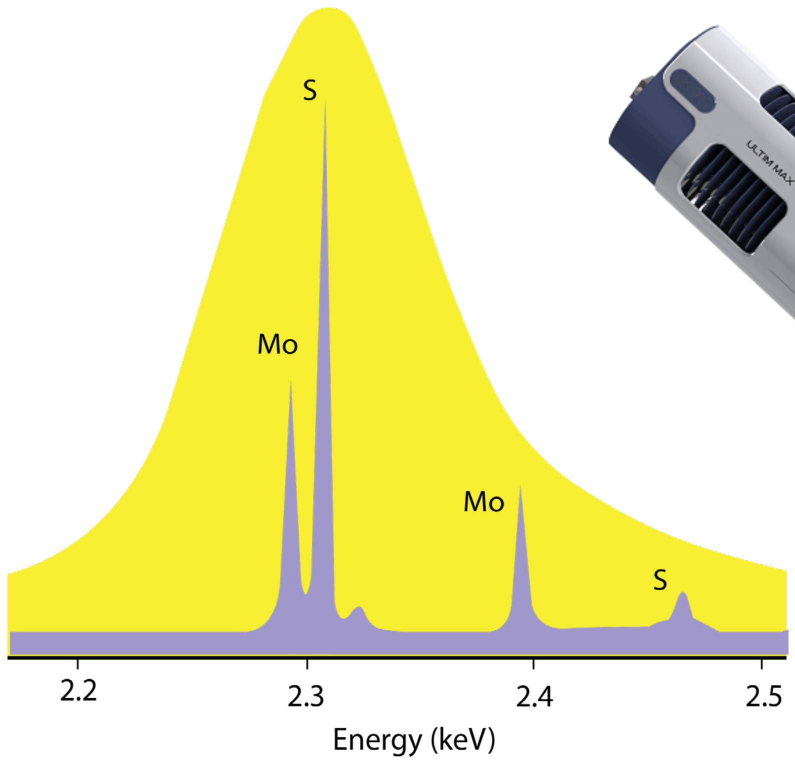
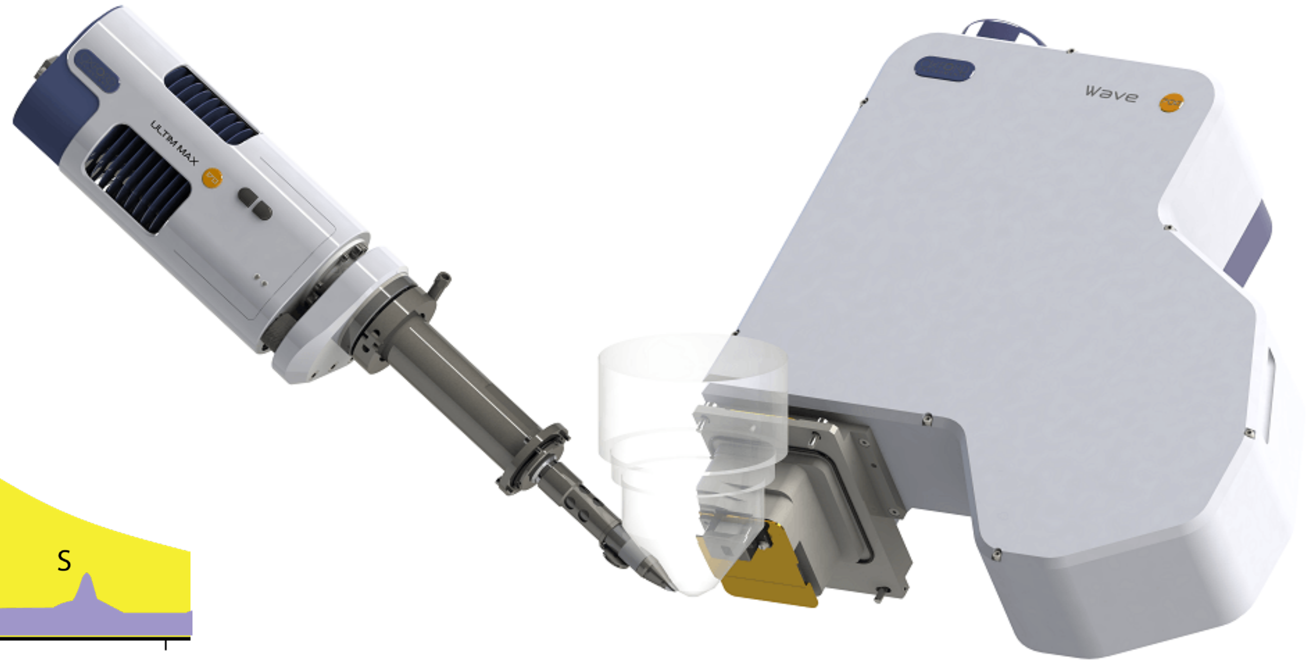
Wavelength Dispersive X-ray Spectroscopy

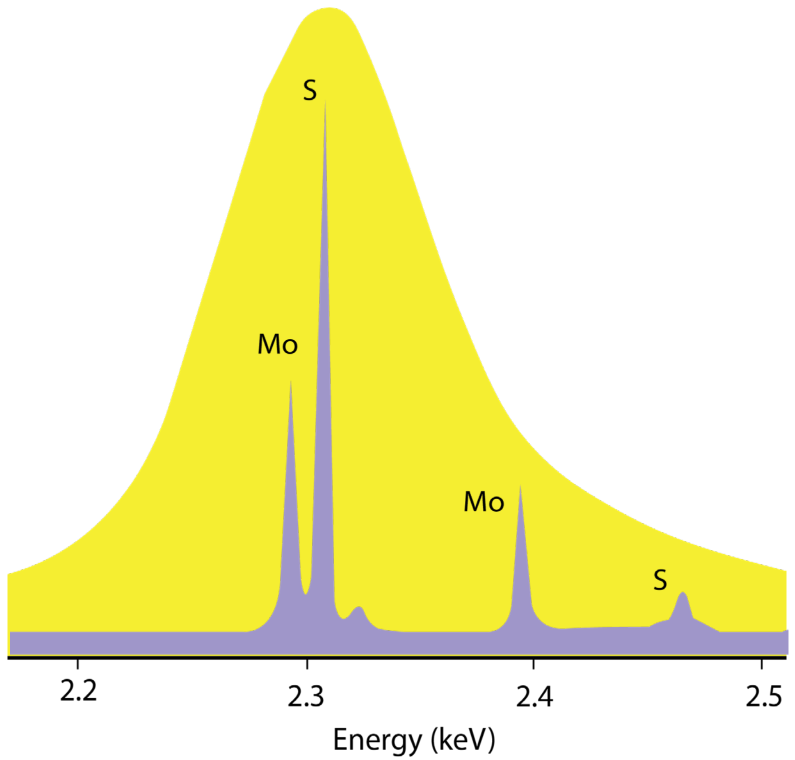




From Oxford Instruments

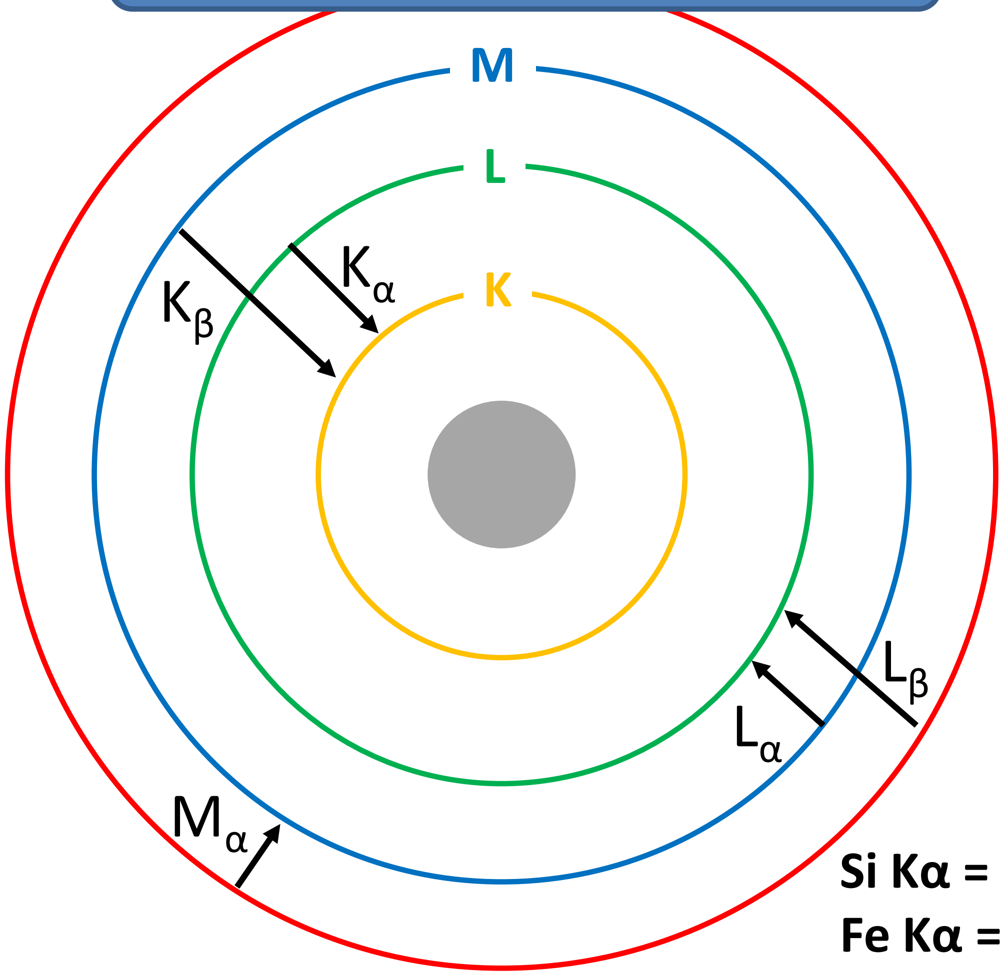
Tirzah Abbott
EPIC-SEM Facility Manager

Outline



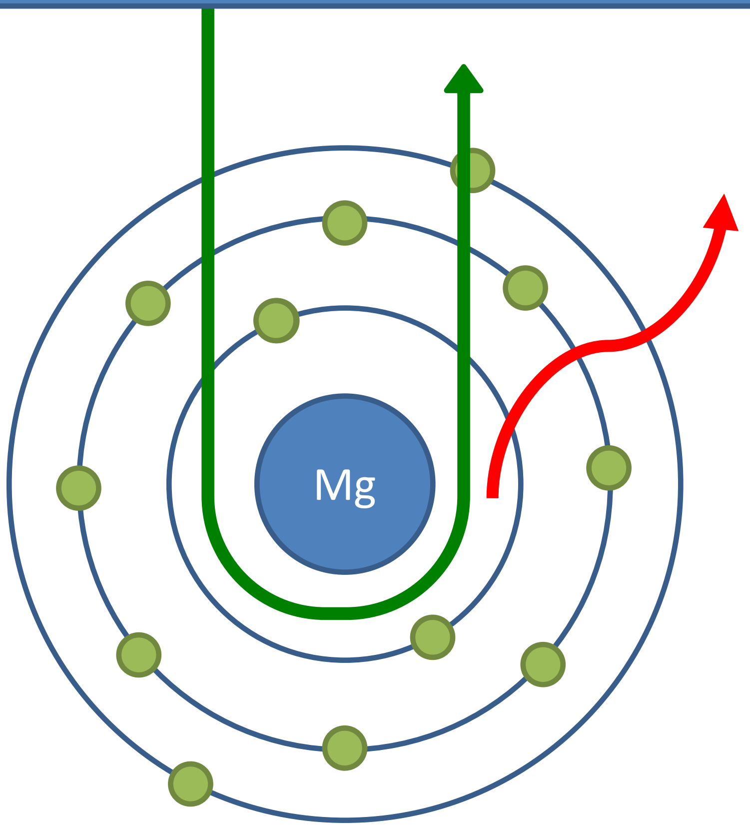
- X-ray emission and detection with EDS in the SEM
- Introduction to wavelength dispersive x-ray spectroscopy
- WDS X-ray detection and Spectrometer
- Examples and available detectors and resources at NU*ANCE*

