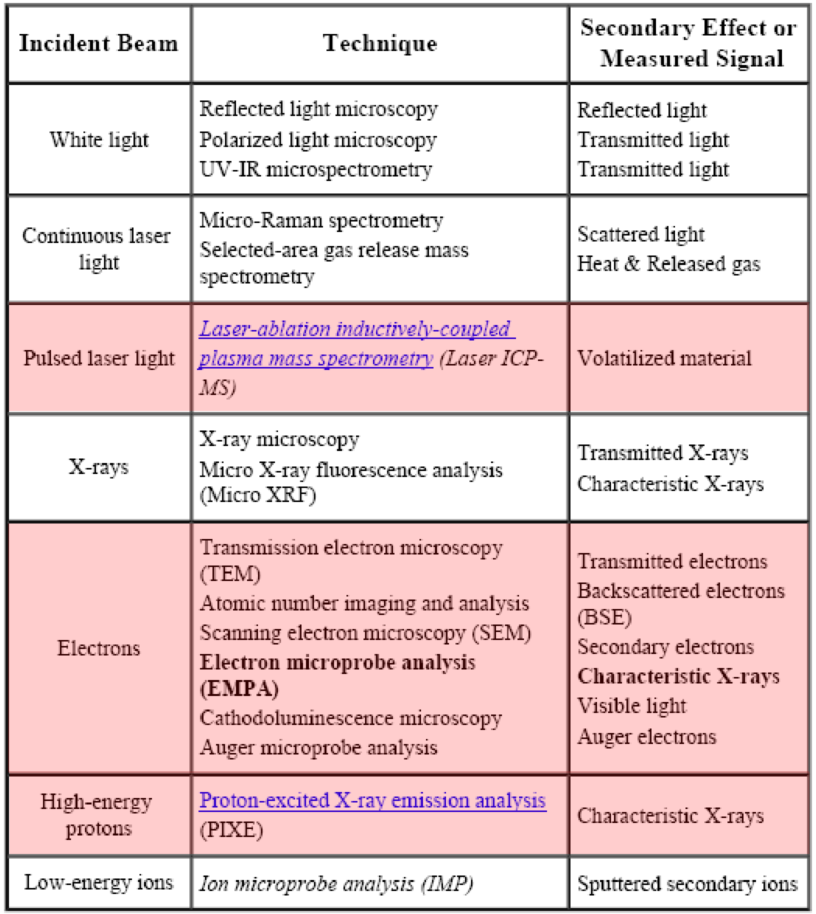
Microbeam Techniques in Geology



Incident Beam	Technique	Secondary Effect or Measured Signal
White light	Reflected light microscopy Polarized light microscopy UV-IR microspectrometry	Reflected light Transmitted light Transmitted light
Continuous laser light	Micro-Raman spectrometry Selected-area gas release mass spectrometry	Scattered light Heat & Released gas
Pulsed laser light	*Laser-ablation inductively-coupled plasma mass spectrometry (Laser ICP-MS)*	Volatilized material
X-rays	X-ray microscopy Micro X-ray fluorescence analysis (Micro XRF)	Transmitted X-rays Characteristic X-rays
Electrons	Transmission electron microscopy (TEM) Atomic number imaging and analysis Scanning electron microscopy (SEM) **Electron microprobe analysis (EMPA)** Cathodoluminescence microscopy Auger microprobe analysis	Transmitted electrons Backscattered electrons (BSE) Secondary electrons **Characteristic X-rays** Visible light Auger electrons
High-energy protons	Proton-excited X-ray emission analysis (PIXE)	Characteristic X-rays
Low-energy ions	*Ion microprobe analysis (IMP)*	Sputtered secondary ions

- Electron microprobe
- Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS)
- Proton-excited X-ray emission analysis (PIXE)

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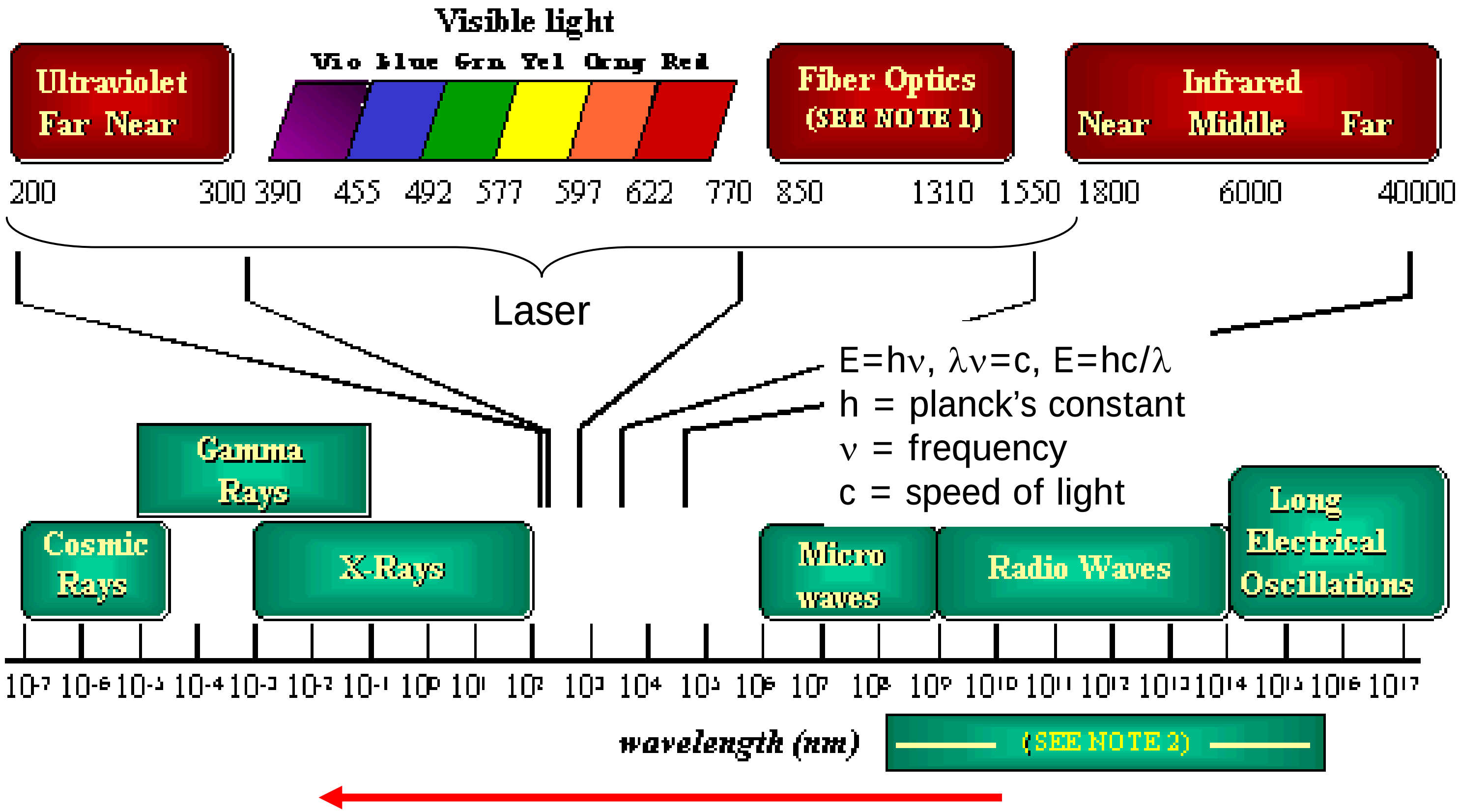
Spectrum chart

