Quantitative Electron Microprobe Analysis

Wavelength Dispersive X-ray Spectrometry (WDS)

Goal: Measurement of concentration of all elements in a microscopic volume

EPMA Analytical procedure

- Sample preparation (mounting, polishing, carbon coating)

Carbon coating non-conducting material

- Setting up the Electron Microprobe

Voltage, beam conditions, spectrometers, etc.

- Qualitative analysis with EDS and WDS

If nothing is known about the chemical composition

- Measurement of X-ray intensities in standards (calibration)

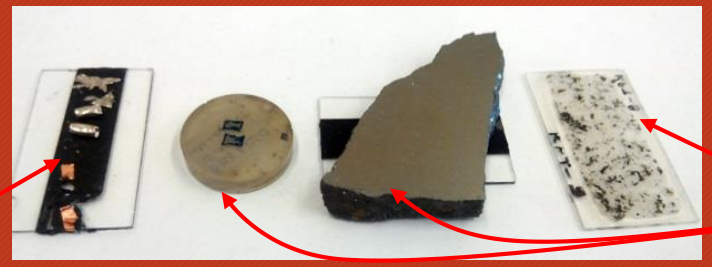
A different standard can be used for each element

- Measurement of X-ray intensities in the specimen and matrix corrections

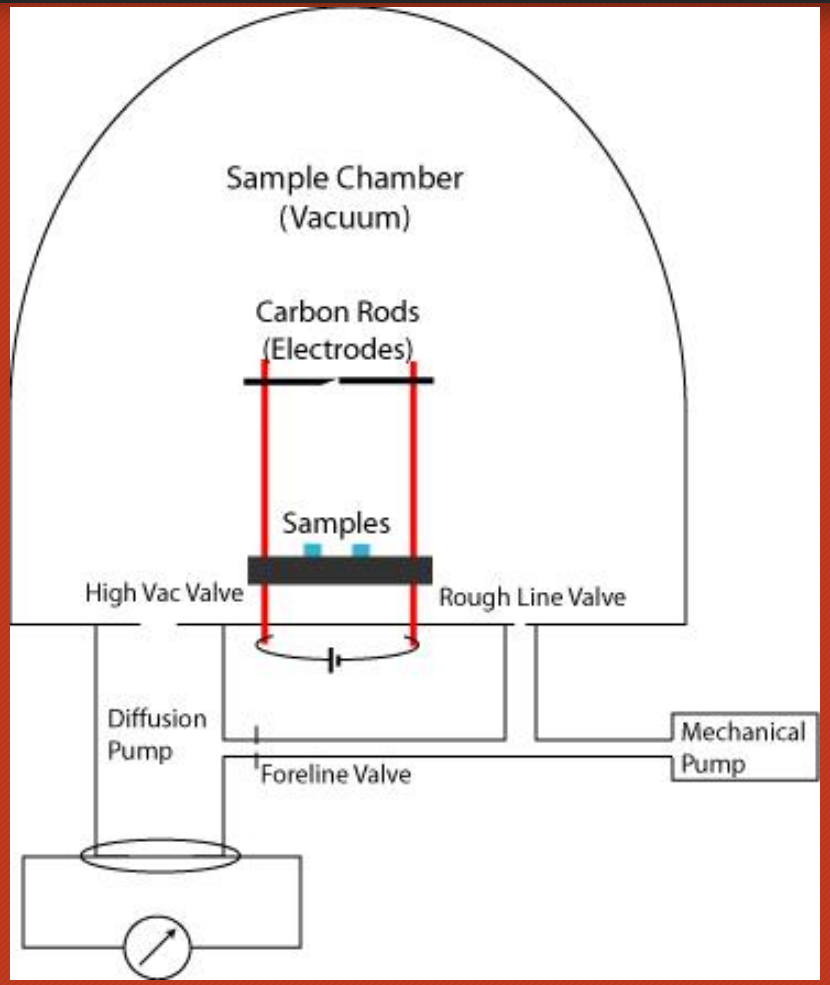
ZAF corrections

Sample preparation

- Sample cut and mounted in epoxy, if necessary
- Coarse polished with 240-600 SiC paper (53-16 μm)
- Fine polished with alumina slurry or diamond paste on cloth (grit size 1.00-0.25 μm)
- Washed with water in ultrasonic cleaner after each polishing step, dried after final step, wiped with ethanol



Carbon coating



25 nm

Thickness is monitored on a polished surface of brass, which is coated with the samples

Setting up the Electron Microprobe
Voltage, filament saturation and beam alignment

- Accelerating voltage
  - *Depends on overvoltage requirement,*

    e.g., FeKα is not emitted with a 5 keV beam because $E_{c(K\text{-}shell)}$=7.111 keV, and U < 1.
  - *For a particular accelerating voltage, overvoltage will be different for different elements. U should be about 2-10.*