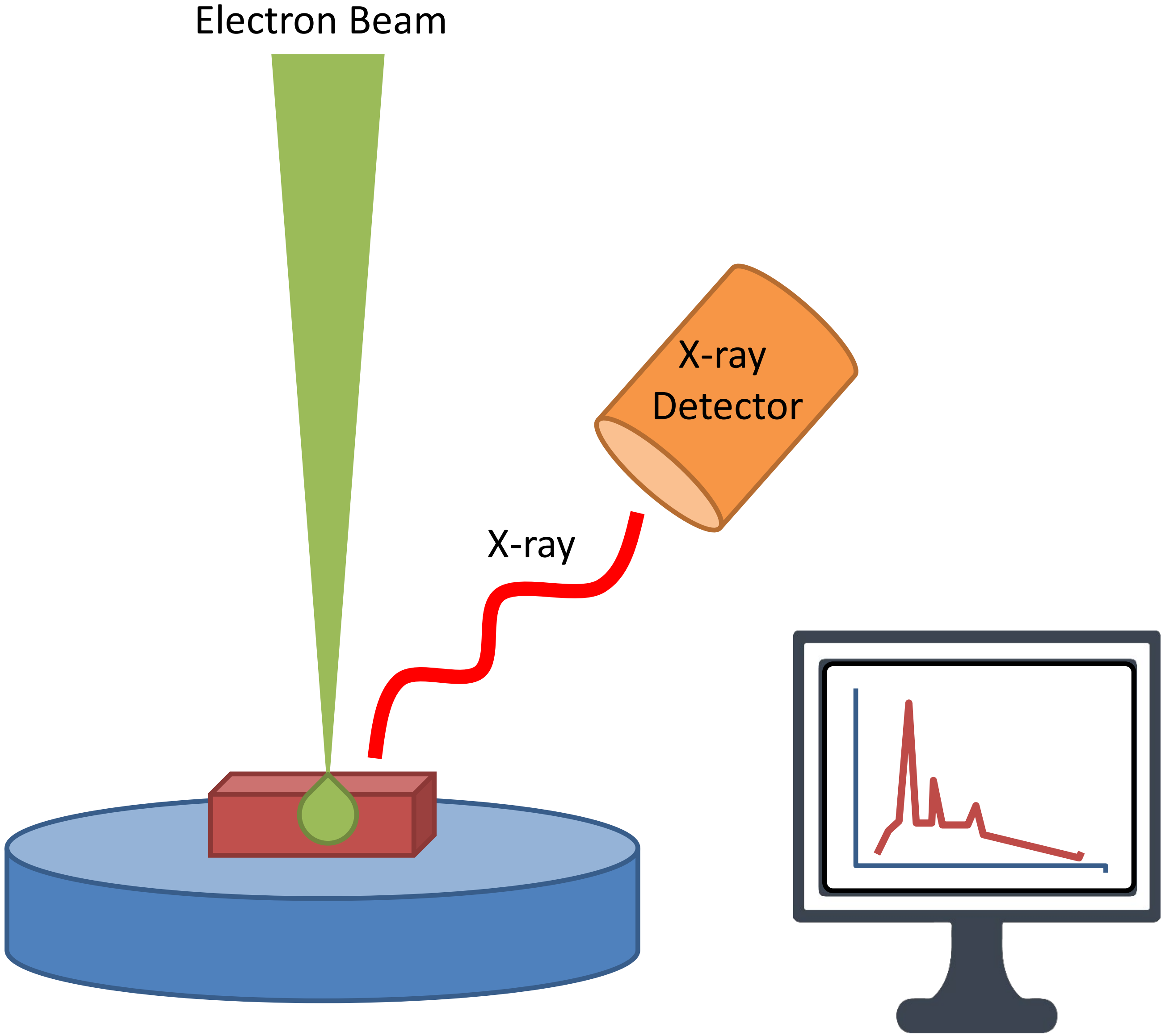
Characteristic X-rays



Si Kα = 1.740 keV
Fe Kα = 6.405 keV

Bremsstrahlung Radiation





Electron beam interacts with sample

↓

X-rays emitted from the sample

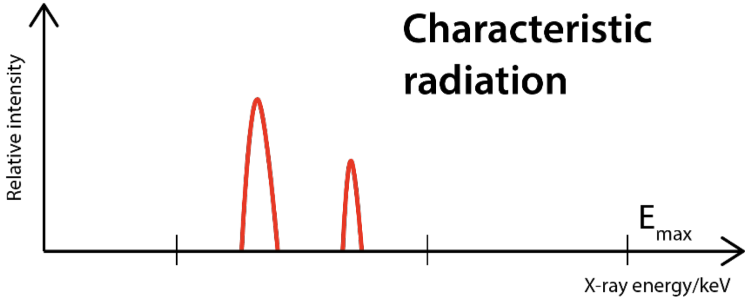
↓

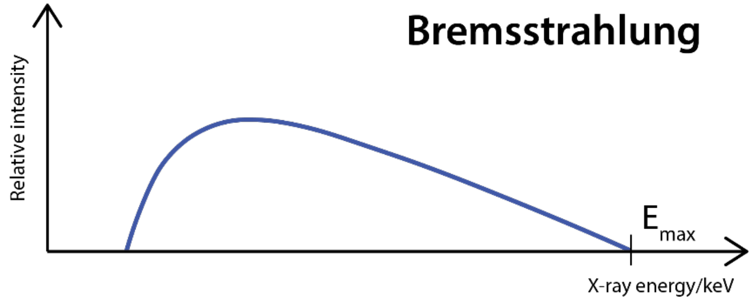
Detector converts x-rays to electrical voltage

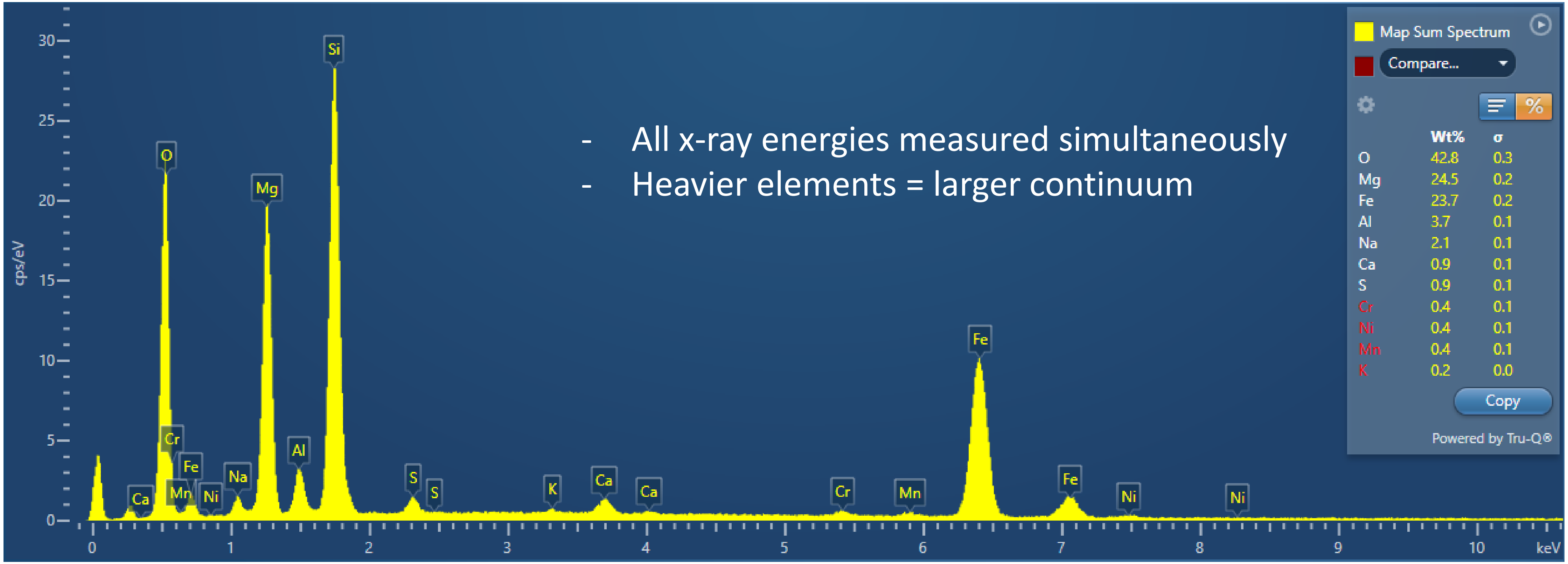
↓

Elemental analysis is done on electrical signals

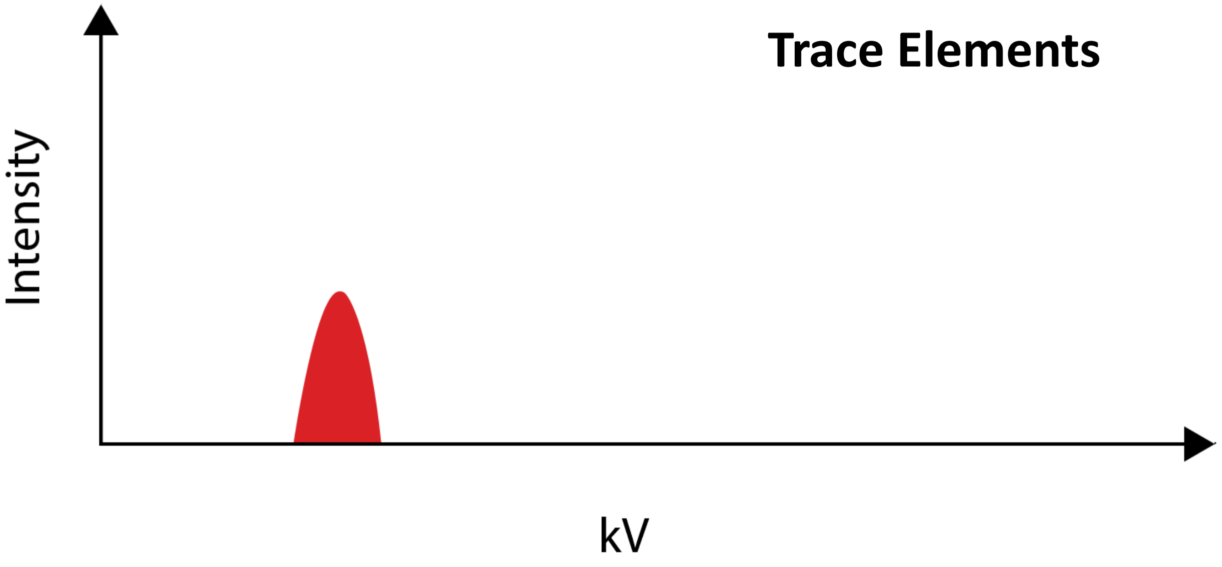
Generating X-Ray Signals

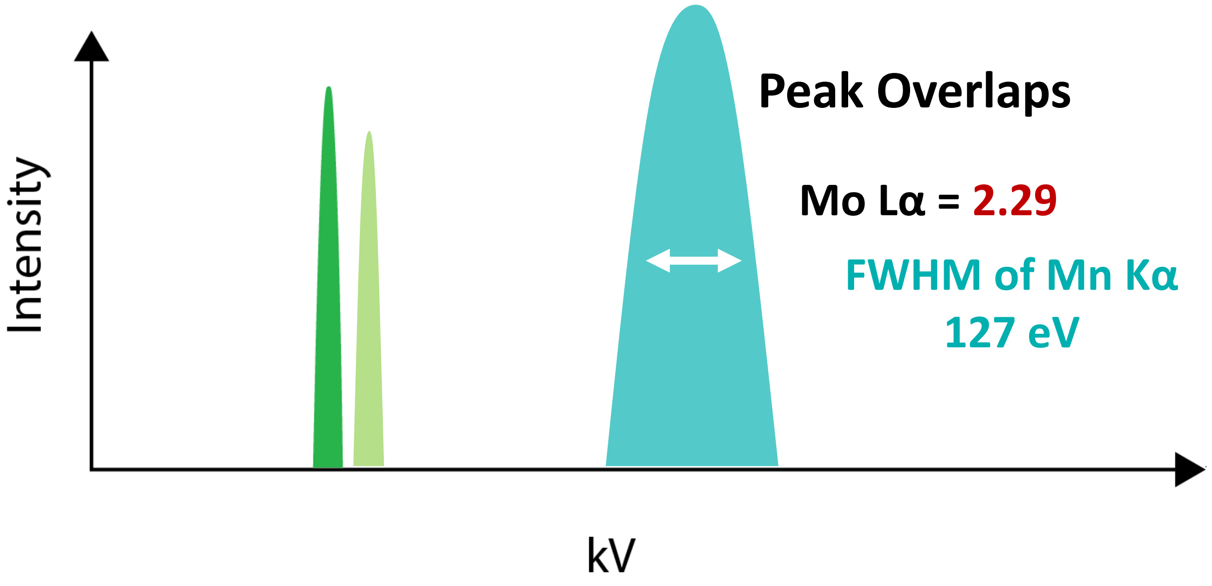






- All x-ray energies measured simultaneously
- Heavier elements = larger continuum