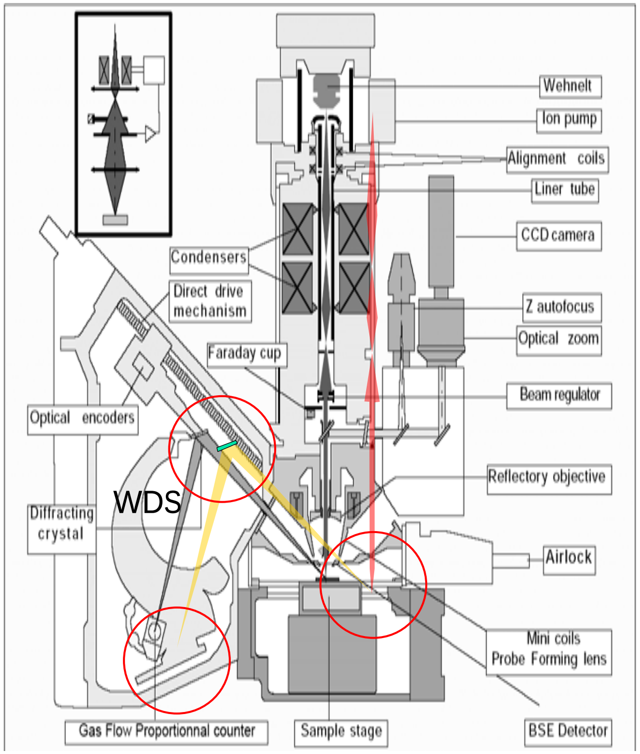


Laser

E=hν, λν=c, E=hc/λ
h = planck's constant
ν = frequency
c = speed of light

Energy and frequency increases

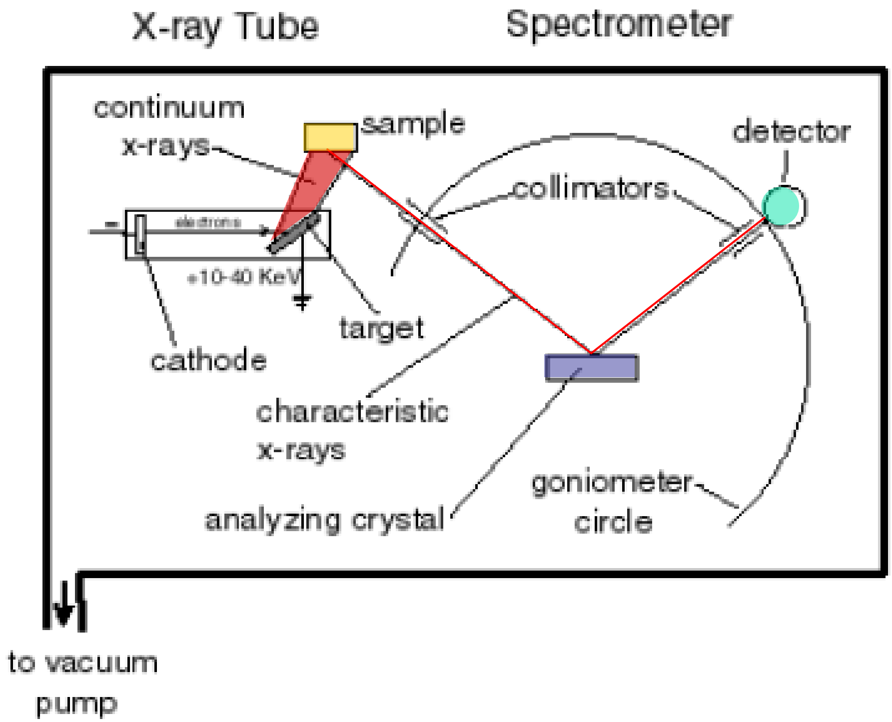
Overview of Electron Microprobe



SE, EDS, CL

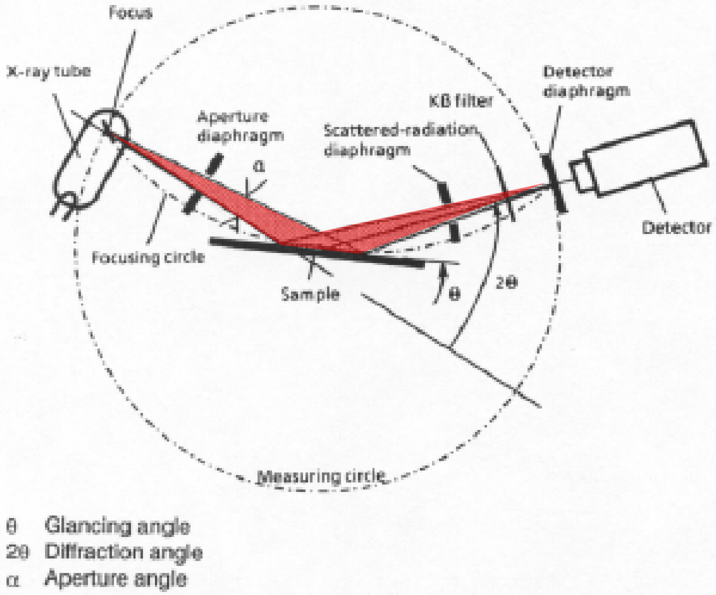
- Use high-energy beam of electrons to generate X-rays characteristic of elements
- Electron beam is collimated and focused by a series of magnetic lenses and apertures
- Filtered by diffracting crystals and counted using detectors
- Can detect elements from ^{5}B to ^{94}Pu down to ~100 ppm
- Non-destructive microbeam method for determining chemical compositions of solid materials

X-ray Fluorescence (XRF)



- Uses X-rays generated by an X-ray tube to excite analytical X-rays from the sample.
- Requires large homogeneous bulk samples, but can determine trace elements to the ppm level.