- Filament saturation and beam alignment
  - *Saturation: filament current is adjusted to ensure saturation*
  - *Gun bias should be properly set to ensure optimum emission*
  - *Shift and tilt alignment: beam current is maximized*
  - *Wobble adjustment: image defocusing should be symmetrical above and below the optimum beam focusing plane. If not, position of the objective lens aperture is adjusted*
  - *Astigmatism correction: image is distorted if the spot is elliptical. Stigmator controls are used to remove distortion*

Setting up the Electron Microprobe
Spectrometer choice

- Crystal/diffractor

  E.g., FeKα ($\lambda_{K\alpha}$ = 0.1937 nm, $E_{FeK\alpha}$ = 6.4 keV) can be diffracted by TAP (2d = 2.5757 nm), PET (2d = 0.8742 nm) and LIF (2d = 0.4027 nm).

  For n = 1, equation $\lambda = 2d\sin\theta$, i.e., $\theta = \sin^{-1}\left(\frac{\lambda}{2d}\right)$, and for R = 140 mm, equation $L = n\lambda\frac{140}{d}$ indicate:

  θ = 4.3° and L = 191.2 mm for TAP

  θ = 12.8° and L = 62.0 mm for PET

  θ = 28.8° and L = 134.6 mm for LIF

  Acceptable ranges for θ and L are 15-55° and 70-230 mm. Therefore, LIF is the correct choice.

- Counter and window

  Xe has a better quantum efficiency for FeKα. So, a Xe counter with a Be window is the right choice.

- SCA settings

  Using LIF/Xe counter and an appropriate collection wire voltage, the CuKα ($E_{CuK\alpha}$ = 8.04 keV) pulse should be set at 5 V by performing PHA. Since $E_{FeK\alpha} = 0.8 \times E_{CuK\alpha}$, the FeK$\alpha$ pulse should be at 0.8 x 5 = 4 V.

- Detector slit

  For higher energy X-rays, smaller slits are recommended. The 300-550 μm slit should be selected.

Setting up the Electron Microprobe
Beam current, counting time and probe diameter

- Beam current and counting time depend on concentration of the element of interest

Higher beam current increases count rate and longer counting time increases total counts (improves precision)

For N counts, the counting uncertainty is $\frac{1}{\sqrt{N}}$ *X 100 %. Counting is more precise as N increases. E.g.,*

For 25 counts, the uncertainty is 20 %

For 100 counts, the uncertainty is 10 %

For 10,000 counts, the uncertainty is 1 %

- Probe diameter

Sometimes necessary to use a defocused beam (large spot size). E.g.,

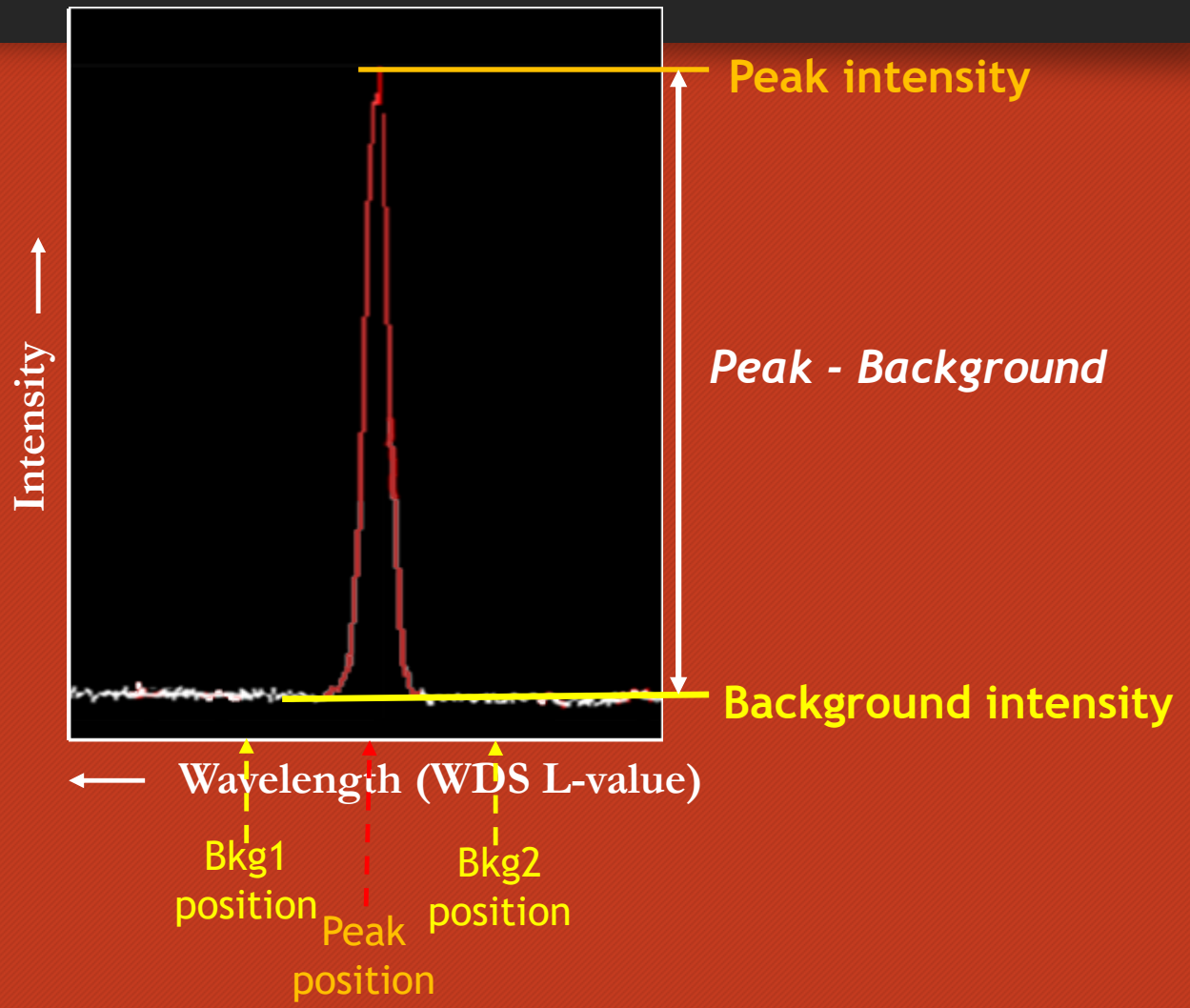
Average composition of fine-grained material (spot size > grain size)