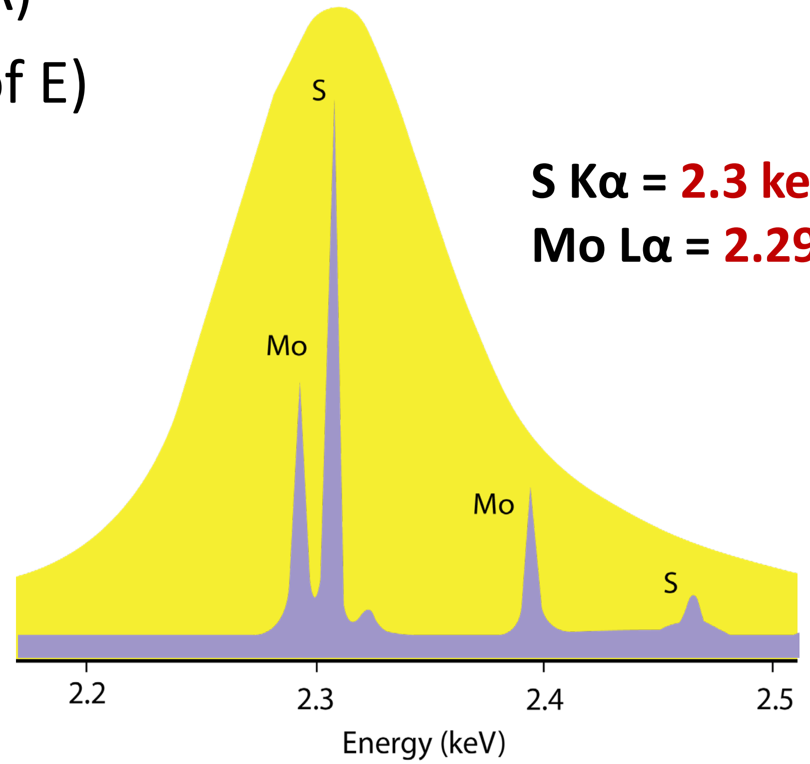
Remove backgrounds for trace elements

- S
  background
  - Lower than 0.1 wt% (1000 ppm) almost impossible with EDS
  - Background is greater in denser materials
- F
  in

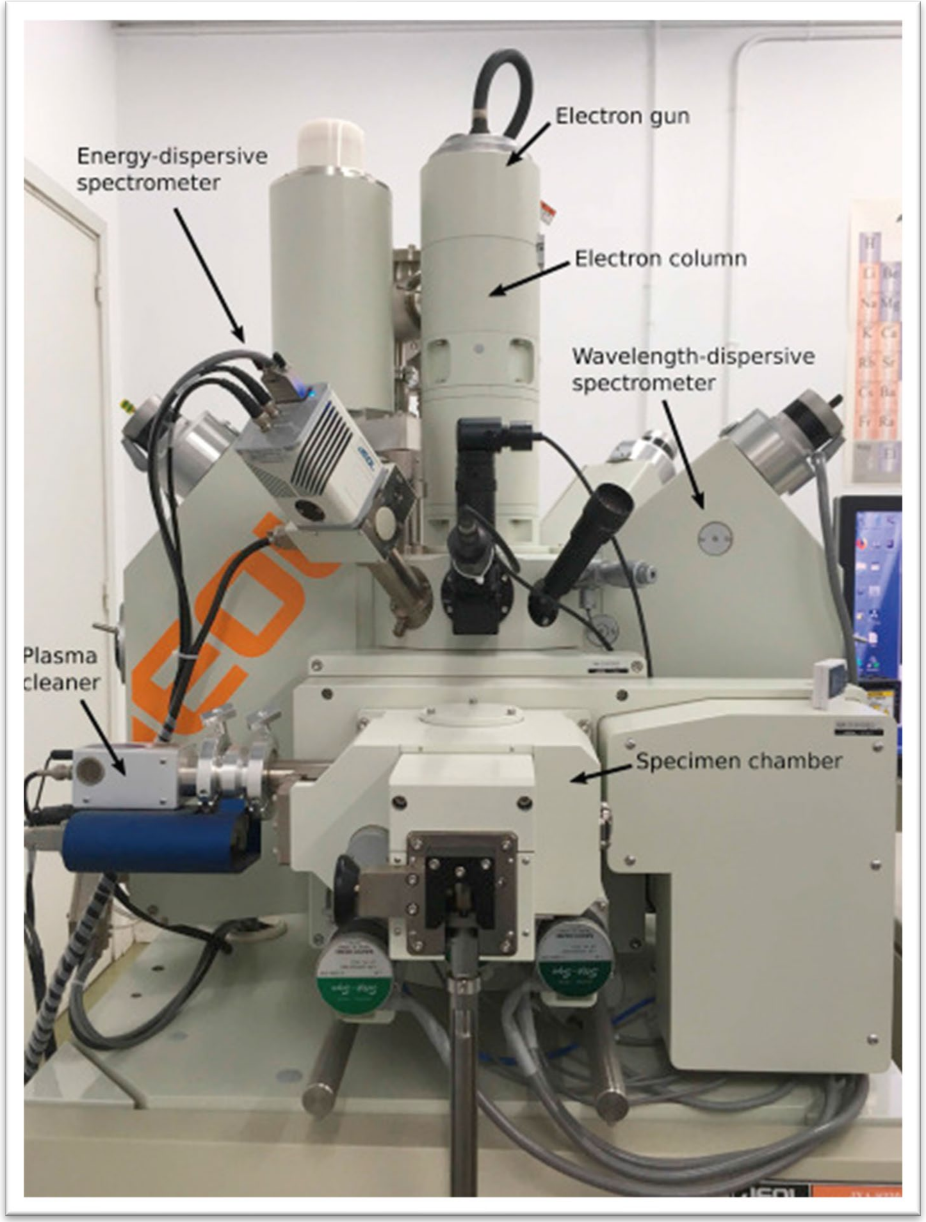
Improve spectral resolution to separate peak overlaps

What is Wavelength Dispersive X-ray Spectroscopy?

- X-ray microanalytical technique used in SEM (EPMA)
- Utilizes Bragg's law of x-ray diffraction (W instead of E)
- Detection limit 10x lower than EDS (0.01 wt%)
- Measures one element at a time with high spectral resolution (2-20 eV)
- Analysis of minor and trace elements and separate peak overlaps
- Point analysis
- Standard based analysis



S Kα = 2.3 keV
Mo Lα = 2.29 keV

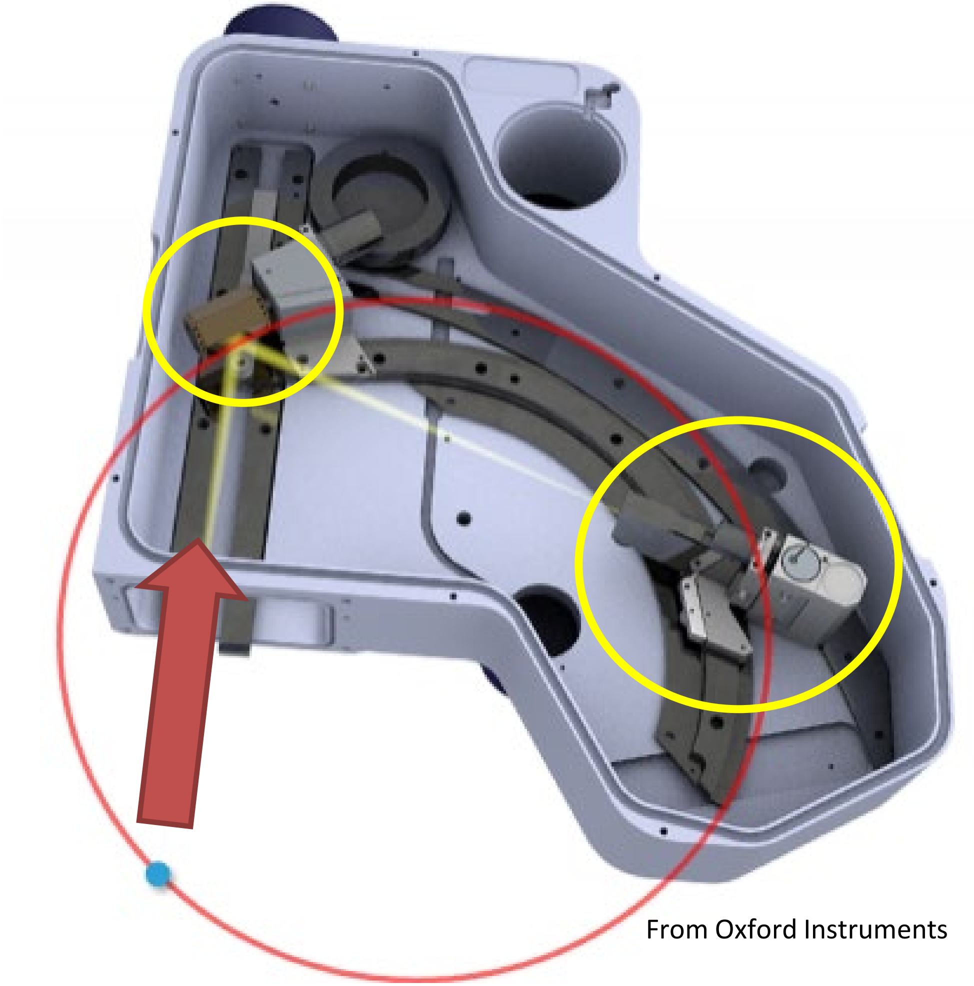

Electron gun
Energy-dispersive spectrometer
Electron column
Wavelength-dispersive spectrometer
Plasma cleaner
Specimen chamber