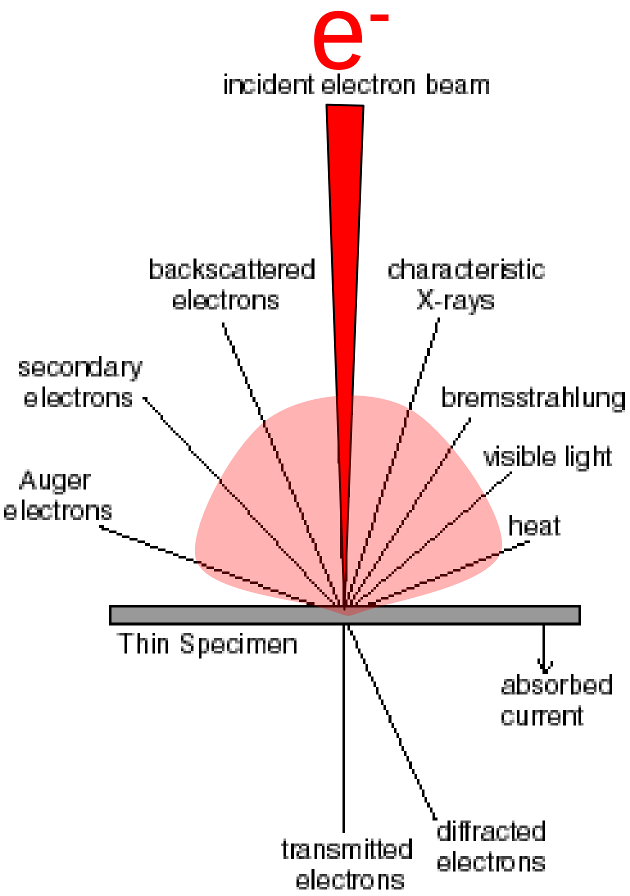
X-ray diffractometer

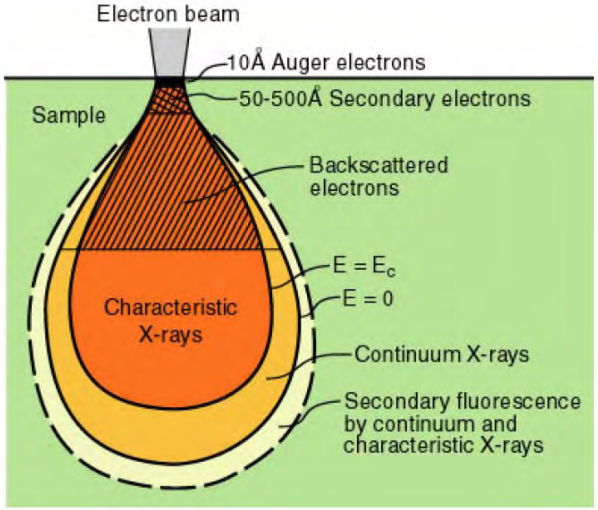


Diffractometer beam path in θ/2θ mode

- Unit cell dimension
- Crystal structure
- Phase identification

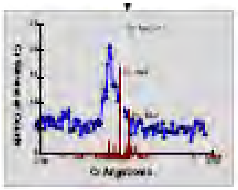
Effects of electron bombardment



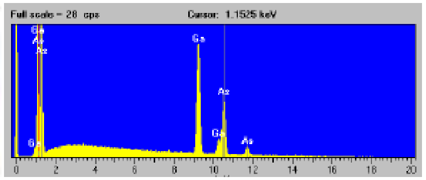


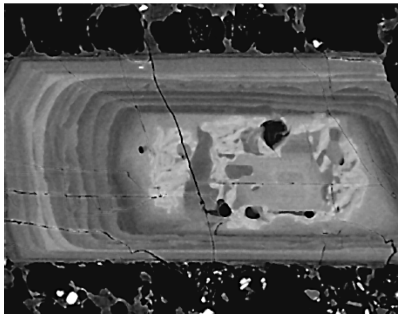
Electron-sample interaction

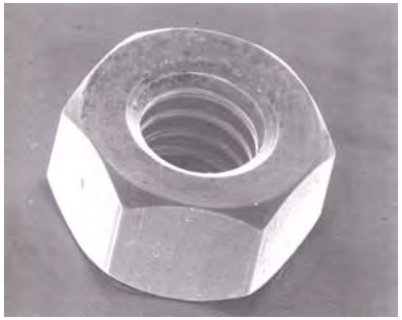
WDS



EDS







- Characteristic X-rays (WDS and EDS)

  Produced by electronic transitions within inner electron shells.

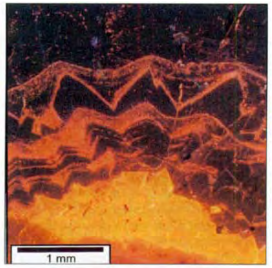
- Backscattered electrons (BSE)

  Primary electrons undergo violent collisions with atoms in the sample and are scattered back from the sample surface. The proportion of backscattered electrons is directly proportional to the mean atomic number of the sample. Backscatter from C is 8%, from U is 50%.

- Secondary electrons (SEM)

  Secondary electrons are produced by ionization of atoms in the sample by interaction with the primary beam. Secondary electrons have low energies, and cannot escape from deep within the sample. Therefore, this electron signal produces the high-resolution morphological images of a sample surface.

Electron-sample interaction



- Cathodoluminescence (CL)

  Visible light emitted by minerals bombarded by electrons. Mechanism depends on the mineral in question.

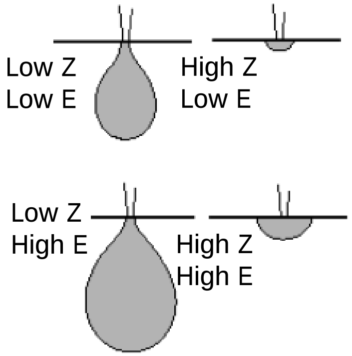
- Continuous X-rays (Continuum X-ray or Bremsstrahulung)

  Most interactions between the primary beam do not produce the characteristic x-rays discussed earlier. Many electrons from the incident beam are simply decelerated by the interactions with outer orbital shell electrons from atoms within the sample. The energy released during these decelerations produces a continuous (or bremsstrahlung) x-ray spectrum. These x-rays are noise, and are undesirable, but unavoidable.

- Auger Electrons

  When an atom is ionized in an inner shell, energy may be released by ejecting another bound electron, instead of producing an x-ray. These electrons can have characteristic energy. Most effective for low atomic number elements (<10).

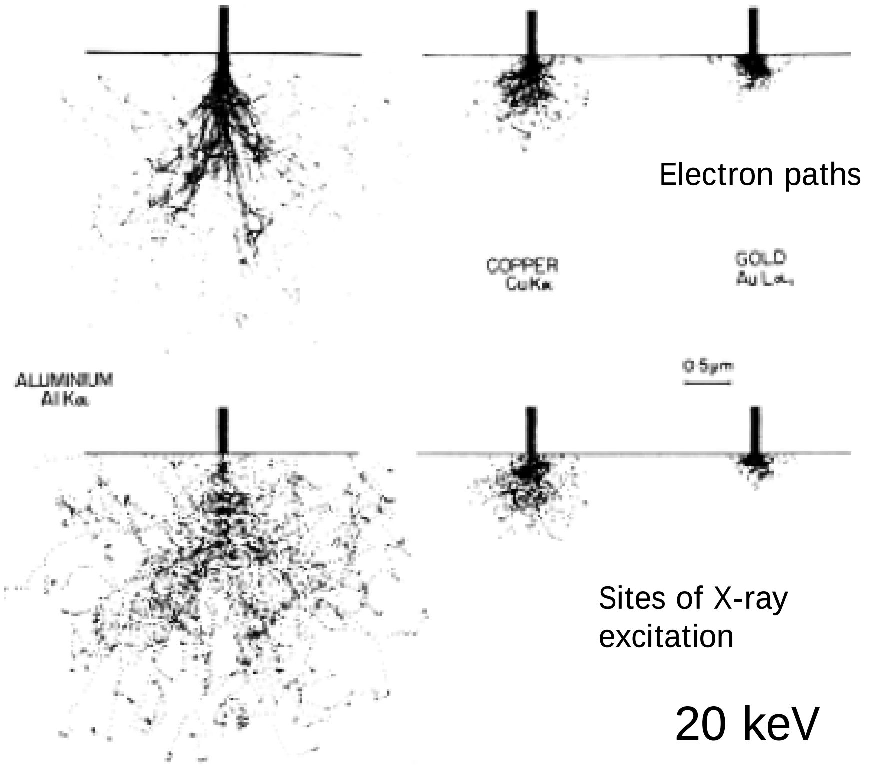
Volume of excitation



$$x\ (\mu m) = \frac{0.1\ E_o^{1.5}}{\rho}$$

where E_o = accelerating voltage (keV), and ρ = density (g/cm^3)