Hydrous, and Na or F containing glass: Na migrates away, F migrates toward the spot (spot size ~ 10 μm)

Standard x-ray intensity measurement (calibration)

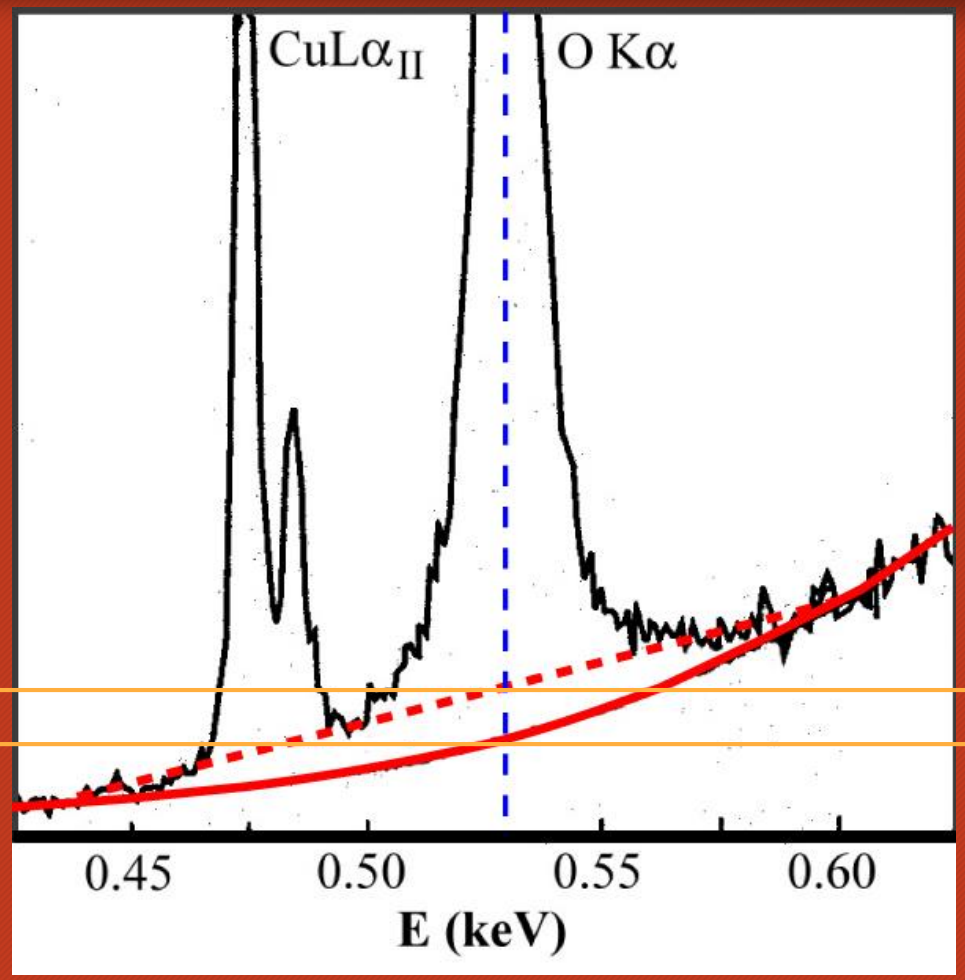
- *Calibration (standard intensity measurement) is performed on standards, a set of homogenous, natural or synthetic compounds with well known composition*
- *A good calibration is essential for **accurate** analysis.*
  It eliminates systematic errors
- *After primary calibration, secondary standards (working standards) are analyzed to make sure the results are as expected*