JEOL

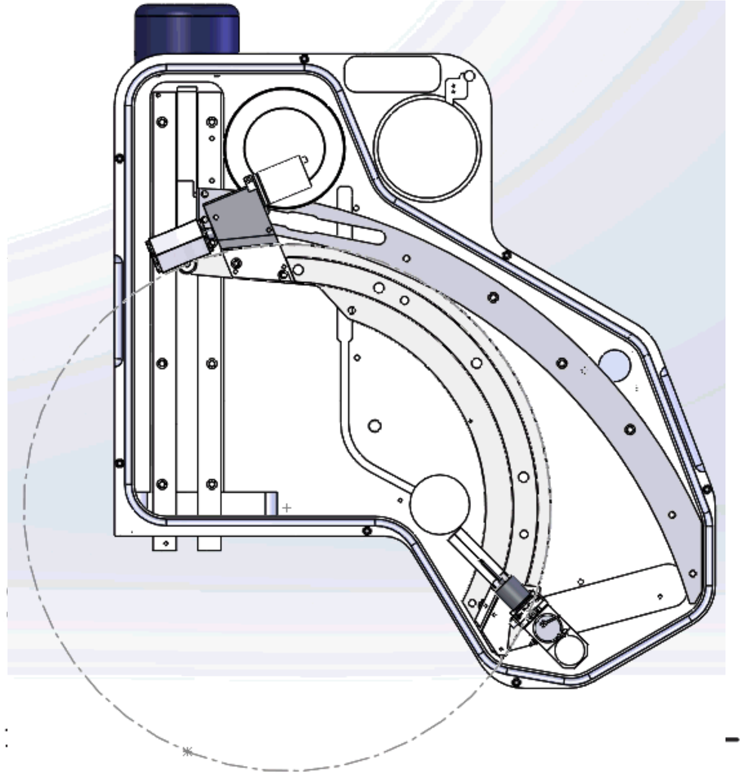
X-rays enter the detector

Diffract at crystal of known d

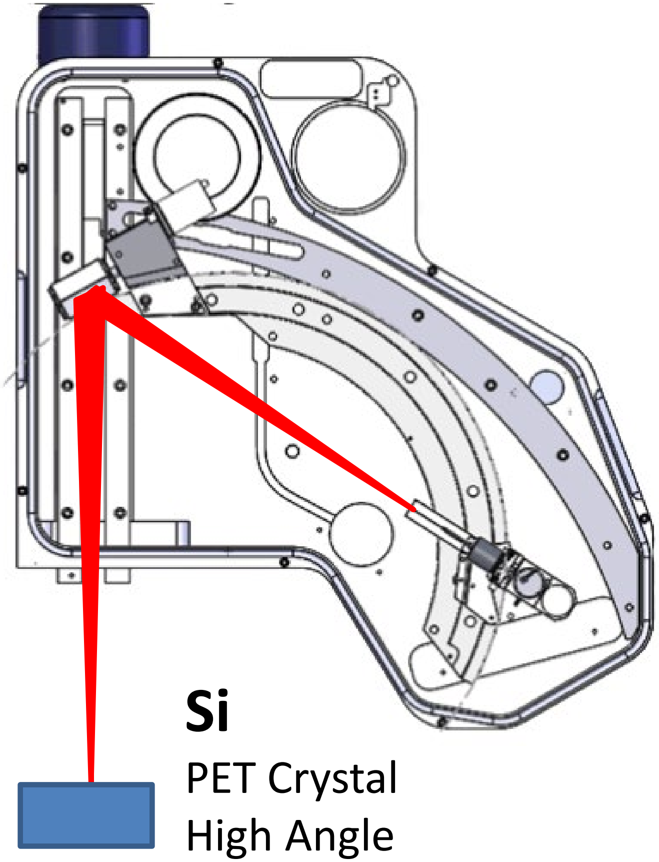
X-rays enter detector and counted

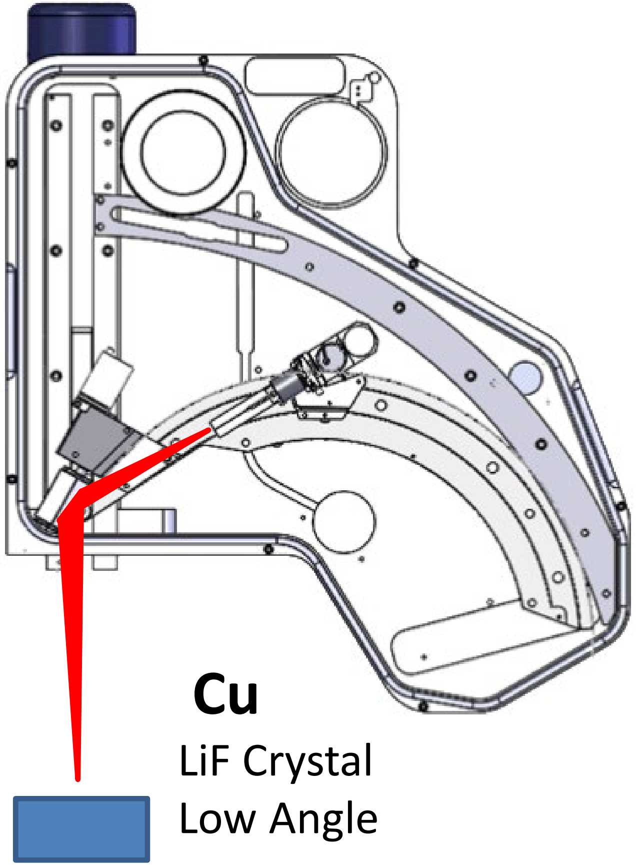


From Oxford Instruments



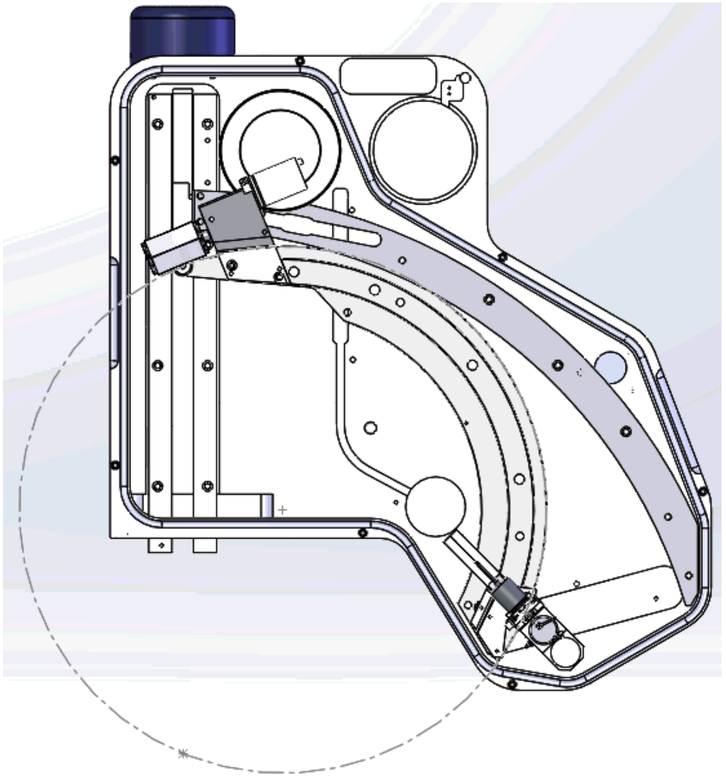
Rowland circle geometry



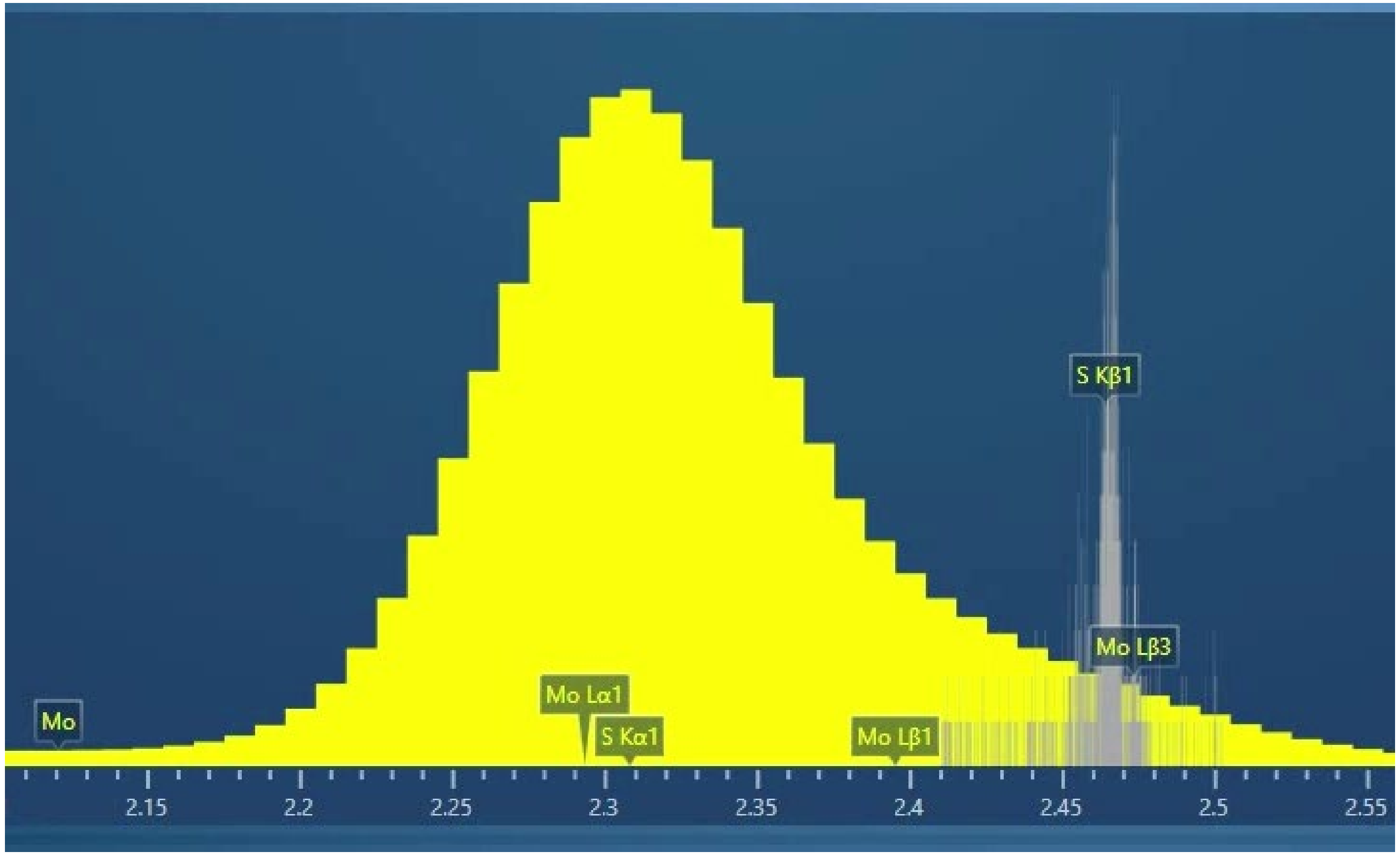


Analyzes one element at a time

Diffraction Crystals

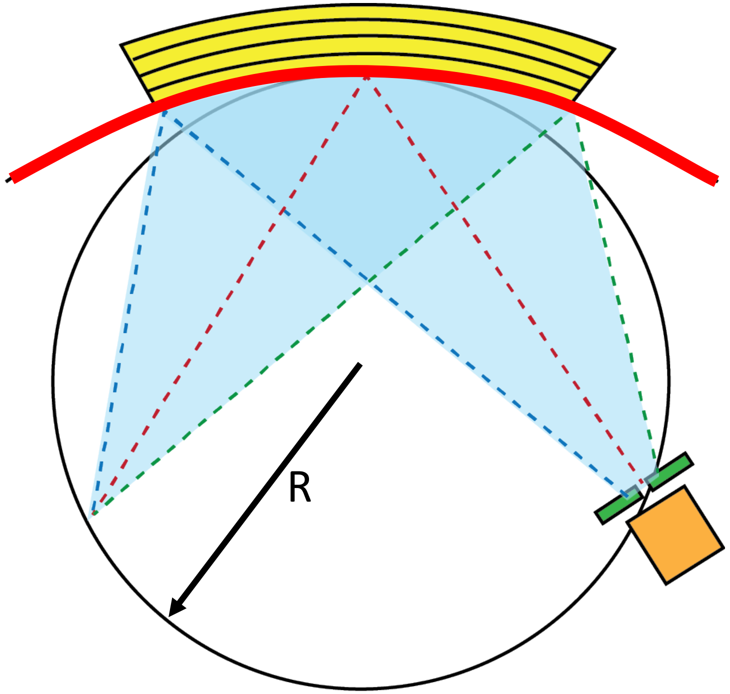


Rowland circle geometry



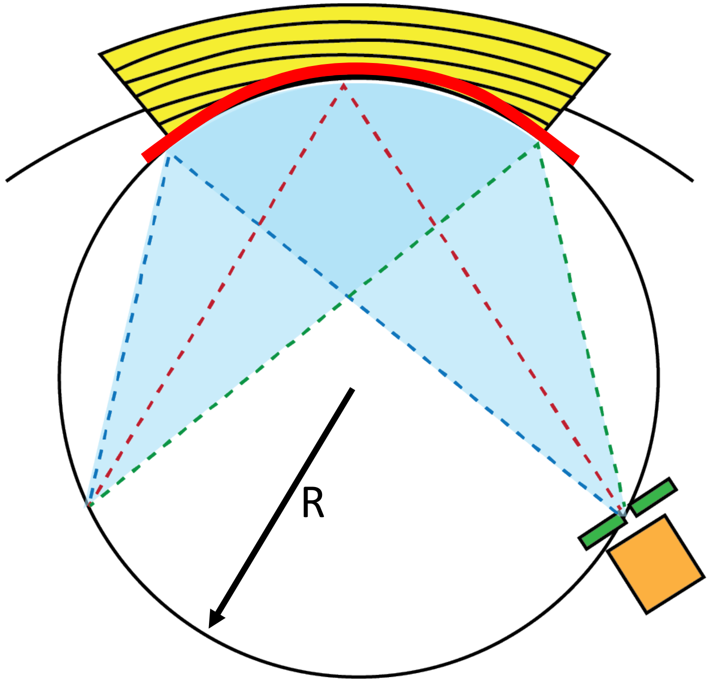
Analyzes a spot – sample stationary

Johann Crystal



Imperfect Convergence
Low sensitivity and low resolution

Johansson Crystal



Perfect Convergence
High sensitivity and high resolution

Crystals

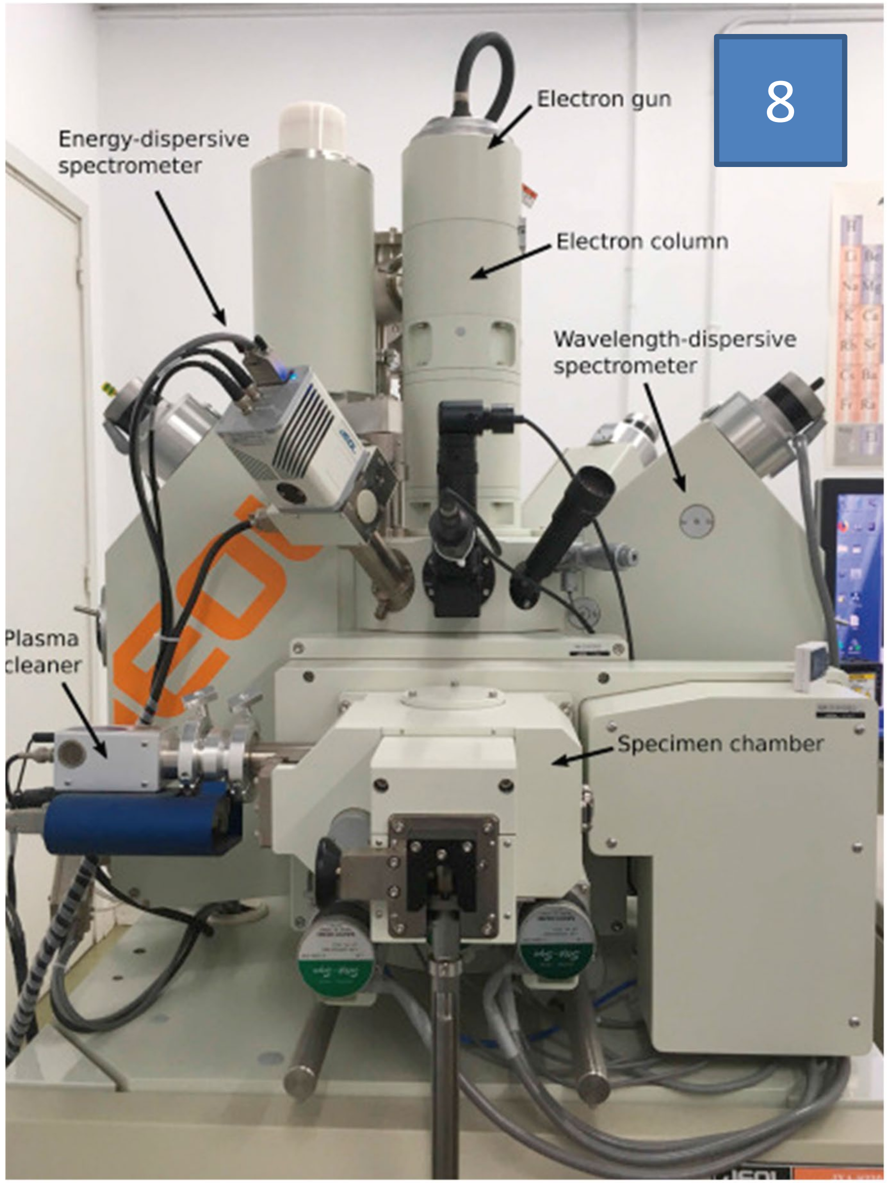
$E = 12.396 / \lambda$

E = energy (keV)
