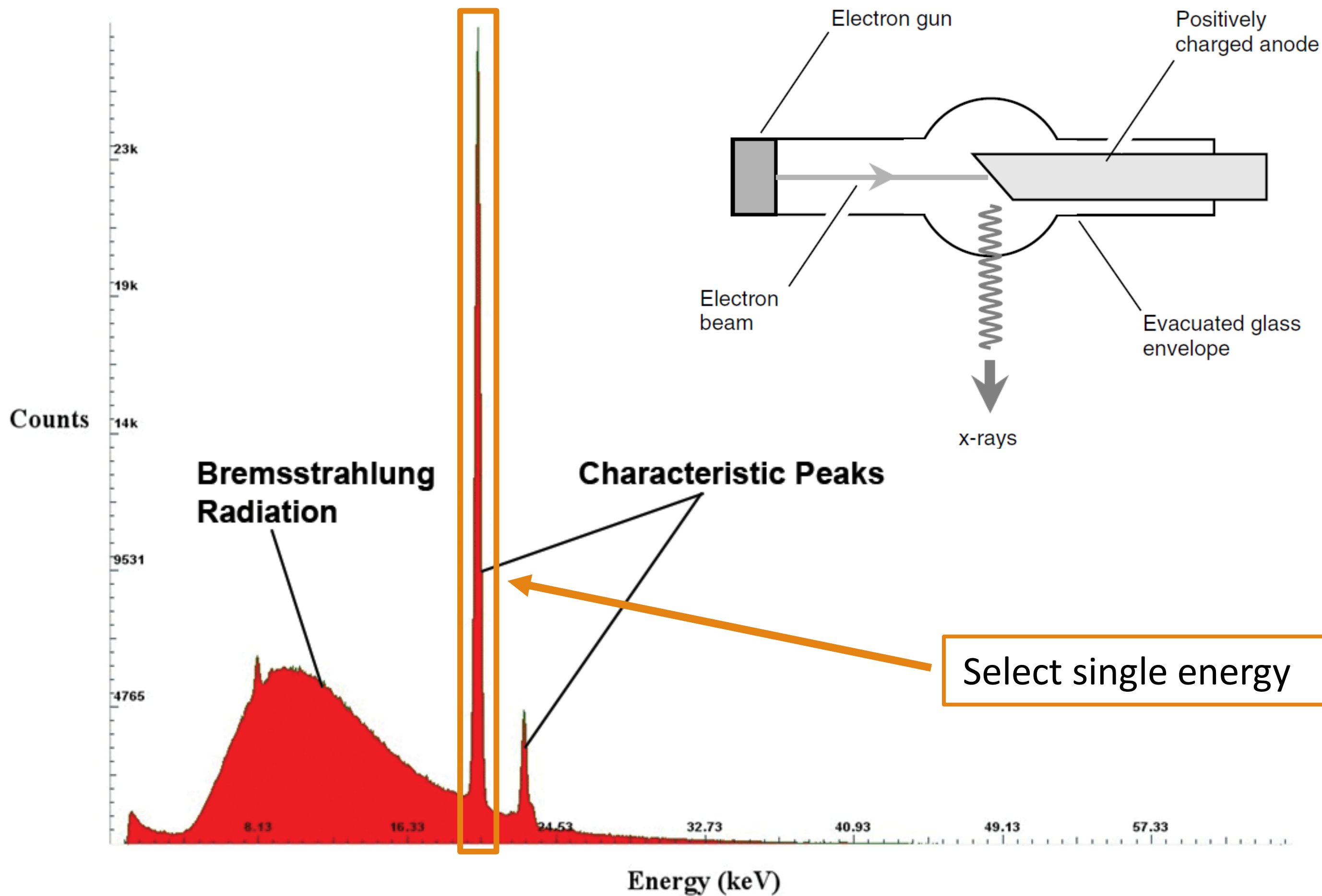


- Chemical state can be identified for each "spot" in image