X-ray intensity measurement



Long counting times are used to achieve statistical precision

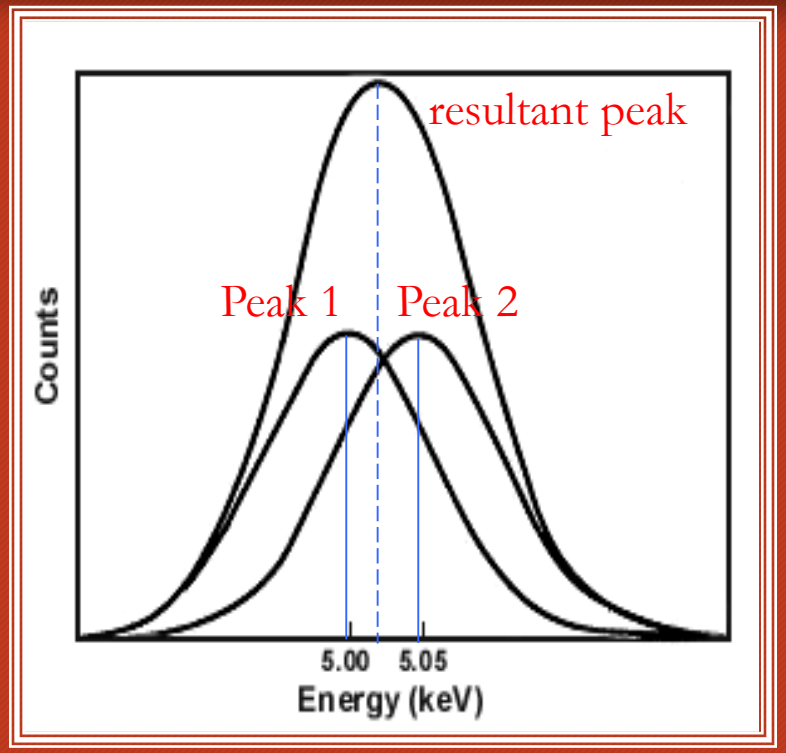
X-ray background measurement: special case