λ = X-ray wavelength (Å)

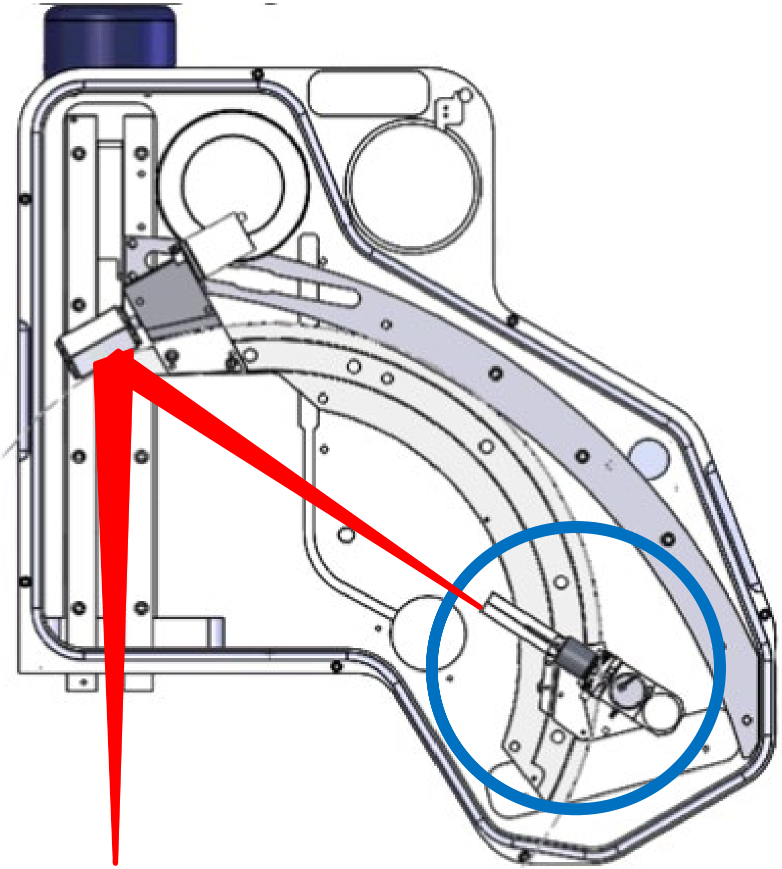
- Multiple crystals needed to span the energy range of elements
- Lattice spacing of the crystal determines energy range
- WD detectors contain many crystals

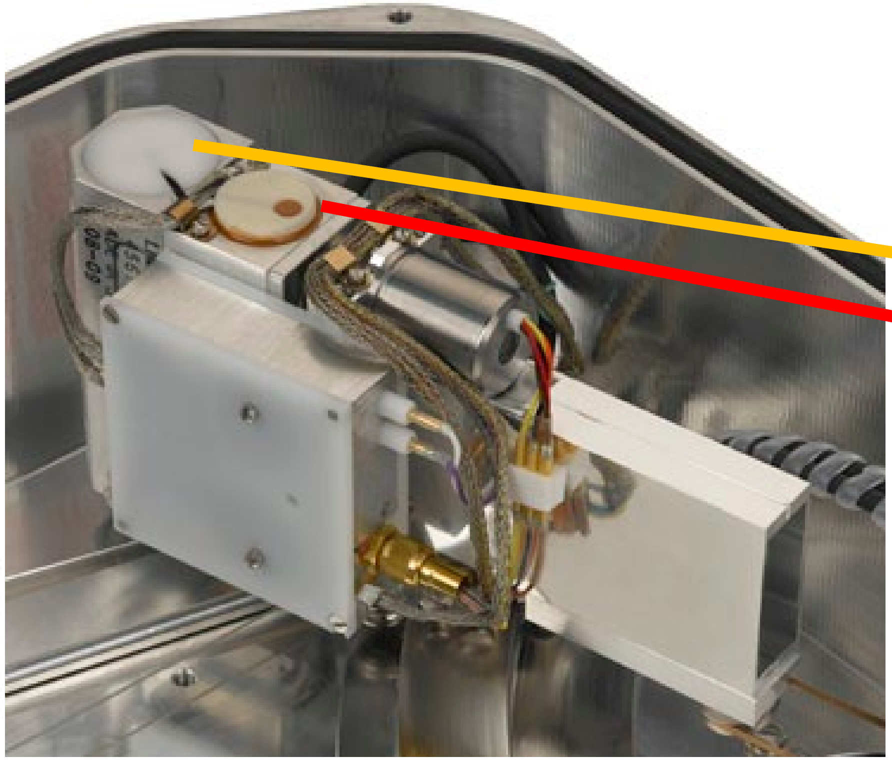
Crystal	2d (nm)	Energy Range (keV)	Element Range (K Line)	Crystal Geometry Type	Optimized Element
LSM200	19.7	0.07 - 0.22	Be to B	Johann	B
LSM-80	7.8	0.17 - 0.56	B to O	Johann	C and N
LSM-60	6.0	0.22 - 0.73	C to F	Johann	O
TAP	2.575	0.52 - 1.70	O to Al	Johansson	
PET	0.8742	1.54 - 4.99	Si to Ti	Johansson	
LiF	0.40267	3.33 – 10.84	Ca to Ge	Johansson	

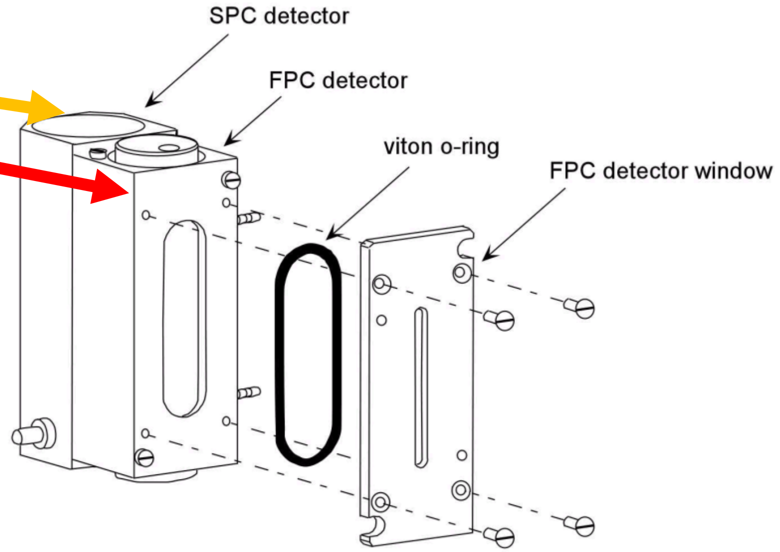
Crystals


8
Electron gun
Energy-dispersive spectrometer
Electron column
Wavelength-dispersive spectrometer
Plasma cleaner
Specimen chamber