Al Cu Au

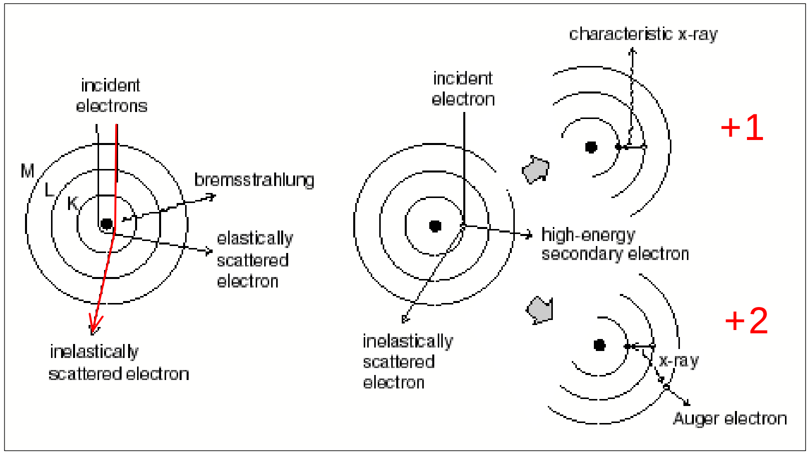


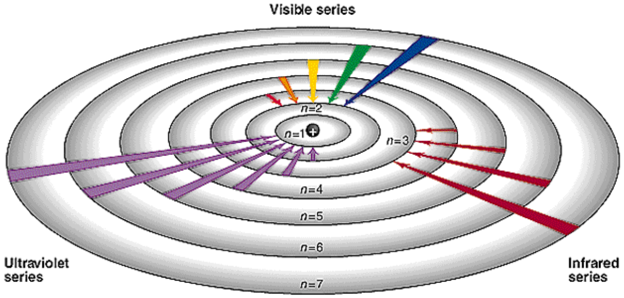
Electron paths

Sites of X-ray excitation

20 keV

Characteristic X-rays

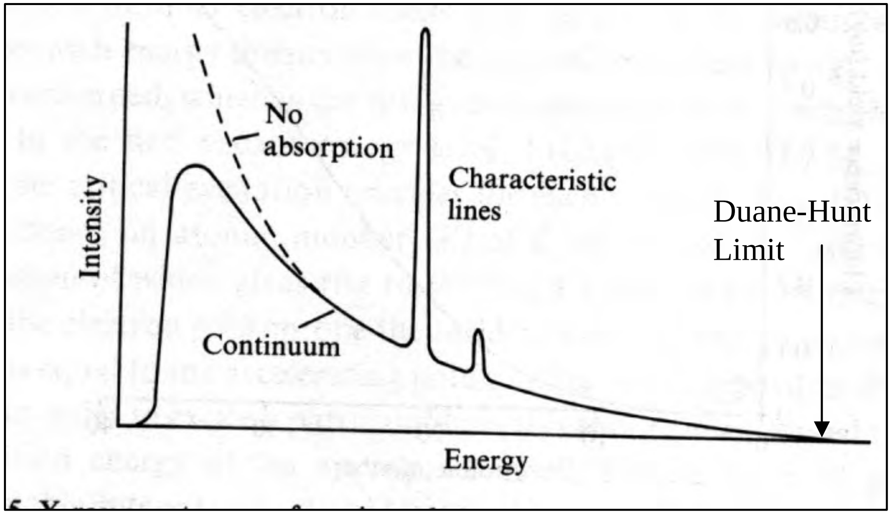




Kα: L to K-shell transition
Kβ: M to K-shell transition
Lα: M to L-shell transition
Lβ: N to L-shell transition
Mα: N to M-shell transition

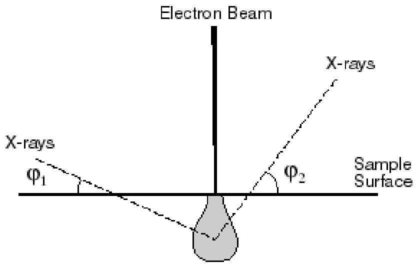
- Elastic Scattering: Trajectory changes but keep velocity
- Inelastic scattering: Keep the same trajectory but changes velocity, forming continuum X-ray (bremsstrahlung, “braking radiation”)
- Inner shell ionization (0.1 %)
- Critical ionization potential (E_c): independent on chemical structure

Continuum X-rays

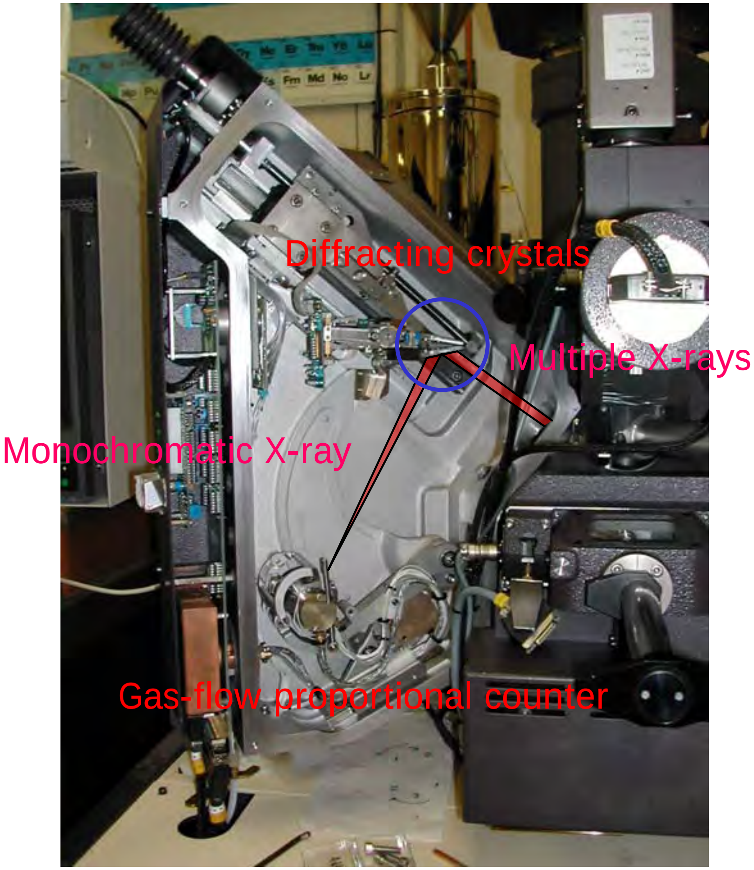


- Primary electrons can decelerate in the Coulombic field of the atom.
- The loss in energy as the electron brakes is emitted as a photon, continuum X-rays.
- The continuum intensity decreases as energy increases.
- The high energy value where the continuum goes to zero is known as the Duane-Hunt limit.
- Background level is a complex function of sample composition.

WDS spectrometers



Take-off angle



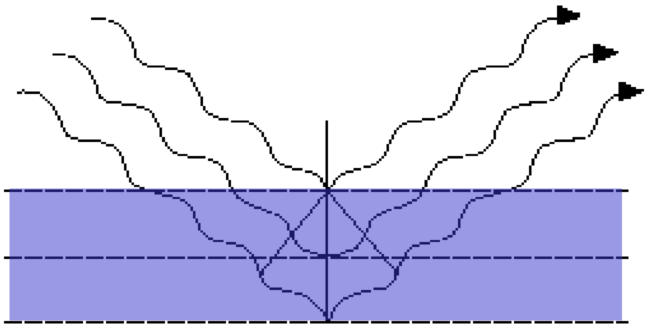
Cameca SX-100

X-rays are dispersed by diffracting crystal with only one wavelength diffracted, with only one wavelength passed to the detector

Detector is a gas-filled (sealed or flow-through) tube where gas is ionized by X-rays, yielding a massive multiplication factor (‘proportional counter’)

An electron microprobe generally has 3-5 spectrometers, with 1-4 crystals in each.