incorrect

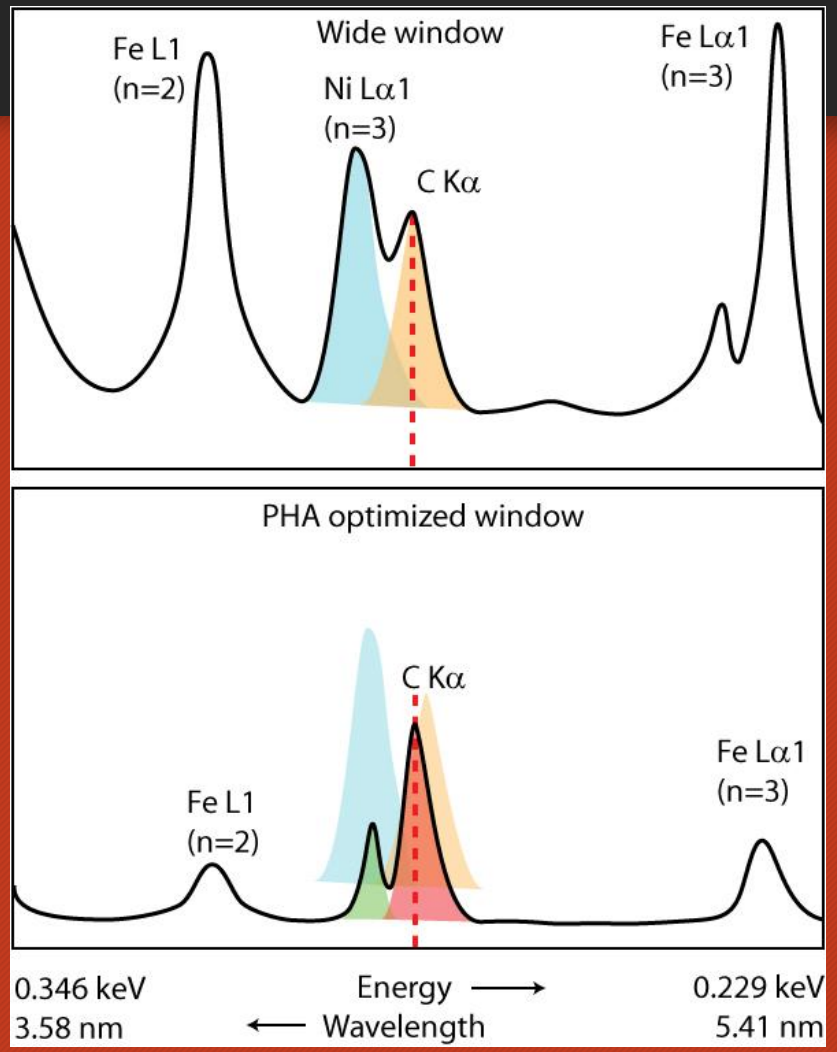
correct

Peak overlap in X-ray spectra



Overlap between Peak 1 and Peak 2 results in a broad single peak

PHA reduces peak and background overlaps



Wide open SCA voltage window

PHA optimized SCA voltage window

Spectrum of carbon steel

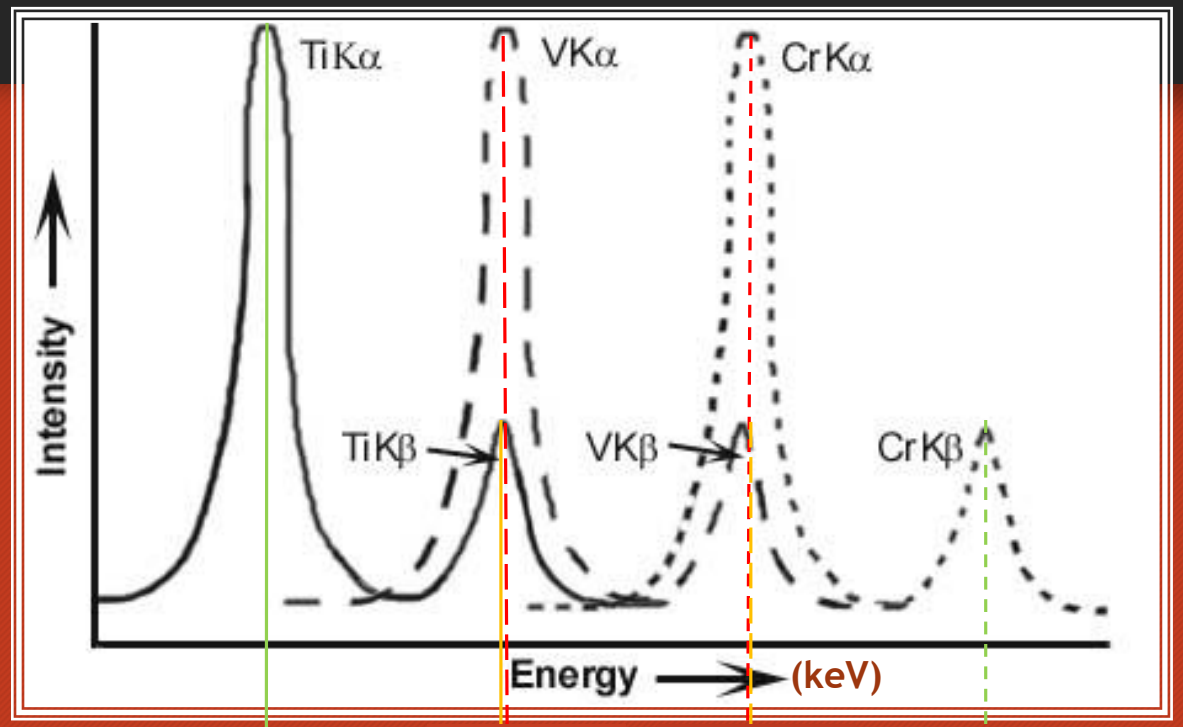
Peak overlap: Kα and Kβ of Ti, V and Cr

		Kα	Kβ
Ti	22	4.508	4.931
V	23	4.949	5.426
Cr	24	5.411	5.946

Element	Atm. No.	K_{α}	K_{β}	K_{ab}	L_{α}	L_{β_1} (*)	L_{β_2} (*)	L_{γ_2} (*)	$L_{\beta\beta ab}$	$L_{\beta ab}$	L_{ab}	M
Li	3	0.052		0.055								
Be	4	0.109		0.112								
B	5	0.183		0.192								
C	6	0.277		0.284								
N	7	0.392		0.400								
O	8	0.525		0.532								
F	9	0.677		0.687								
Ne	10	0.848		0.867								
Na	11	1.041		1.071								
Mg	12	1.253		1.303								
Al	13	1.486		1.560								
Si	14	1.739		1.840								
P	15	2.013	2.139(4)	2.143								
S	16	2.307	2.465(7)	2.470								
Cl	17	2.621	2.815(5)	2.819								
Ar	18	2.957	3.190(10)	3.202								
K	19	3.312	3.589(10)	3.607								
Ca	20	3.690	4.012(10)	4.037	0.341							
Sc	21	4.088	4.460(13)	4.488	0.395							
Ti	22	4.508	4.931(13)	4.964	0.452							
V	23	4.949	5.426(13)	5.463	0.511							
Cr	24	5.411	5.946(12)	5.988	0.573							
Mn	25	5.894	6.489(13)	6.536	0.637							
Fe	26	6.398	7.057(13)	7.110	0.705							
Co	27	6.924	7.648(13)	7.708	0.776							
Ni	28	7.471	8.263(13)	8.330	0.851							
Cu	29	8.040	8.904(13)	8.979	0.930							
Zn	30	8.630	9.570(13)	9.660	1.012							
Ga	31	9.241	10.262(14)	10.336	1.098							
Ge	32	9.874	10.978(14)	11.102	1.188							
As	33	10.530	11.722(15)	11.862	1.282							
Se	34	11.207	12.494(16)	12.652	1.419							
Br	35	11.907	13.286(16)	13.468	1.480							
Kr	36	12.631	14.107(16)	14.322	1.586							
Rb	37	13.373	14.956(16)	15.200	1.694							