OXFORD INSTRUMENTS



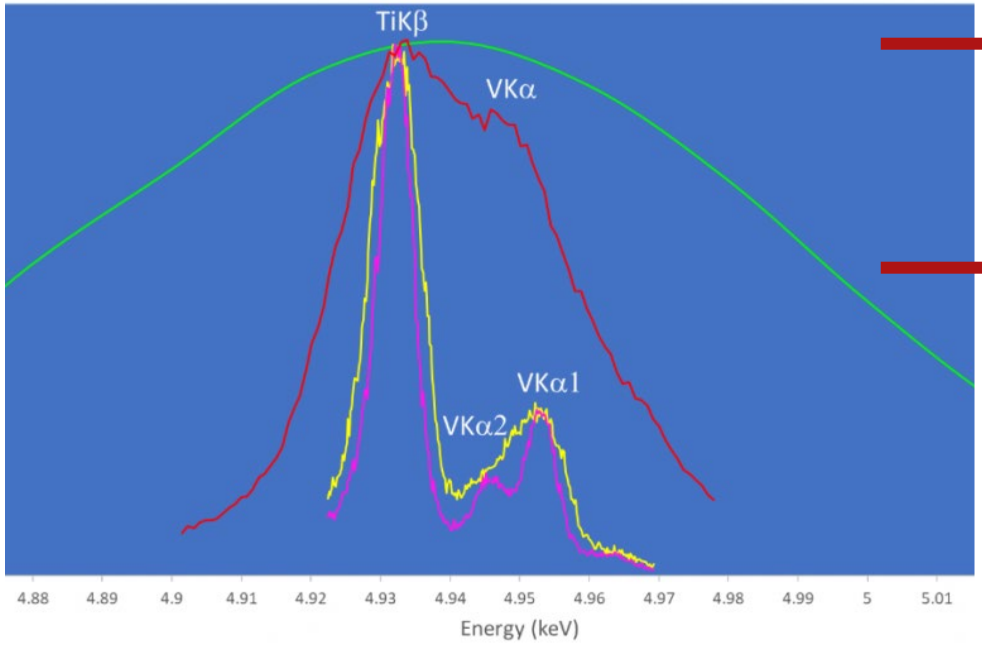


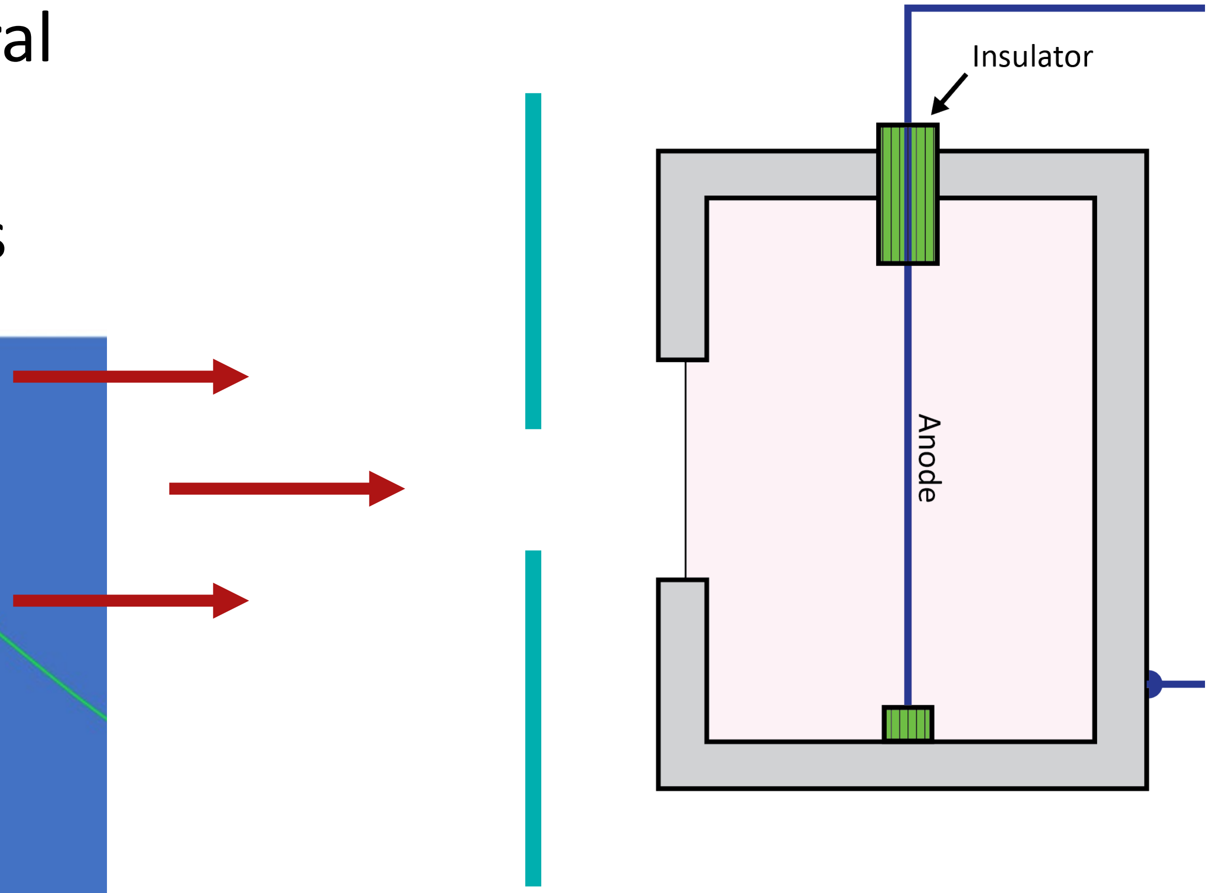


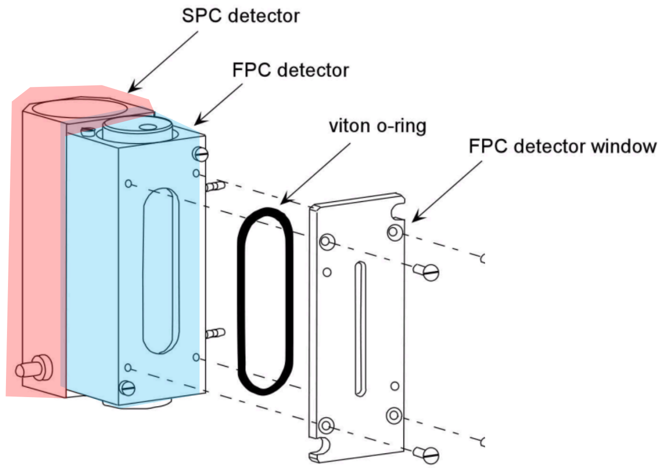
From Oxford Instruments

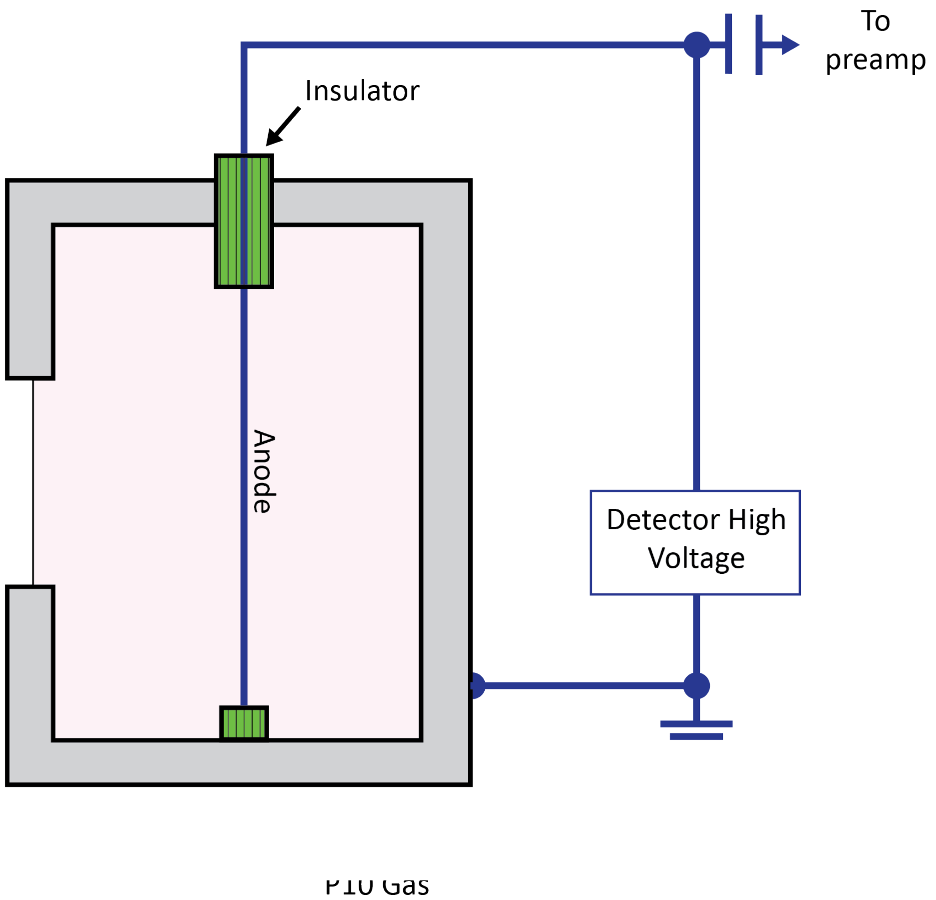
Entrance slit

- **Smaller** – increased spectral resolution
- **Wider** – more x-ray counts







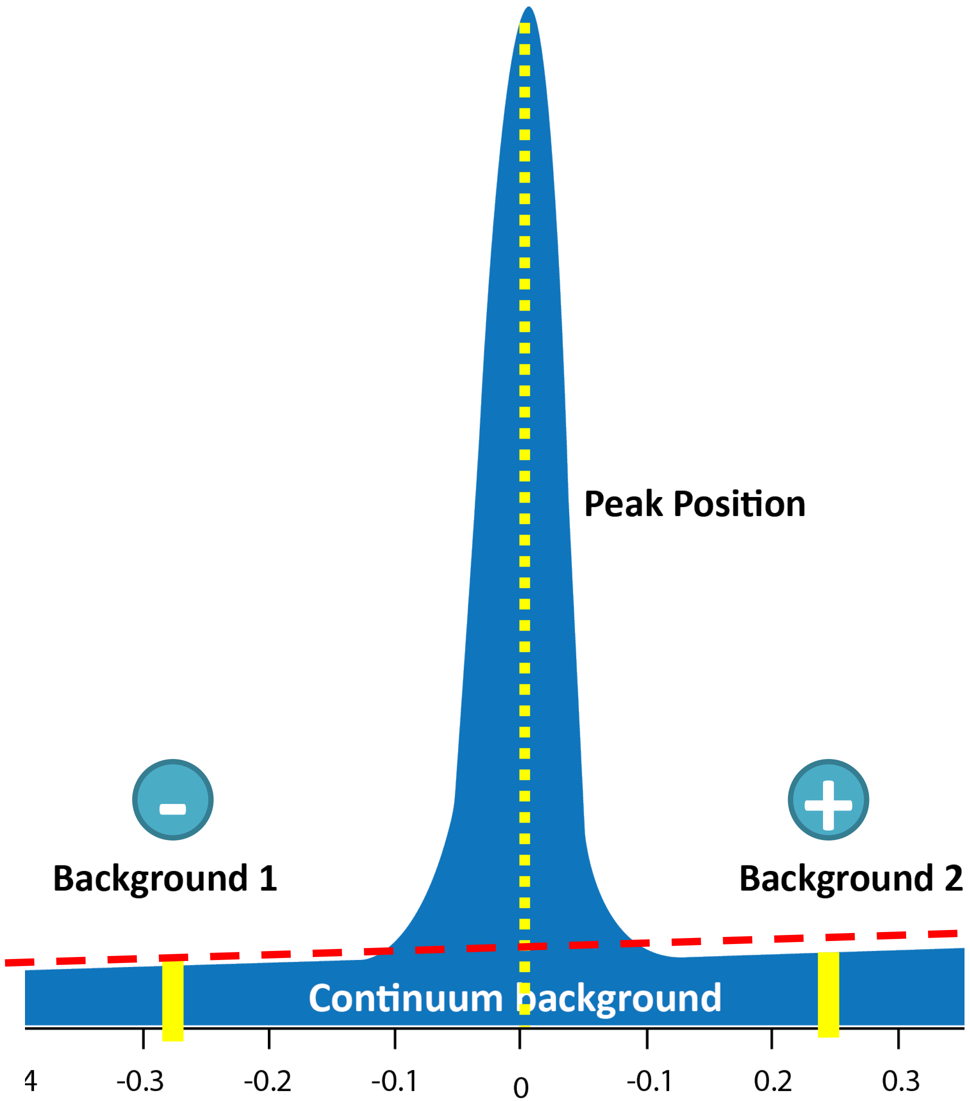


Sealed Proportional Counter (SPC)