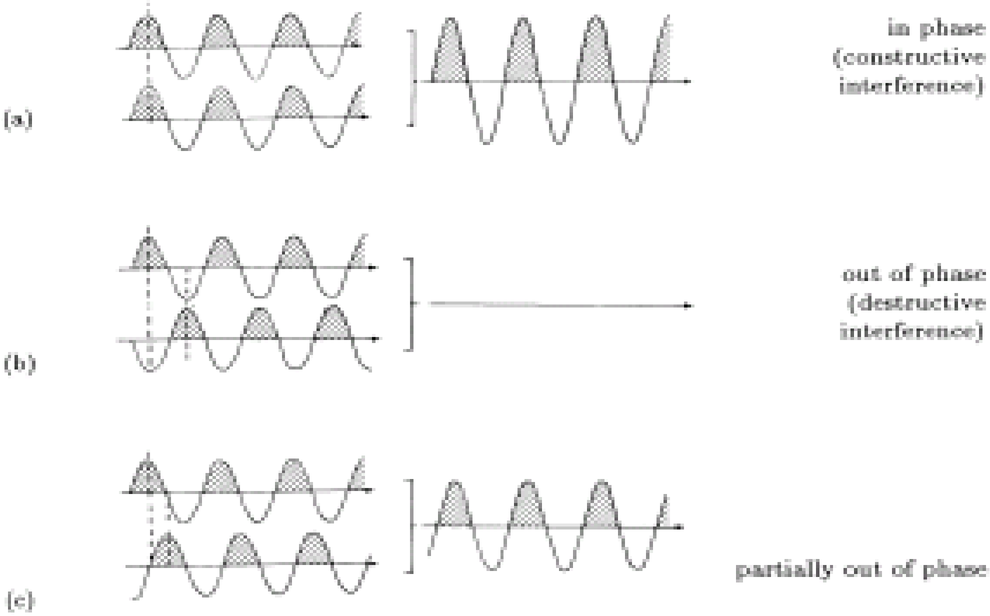
Diffraction of X-rays



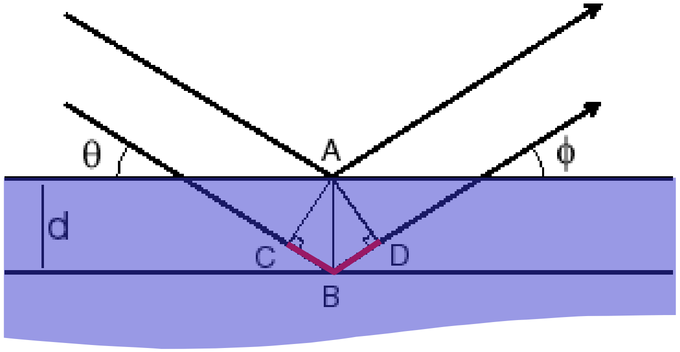
X-rays from sample

X-ray to detector

Diffracting crystal



Bragg's Law



CB = BD = d sinθ

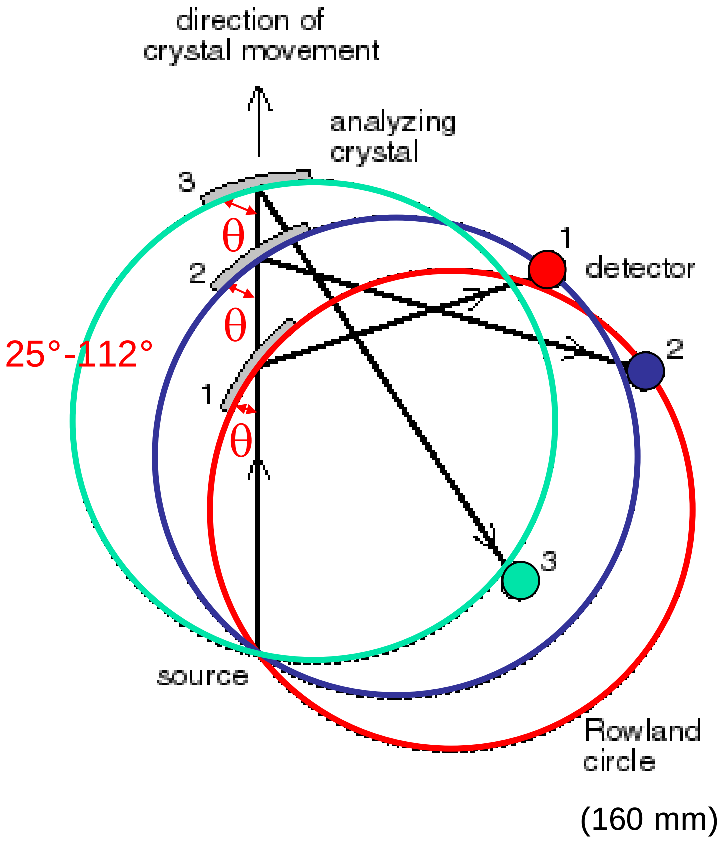
$$n\lambda = 2d \sin\theta$$

where, n = an integer (1, 2, 3…),
λ = wavelength,
d = d-spacing of the crystal,
and θ = incident angle (measured from crystal surface)

High order interference

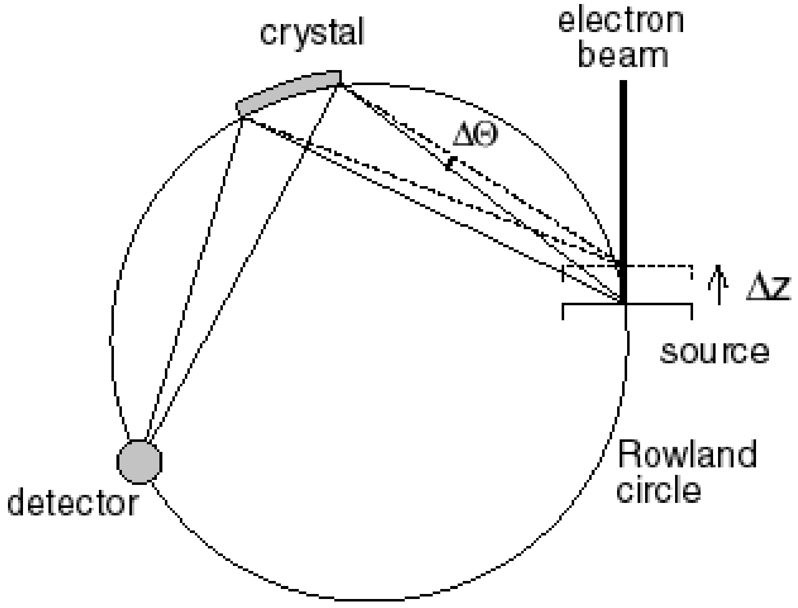
n can be >1, so other elements can cause interference if their wavelengths are at an integral fraction of the desired wavelength

Spectrometer geometry



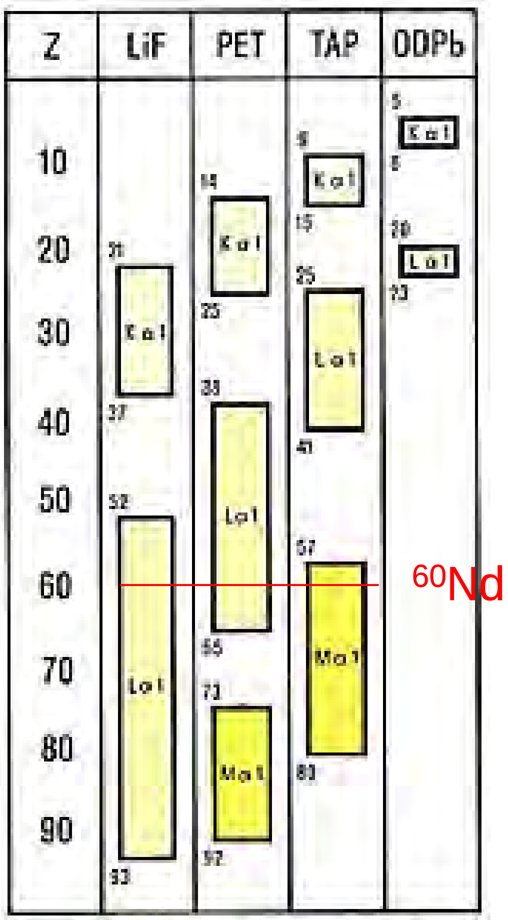
- Linear-focusing drive to change incident angles
- Sample, diffracting crystal, and detector lie on a circle (the Rowland circle).
- The distance of diffracting crystals to sample determines X-rays to be collected.

Bragg defocusing



- Changing take-off angle and thus X-ray counts reduced
- EDS is not focus sensitive

Diffracting crystals

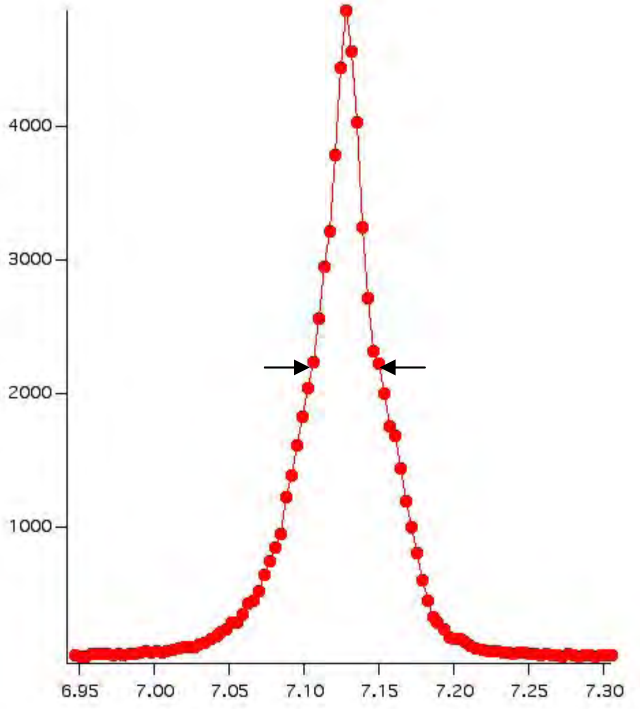


- The most commonly used crystals are:
  Lithium fluoride (LIF), 2d = 4.028 Å
  Pentaerythritol (PET), 2d = 8.742 Å
  Thallium acid pthalate (TAP), 2d = 25.75 Å