Sr	38	14.140	15.830(16)	16.104	1.806							
Y	39	14.931	16.731(17)	17.035	1.922							
Zr	40	15.744	17.660(18)	17.996	2.042	2.124(45)						
Nb	41	16.581	18.729(8)	18.984	2.166	2.257(45)						
Mo	42	17.441	19.599(17)	20.001	2.293	2.394(45)						
Tc	43	18.325	20.608(16)	21.044	2.424	2.536(45)						
Ru	44	19.233	21.646(16)	22.116	2.558	2.683(45)						
Rh	45	20.165	22.712(16)	23.216	2.696	2.834(40)	3.001(25)					
Pd	46	21.121	23.806(17)	24.344	2.838	2.990(40)	3.171(25)					
Ag	47	22.101	24.928(17)	25.512	2.984	3.150(40)	3.347(25)					
Cd	48	23.106	26.081(18)	26.711	3.133	3.316(42)	3.528(25)			3.537	3.727	4.018
In	49	24.136	27.260(18)	27.937	3.286	3.487(75)	3.713(17)			3.730	3.939	4.237
Sn	50	25.191	28.467(19)	29.190	3.443	3.662(75)	3.904(17)			3.928	4.157	4.464
Sb	51	26.271	29.396(19)	30.481	3.604	3.843(75)	4.100(17)			4.132	4.381	4.698
Te	52	27.468	30.974(19)	31.811	3.769	4.029(75)	4.301(17)			4.341	4.612	4.939
I	53	28.607	32.272(19)	33.167	3.937	4.220(75)	4.507(17)			4.558	4.853	5.191
Xe	54	29.774	33.600(20)	34.590	4.109	4.420(50)	4.720(20)			4.781	5.103	5.452
Cs	55	30.968	34.960(20)	35.987	4.286	4.619(50)	4.935(20)			5.011	5.357	5.720
Ba	56	32.188	36.354(21)	37.452	4.465	4.827(50)	5.156(20)			5.246	5.622	5.995
La	57	33.436	37.771(21)	38.934	4.650	5.041(50)	5.383(20)			5.483	5.888	6.267
Ce	58	34.714	39.223(21)	40.453	4.839	5.261(50)	5.612(20)			5.723	6.160	6.547
Pr	59	36.020	40.771(21)	42.002	5.033	5.488(50)	5.849(20)			5.962	6.438	6.833
Nd	60	37.355		43.574	5.229	5.721(50)	6.088(20)			6.208	6.722	7.128
Pm	61	38.718		45.198	5.432	5.960(50)	6.338(20)			6.459	7.013	7.434
Sm	62	40.111		46.849	5.635	6.204(50)	6.586(20)			6.716	7.312	7.747
Eu	63				5.845	6.455(50)	6.842(20)			6.979	7.618	8.059
Gd	64				6.056	6.712(50)	7.102(20)			7.242	7.930	8.385
Tb	65				6.272	6.977(50)	7.365(20)			7.514	8.251	8.715