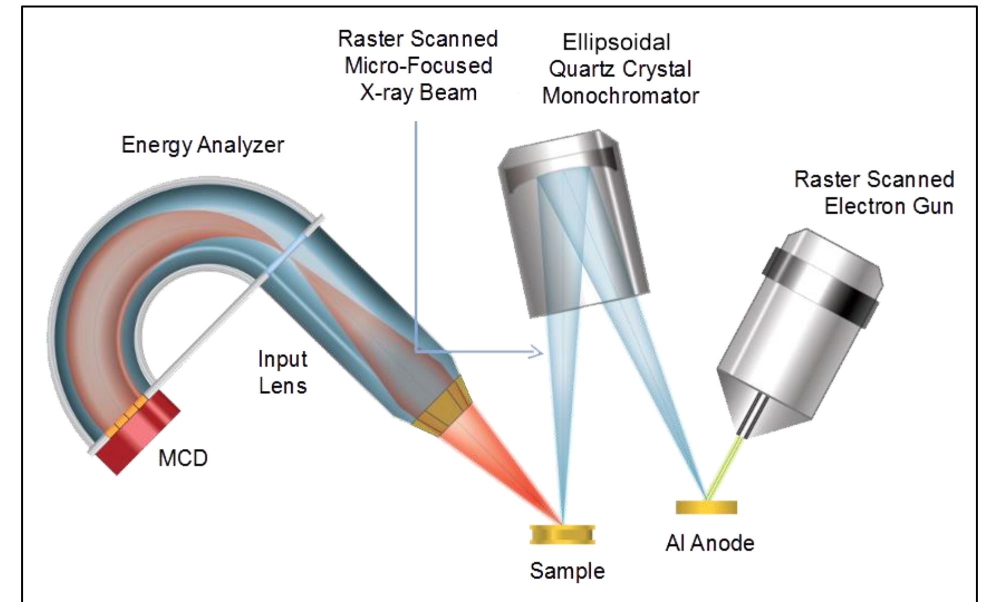


X-Ray production



- 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:

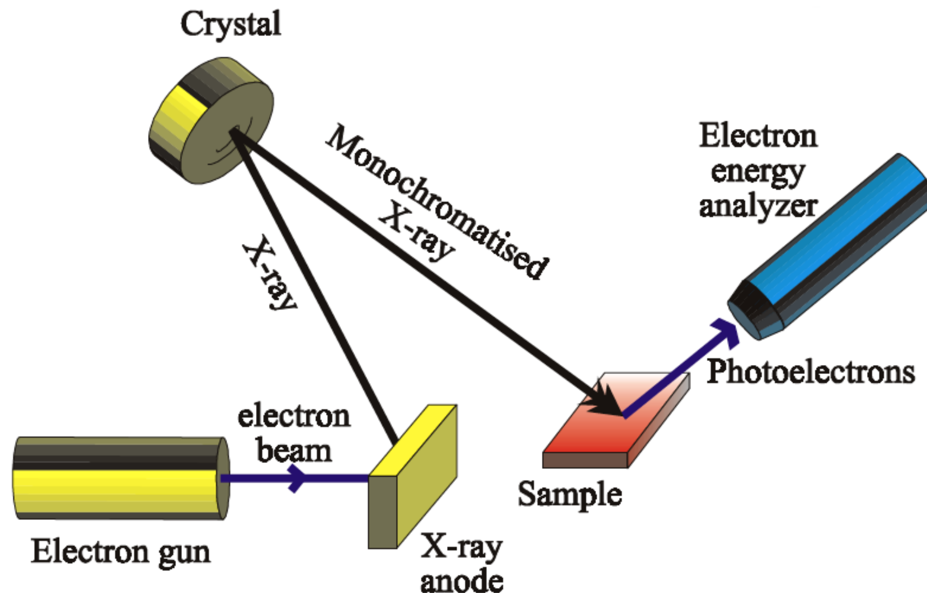
- 10-40 times lower intensity

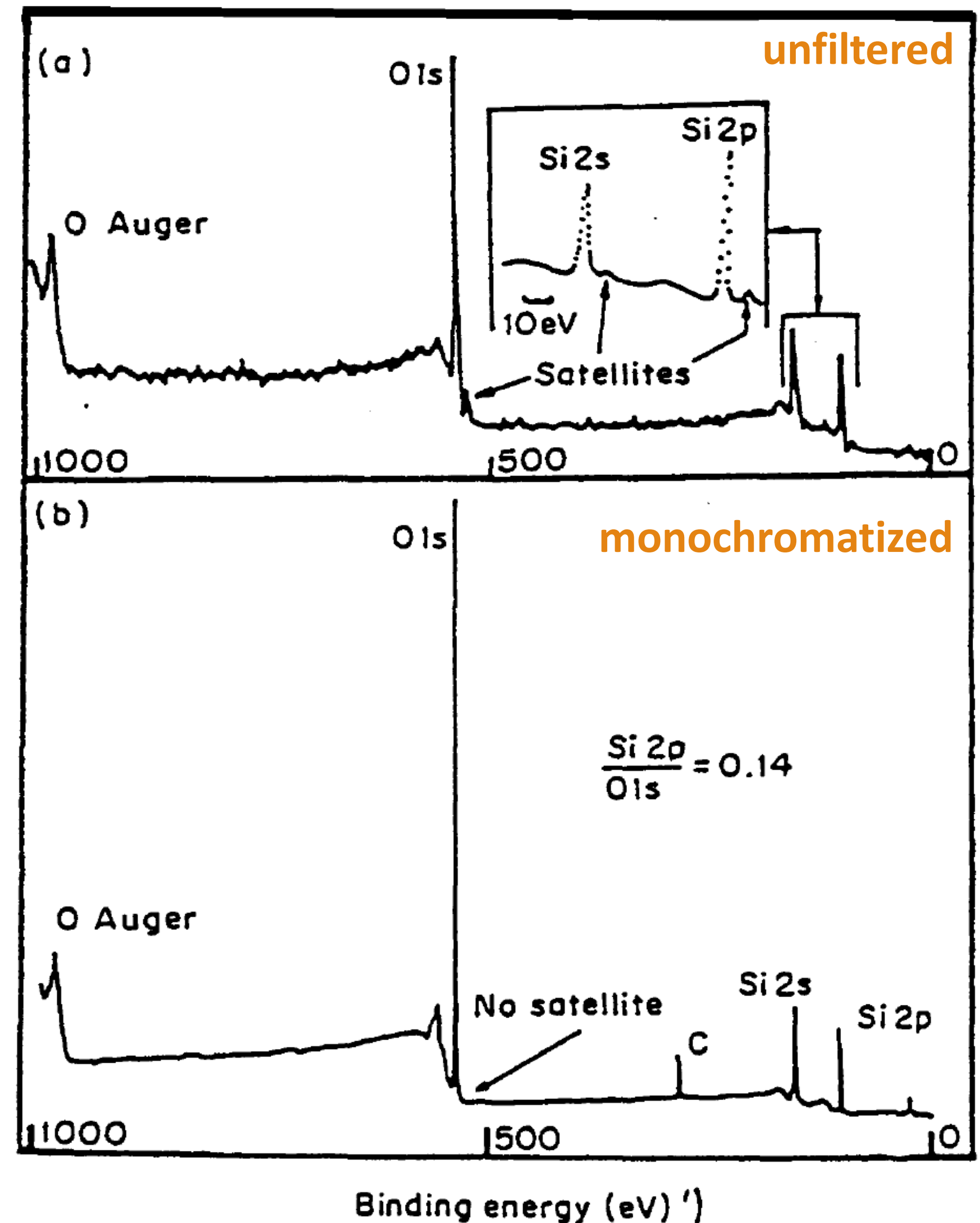
Bragg diffraction:

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

For Al K_α:
λ = 8.3 Å

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





Synchrotron sources

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