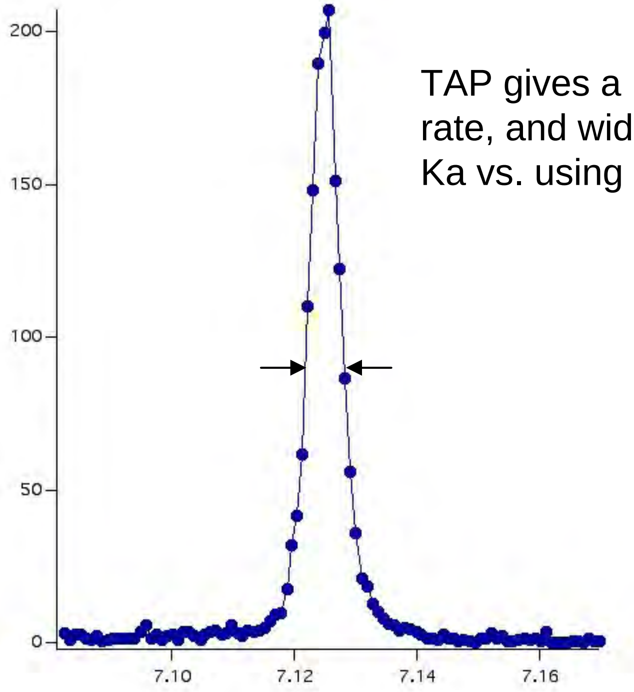
Which crystals to use?

Time and money (resolution vs. count rate)
Interferences vs. counting statistics (sharper peaks usually have lower count rates)
Stability (thermal coefficient of expansion)
Sensitivity to de-focussing
Peak shape/shift

Diffracting Crystal comparison



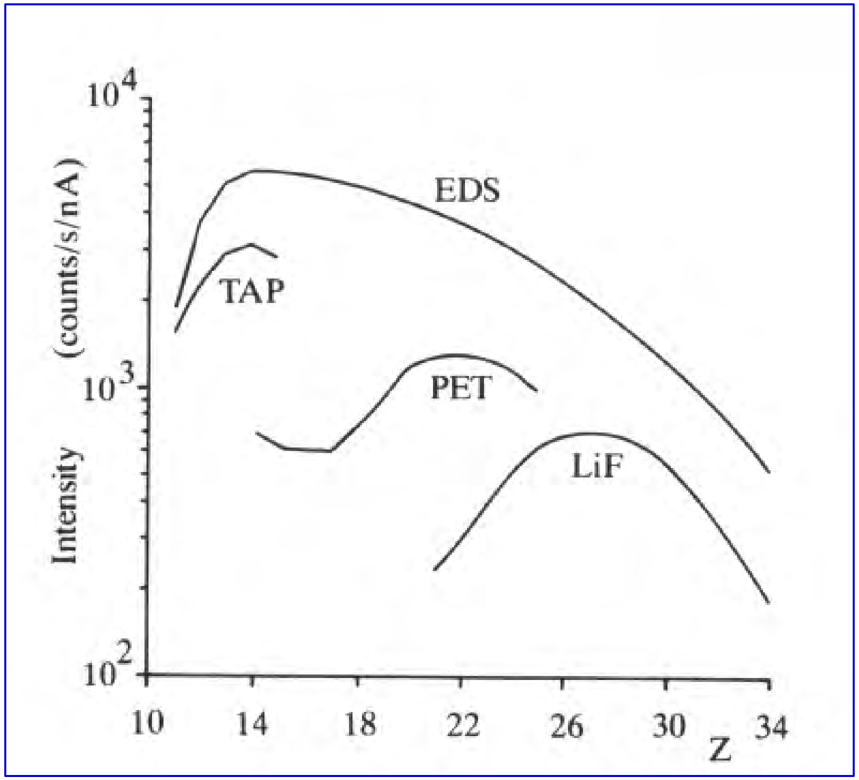
Si Kα on TAP sin θ = 27714
P/B= 4862/40=122 FWHM=0.038 Å



Si Kα on PET sin θ = 81504
P/B= 207/1.3=159 FWHM=0.006 Å

TAP gives a higher count rate, and wider peak for Si Ka vs. using PET

Spectrometer efficiency



- A function of the solid angle subtended by the crystal, reflection efficiency, and detector efficiency
- WDS spectrometer has ~10% the collection efficiency relative to the EDS detector

Gas-flow proportional detector

- Convert X-ray photons through ionization into voltage pulses
- X-rays passing through the Ar gas filled detector produce a trail of ion pairs ($Ar^+ + e^-$), with number of pairs proportional to the X-ray energy
- If the X-ray energy is >3206 eV it can knock out an Ar K electron, with L shell electron falling in its place, forming escape peak.
- Dead time correction

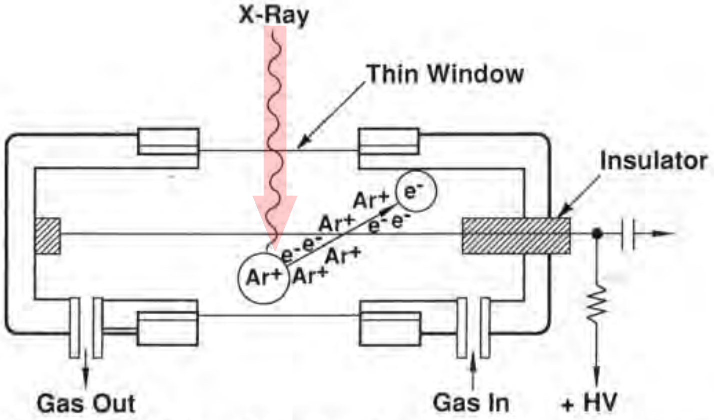


Figure 5.7. Schematic drawing of a gas flow proportional counter.

Detector amplification

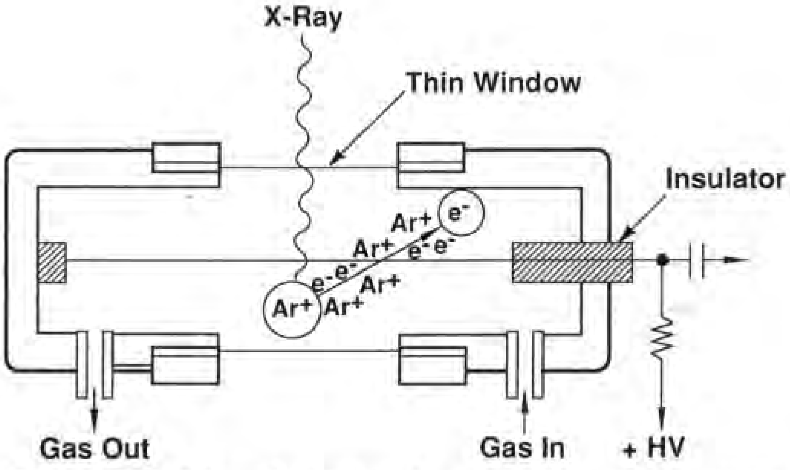
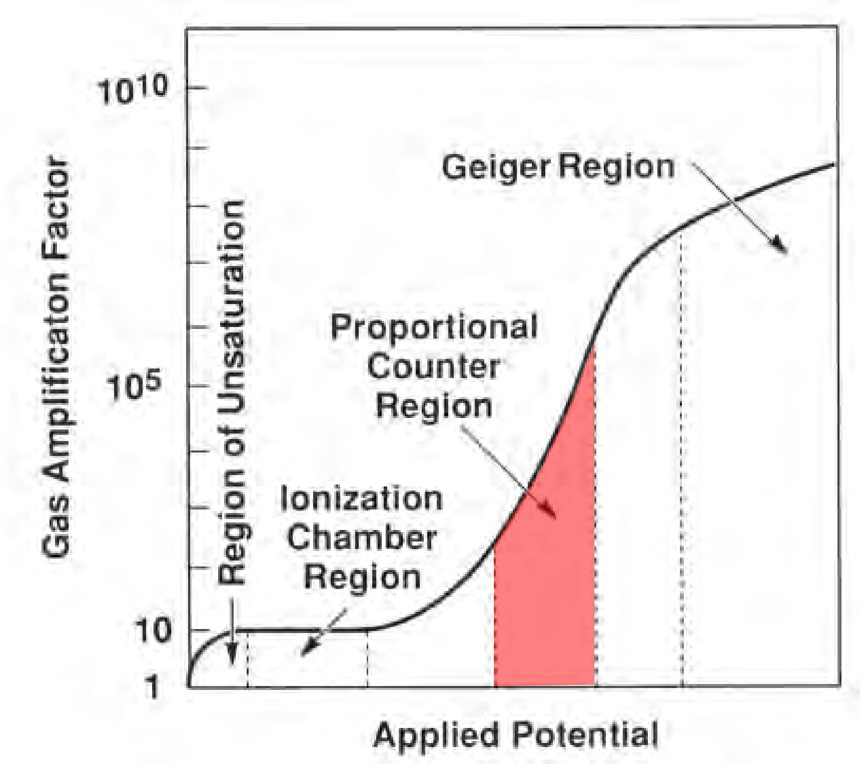