Dy	66				6.494	7.246(50)	7.634(20)			7.880	8.582	9.050
Ho	67				6.719	7.524(50)	7.910(20)			8.066	8.915	9.398
Er	68				6.947	7.809(50)	8.188(20)			8.356	9.260	9.756
Tm	69				7.179	8.100(50)	8.467(20)	9.424(5)		8.648	9.615	10.119
Yb	70				7.414	8.400(50)	8.757(20)	9.778(5)		8.942	9.974	10.489
Lu	71				7.654	8.708(50)	9.038(20)	10.142(6)		9.247	10.343	10.872
Hf	72				7.898	9.021(50)	9.346(20)	10.514(10)		9.556	10.734	11.272
Ta	73				8.145	9.342(50)	9.650(20)	10.893(10)		9.875	11.130	11.680
W	74				8.396	9.671(50)	9.960(20)	11.284(10)		10.198	11.537	12.098
Re	75				8.651	10.008(50)	10.274(20)	11.683(10)		10.529	11.953	12.529
Os	76				8.910	10.354(50)	10.597(20)	12.093(10)		10.866	12.379	12.969
Ir	77				9.174	10.706(50)	10.919(20)	12.510(10)		11.210	12.818	13.421
Pt	78				9.441	11.069(50)	11.249(20)	12.940(10)		11.560	13.270	13.880
Au	79				9.712	11.440(50)	11.583(20)	13.379(10)		11.919	13.734	14.351
Hg	80				9.987	11.821(50)	11.922(20)	13.828(10)		12.284	14.212	14.840
Ti	81				10.267	12.211(50)	12.270(20)	14.289(10)		12.658	14.698	15.340
Pb	82				10.550	12.612(50)	12.621(20)	14.762(10)		13.038	15.203	15.852
Bi	83				10.837	13.021(50)	12.978(20)	15.245(10)		13.424	15.717	16.373
Po	84				11.129	13.445(50)	13.338(20)	15.741(10)		13.817	16.244	16.935
At	85				11.425	13.874(50)	14.065(10)	16.249(10)		14.215	16.784	17.490
Rn	86				11.725	14.313(50)	14.509(10)	16.768(10)		14.618	17.337	18.058
Fr	87				12.029	14.768(50)	14.448(20)	17.300(10)		15.028	17.904	18.638
Ra	88				12.338	15.233(50)	14.839(20)	17.845(10)		15.441	18.482	19.234
Ac	89				12.650	15.710(50)	15.929(10)	18.405(10)		15.865	19.078	19.842
Th	90				12.967	16.199(50)	15.621(20)	18.979(10)		16.296	19.679	20.459
Pa	91				13.288	16.699(50)	16.022(20)	19.565(10)		16.765	20.358	21.168
U	92				13.612	17.217(50)	16.425(20)	20.164(10)		17.162	20.943	21.766