- Sealed Xe gas
- Performs best with high Energy X-rays (>Fe Kα)

Flow Proportional Counter (FPC)

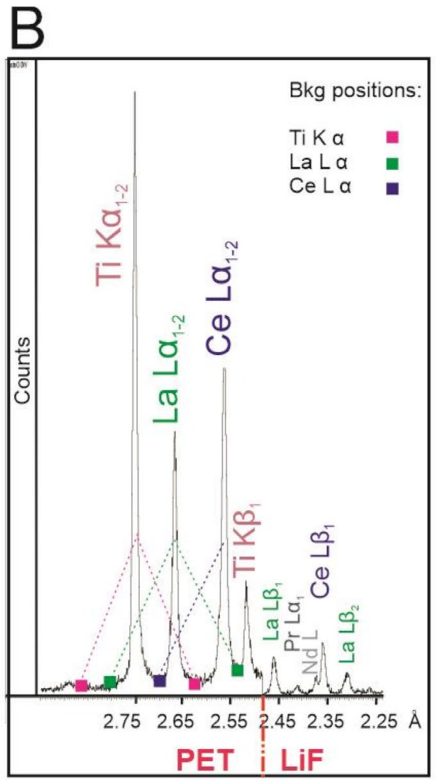
- Flowing P-10 (10% CH_4 balance Ar)
- Performs best on low Energy x-rays (<Fe Kα)



A

			- bckg	Peak	+bckg
PET 2.4828 - 7.400 Å	Ti Kα	Å	2.63	**2.7497**	2.86
		keV	4.7142	**4.509**	4.3201
	La Lα	Å	2.5299	**2.6656**	2.8099
		keV	4.9007	**4.6512**	4.4124
	Ce Lα	Å	*	**2.5615**	2.7
		keV		**4.8402**	4.592
	V Kα	Å	2.4	**2.5048**	2.6199
		keV	5.166	**4.9498**	4.7324
LiF 1.1436 - 2.4827 Å	Pr Lα	Å	2.3299	**2.463**	2.5999
		keV	5.3214	**5.0338**	4.7688
	Nd Lα	Å	2.24	**2.3703**	2.5099
		keV	5.535	**5.2307**	4.9398
	Sm Lα	Å	2.0699	**2.1998**	2.3399
		keV	5.9898	**5.6361**	5.2986

B



The Effect of X-ray Energy Overlaps on the Microanalysis of Chevkinite (Ce, La, Ca, Th)$_4$(Fe^{2+}, Mg)$_2$(Ti, Fe^{3+})$_3$Si$_4$O$_{22}$ Using SEM EDS-WDS

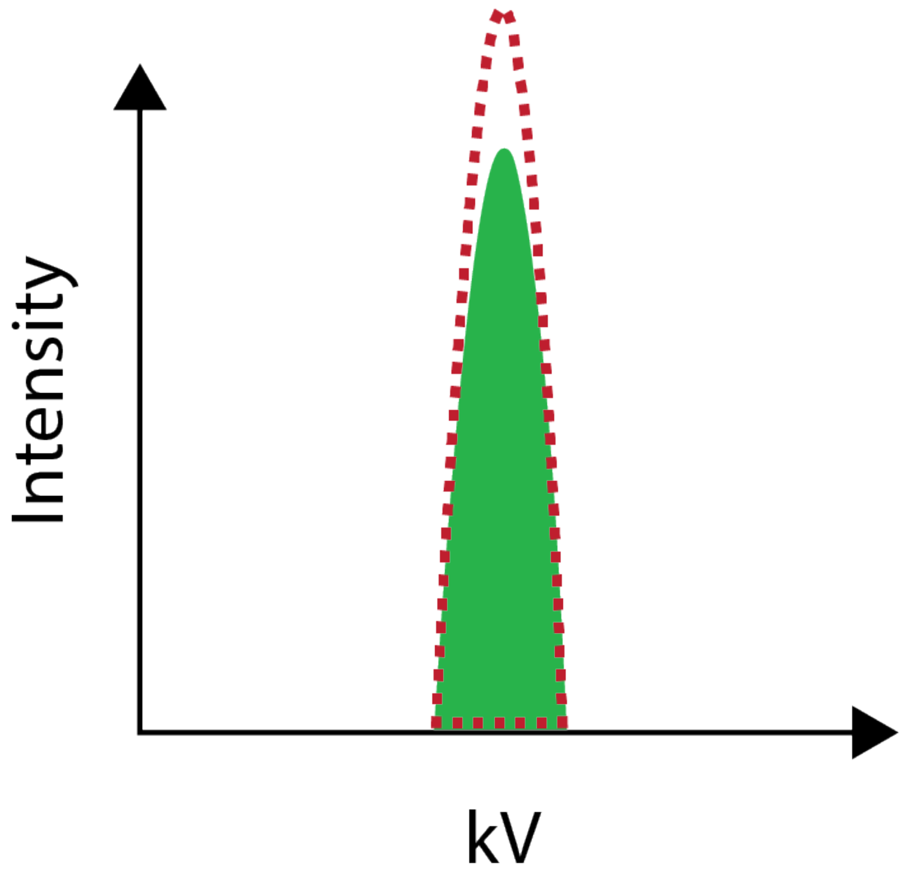
Lacinska et al., 2021

WD Quantification

$$\frac{C^{A}_{unk}}{C^{A}_{stan}} \approx \frac{I^{A}_{unk}}{I^{A}_{stan}} = k_A$$

$$C_{A\,(unk)} = k_A C_{A\,(stan)}$$

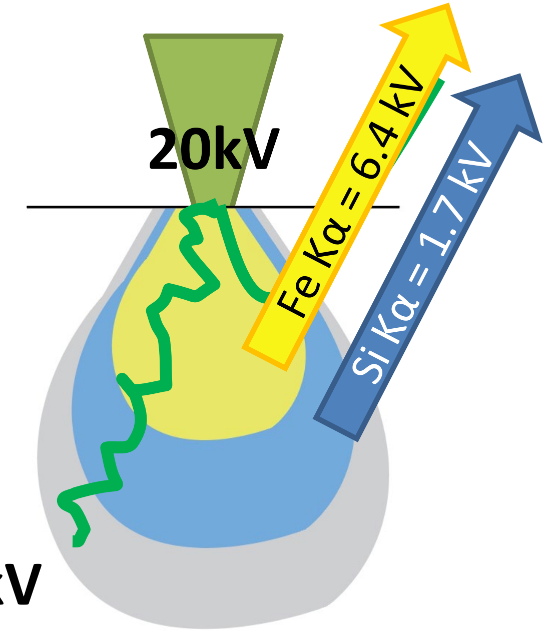
$$C_{A\,(unk)} = k_A \frac{ZAF_i^{stan}}{ZAF_i^{unk}} C_{A\,(stan)}$$



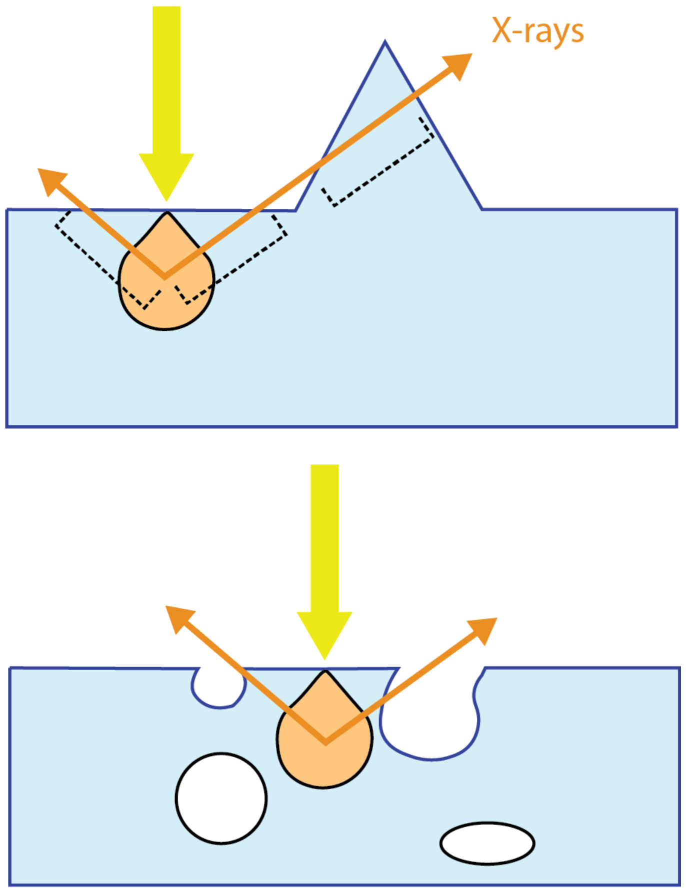
Matrix Effects

Mean Atomic Mass (Z)

- Backscattering – BSE do not generate x-rays
- Stopping power

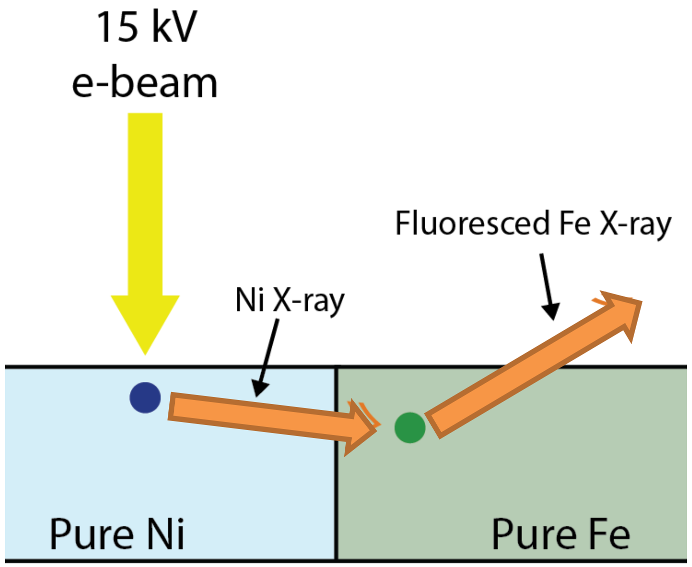


Absorption (A)



Fluorescence (F)

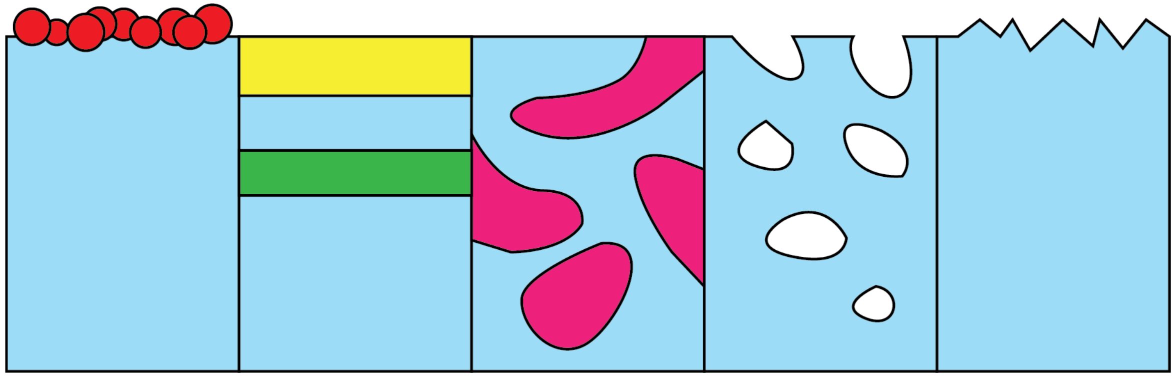
- X-ray traveling through sample has energy $E_x > E_c$ of element B



$E_{NiK\alpha} = 7.47$ kV FeKα $E_c = 7.11$ kV

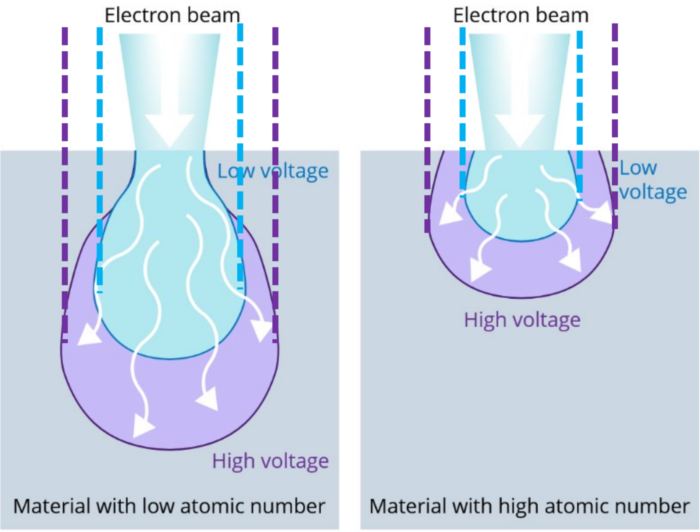
Quantitative WDS (and EDS!)