Figure 5.7. Schematic drawing of a gas flow proportional counter.

- It takes 16 eV to produce one Ar+ and an electron pair, but the effective value is 28 eV.
- For Mn Ka (2895 eV), 210 ion pairs are initially created per X-ray
- All 210 electrons are accelerated toward the center anode (which has a positive voltage [bias] of 1200-2000v) and produces many secondary ionizations.
- This yields a very large amplification factor (~10^5), and has a large dynamic range (0-50,000 counts/sec).

WDS detector

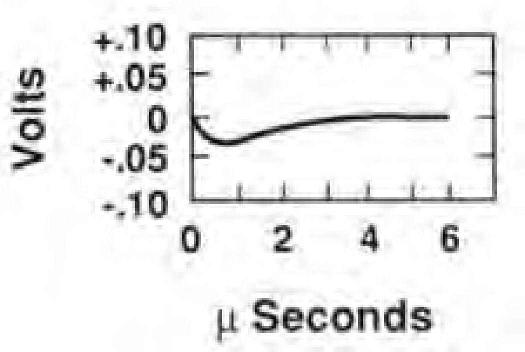


The bias on the anode in the gas proportional counter needs to be adjusted to be in the proportional range.

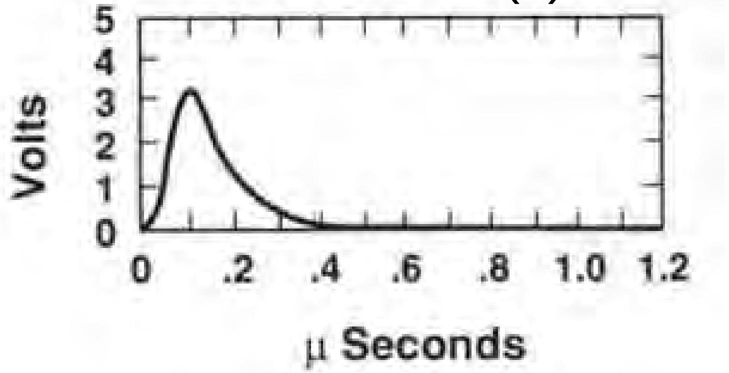
Too high bias can produce a Geiger counter effect.

Too low produces no amplification.

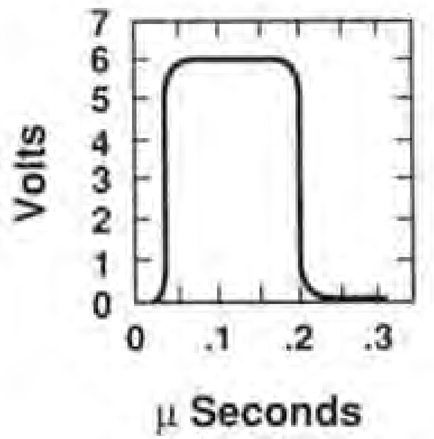
WDS pulse processing



(1)



(2)



Each pulses (charges) generated in the tube are (1) amplified and (2) shaped (bottom).

Each figure is for one (the same) pulse.

Ar escape peak

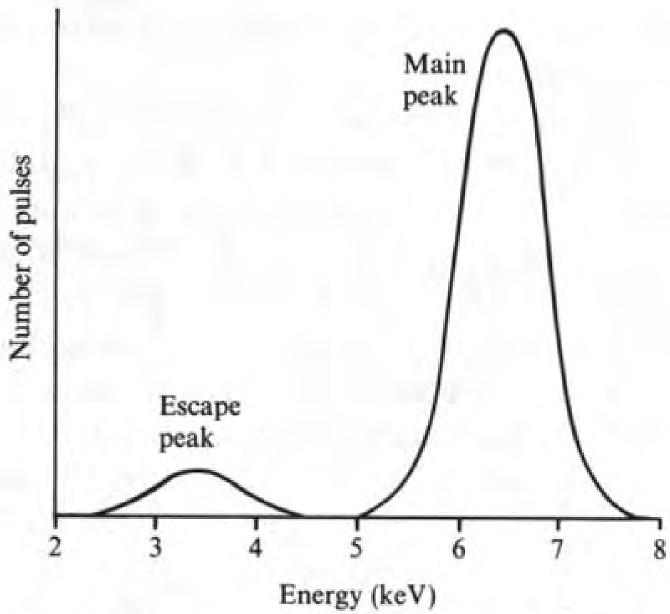
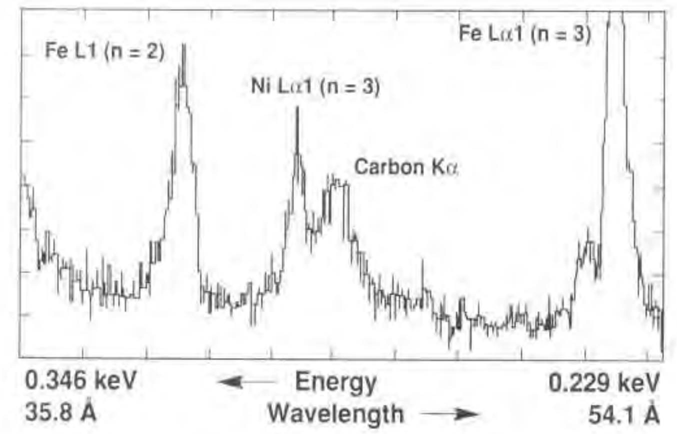


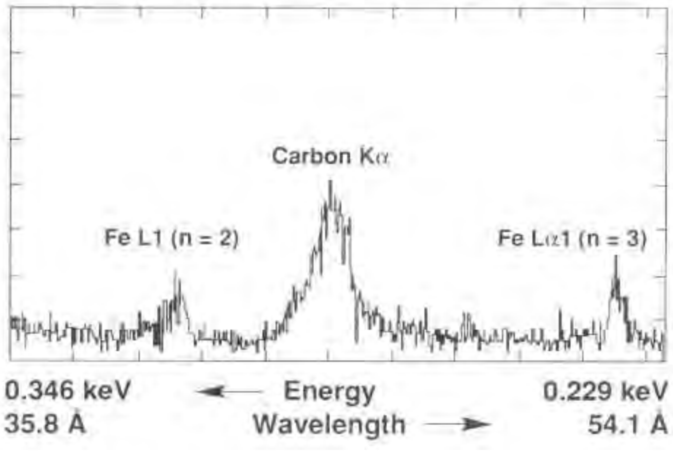
Fig. 7.8 Argon escape peak for Fe Kα X-rays.