Element	Atm. No.	M
Cd	48	0.606
In	49	
Sn	50	0.691
Sb	51	0.733
Te	52	0.778
I	53	
Xe	54	
Cs	55	
Ba	56	0.972
La	57	0.833
Ce	58	0.883
Pr	59	0.929
Nd	60	0.978
Pm	61	
Sm	62	1.081
Eu	63	1.131
Gd	64	1.185
Tb	65	1.240
Dy	66	1.293
Ho	67	1.347
Er	68	1.405
Tm	69	1.462
Yb	70	1.521
Lu	71	1.581
Hf	72	1.644
Ta	73	1.709
W	74	1.774
Re	75	1.842
Os	76	1.914
Ir	77	1.977
Pt	78	2.048
Au	79	2.121
Hg	80	2.195
Ti	81	2.267
Pb	82	2.342
Bi	83	2.419
Po	84	
At	85	
Rn	86	
Fr	87	
Ra	88	
Ac	89	
Th	90	2.991
Pa	91	3.077
U	92	3.165

Peak overlap correction for Ti-V-Cr



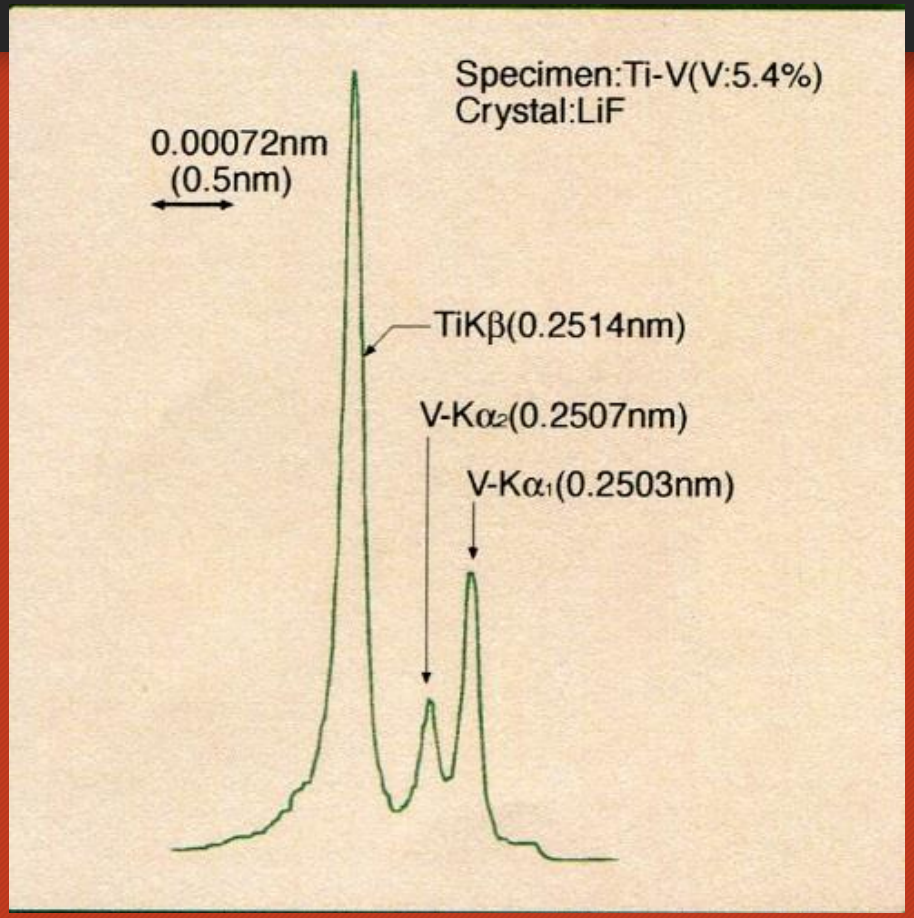
4.508 4.949 5.411

4.931 5.426 4.946

$$I^{\text{corr}}_{\text{VK}\alpha} = I^{\text{meas}}_{\text{VK}\alpha} - \frac{I^{\text{meas}}_{\text{TiK}\alpha}}{I^{\text{Ti - std}}_{\text{TiK}\alpha}} I^{\text{Ti - std}}_{\text{VK}\alpha}$$

$$I^{\text{corr}}_{\text{CrK}\alpha} = I^{\text{meas}}_{\text{CrK}\alpha} - \frac{I^{\text{corr}}_{\text{VK}\alpha}}{I^{\text{V - std}}_{\text{VK}\alpha}} I^{\text{V - std}}_{\text{CrK}\alpha}$$

Peak resolution with LIF



XCE type spectrometer with Xe counter

LIF is able to resolve the TiKβ, VKα_1 and VKα_2 peaks

EPMA Quantitative analysis

X-ray intensity is proportional to the concentration, $C \propto I$

$$\frac{C_i}{C_{(i)}} \propto \frac{I_i}{I_{(i)}}$$

C_i , I_i : concentration and intensity in sample

$C_{(i)}$, $I_{(i)}$: concentration and intensity in standard

$$\frac{I_i}{I_{(i)}} = k_i \text{ (k - ratio)}$$

$$\frac{C_i}{C_{(i)}} = k_i \cdot [\text{ZAF}]_i$$

ZAF Matrix corrections:

Z: Atomic Number correction

A: Absorption correction

F: Fluorescence correction

Typical quantitative analysis output

k-ratio | Element Wt% | Oxide Wt% | Atomic proportion

Element		k-Ratio	El-Wt%	MDLel%	Ox-Wt%	MDLox%	At-Prop	Error%
SiO2	Ka	0.9119	17.30	0.03	37.01	0.05	2.960	0.68%
TiO2	Ka	0.0021	0.13	0.05	0.22	0.09	0.013	20.28%
Al2O3	Ka	0.5200	11.46	0.03	21.66	0.05	2.042	0.86%
Cr2O3	Ka	0.0000	0.00	0.06	0.00	0.08	0.000	99.00%
FeO	Ka	1.0431	21.43	0.07	27.57	0.09	1.844	1.58%
MnO	Ka	0.0809	2.89	0.08	3.73	0.11	0.253	4.29%
MgO	Ka	0.0781	1.36	0.02	2.26	0.04	0.269	2.93%
CaO	Ka	0.3565	5.20	0.04	7.28	0.05	0.624	1.82%
Na2O	Ka	0.0011	0.01	0.04	0.02	0.05	0.003	99.00%
O			39.95				12.000	
Total:			99.75		99.75	Cation:	8.007	

Minimum detection limit (El-Wt%)

Minimum detection limit (Ox-Wt%)

Uncertainty

Cation Sum based on a certain #O

Typical quantitative analysis output

Element	Oxide Wt%	Atomic proportion
	Ox-Wt%	At-Prop
SiO2	37.01	2.960
TiO2	0.22	0.013
Al2O3	21.66	2.042
Cr2O3	0.00	0.000
FeO	27.57	1.844
MnO	3.73	0.253
MgO	2.26	0.269
CaO	7.28	0.624
Na2O	0.02	0.003
O		12.000
Total:	99.75	8.007

- *A typical mineral analysis reports Oxide wt% and Atomic proportions*
- *The wt% total and cation sum give us an idea of the quality of the analysis*
- *Atomic proportions give us the formula:* $Mg_{0.27}Fe_{1.84}Mn_{0.25}Ca_{0.62}Al_{2.04}Si_{2.96}O_{12}$ *(garnet)*