- Flat
- Homogenous
- Beam stable
- Good standards
  - As much like you sample as possible so they have similar matrix effects



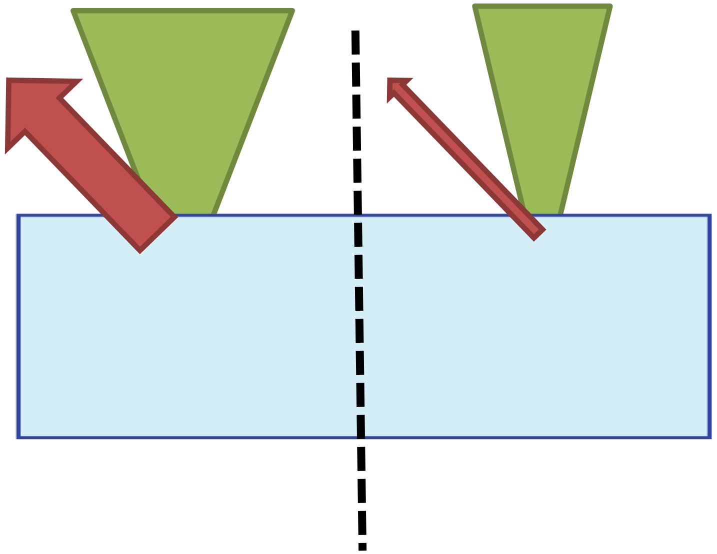
Accelerating Voltage

- Choose appropriate kV
- Typically, >15 kV
- Overvoltage
- Spatial resolution

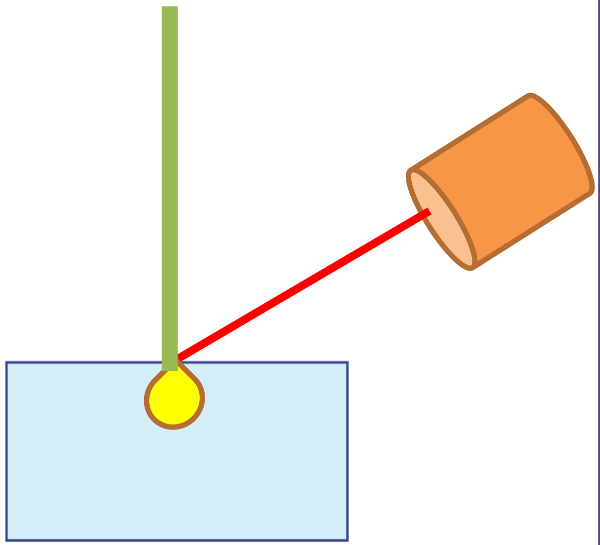


Probe Current

- If your sample can handle it, a higher probe current = more x-ray counts



Working Distance



Applications

- Materials science
- Metals and alloys
- Geology and petrology
- Aerospace automotives
- Energy generation and storage
- Life sciences
- Semiconductors

	Olivine analysis		Element wt.%							
			Si	Fe	Ni	Mn	Mg	Ca	O	Total
Published EPMA data	Electron microprobe	Average	16.87	25.90	0.03	0.42	18.25	0.02	38.79	100.28
		1σ	*0.085*	*0.396*	*0.011*	*0.021*	*0.211*	*0.008*	*0.172*	*0.474*
Data collected with **AZtecWave**	SEM WDS-only	Average	16.79	25.39	0.04	0.43	18.56	0.01	38.75	99.97
		1σ	*0.327*	*0.309*	*0.014*	*0.027*	*0.310*	*0.004*	*0.268*	*0.487*
	SEM EDS+WDS	Average	17.02	25.24	0.04	0.43	18.14	0.01	38.69	99.57
		1σ	*0.059*	*0.320*	*0.014*	*0.027*	*0.204*	*0.004*	*0.118*	*0.201*

EPMA reference - Gardner, R.L., Piazolo, S., Daczko, N.R. and Trimby, P., 2020. Microstructures reveal multistage melt present strain localisation in mid-ocean gabbros. Lithos, 366, p.105572.

From Oxford Instruments

Seddio, 2016

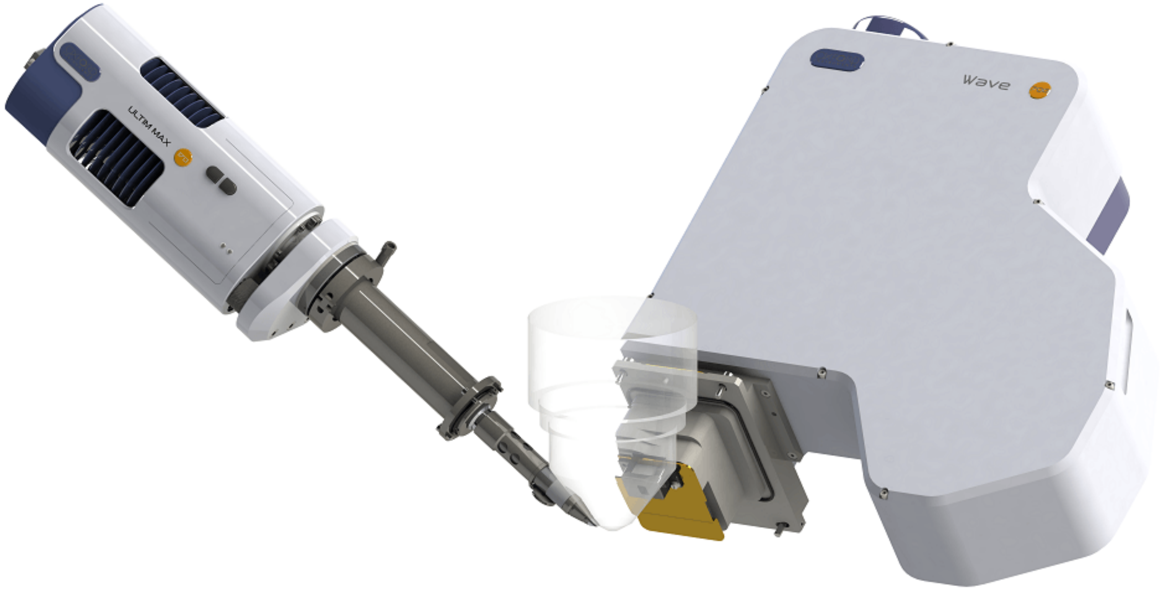
- EDS for major
- WDS for minor

- WDS is a longer analysis, so only use it for trace elements or peak overlap makes it faster!

Example quantitative results obtained for a ref. glass standard with elements <0.2 wt. %:
(Un-normalised analytical totals, oxygen calculated by stoichiometry)

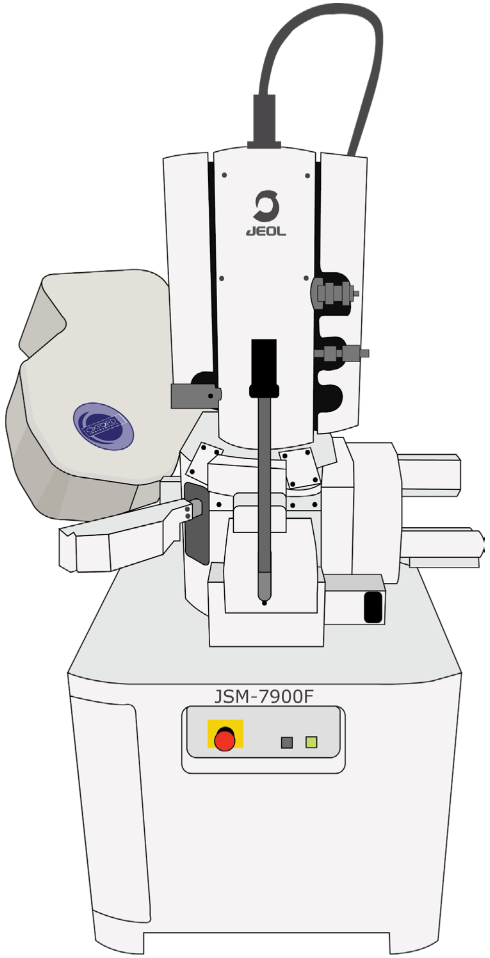
Element	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	As	Ba	Total
Reference (wt. %)	46.1	9.44	0.16	1.46	33.22	0.05	1.67	7.64	0.008	0.03	0.02	0.11	99.9
Technique	Cal.	EDS	WDS	EDS	EDS	WDS	EDS	EDS	WDS	WDS	WDS	WDS	-
Ave. (wt. %) (4 points)	46.02	8.86	0.154	1.51	33.46	0.033	1.58	7.43	0.008	0.028	0.020	0.085	99.2
1σ	0.08	0.09	0.004	0.03	0.06	0.002	0.01	0.07	0.001	0.001	0.001	0.011	0.2

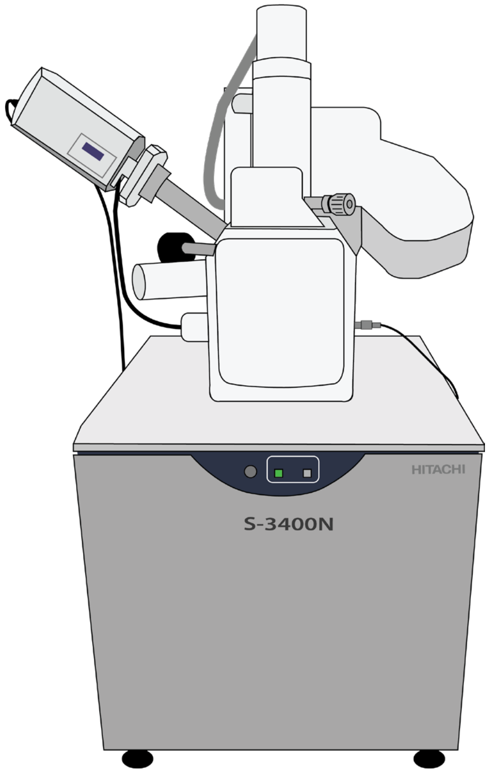
From Oxford Instruments



WDS at NUANCE

JEOL JSM 7900F OI Wave 700	
LSM-200	Be to B
LSM-60	C to F
TAP	O to Al
PET	Si to Ti
LiF	Ca to Ge





Hitachi S-3400 OI Wave 500	
LSM-80	B to O
TAP	O to Al
PET	Si to Ti
LiF	Ca to Ge

EPIC has a metals and minerals standard block – it is always better to have a standard like your sample!

Thank you!

Thank you, Rosie Jones
from Oxford Instruments

From Oxford Instruments

Tirzah Abbott

SEM Facility Manager

Tirzah.abbott@northwestern.edu