- There is a probability that a small number of Ar Ka X-rays produced by the incident X-ray (here, Fe Ka) will escape out of the counting tube. If this happens, then those affected Fe Ka X-rays will have pulses deficient by 2958 eV.

Integral vs. differential PHA



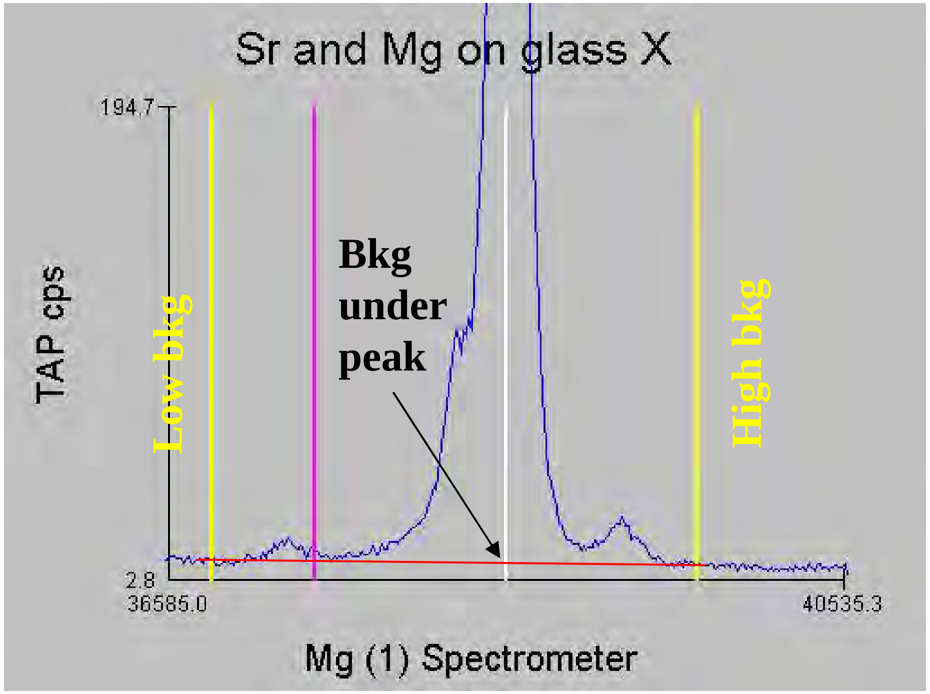
Integral



Differential

- Analysis of ‘light elements’ such as C is complicated because of the long wavelength (44 Å) which means that higher order reflections of many elements can interfere.
- By setting the detector electronics to the discrimination mode (“differential”), bottom, the higher order lines are strongly (but not totally) suppressed.

Spectrum = characteristic + continuum



Peak position must be precisely found

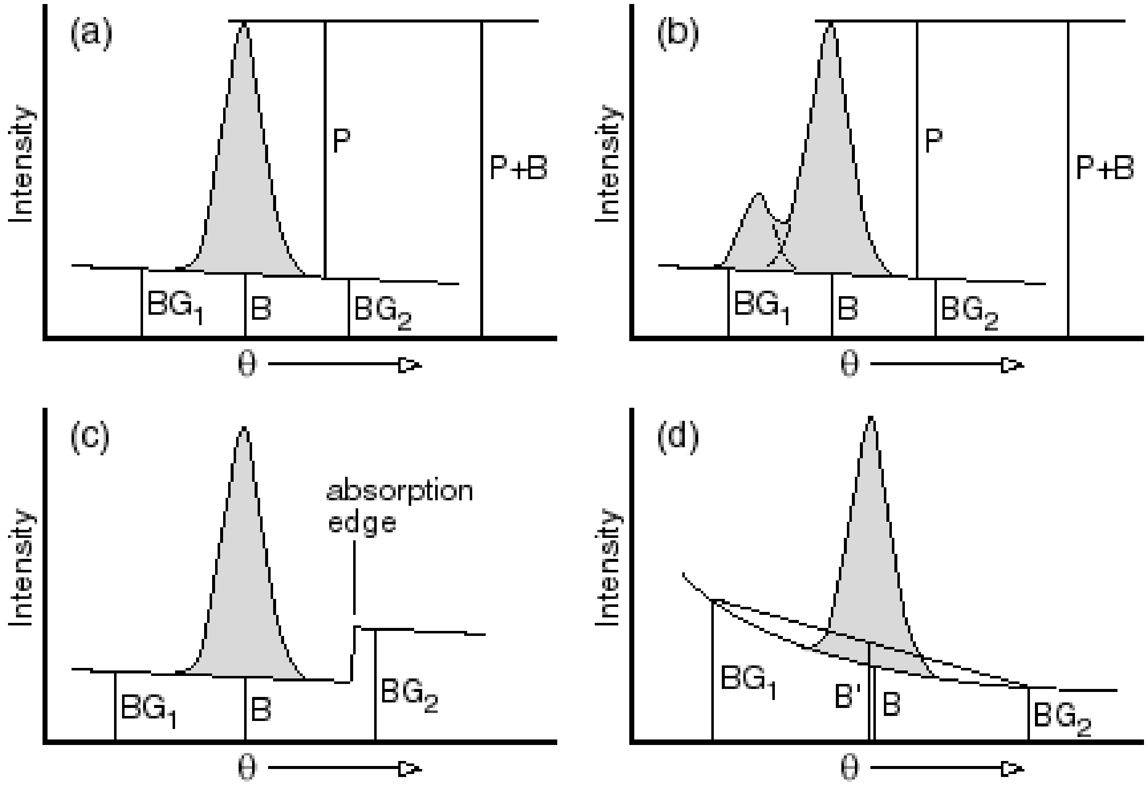
Background positions must be found in order to estimate the continuum level at the peak position

Background level increases with increasing mean atomic number of the specimen

Background offsets

Linear Bkg

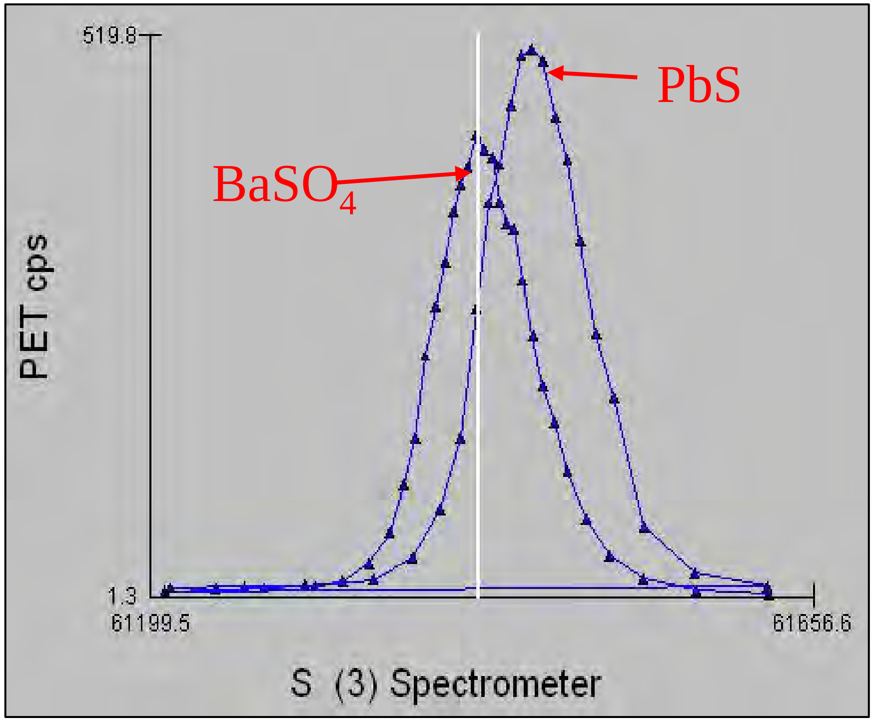
Interference on Bkg



Absorption edge

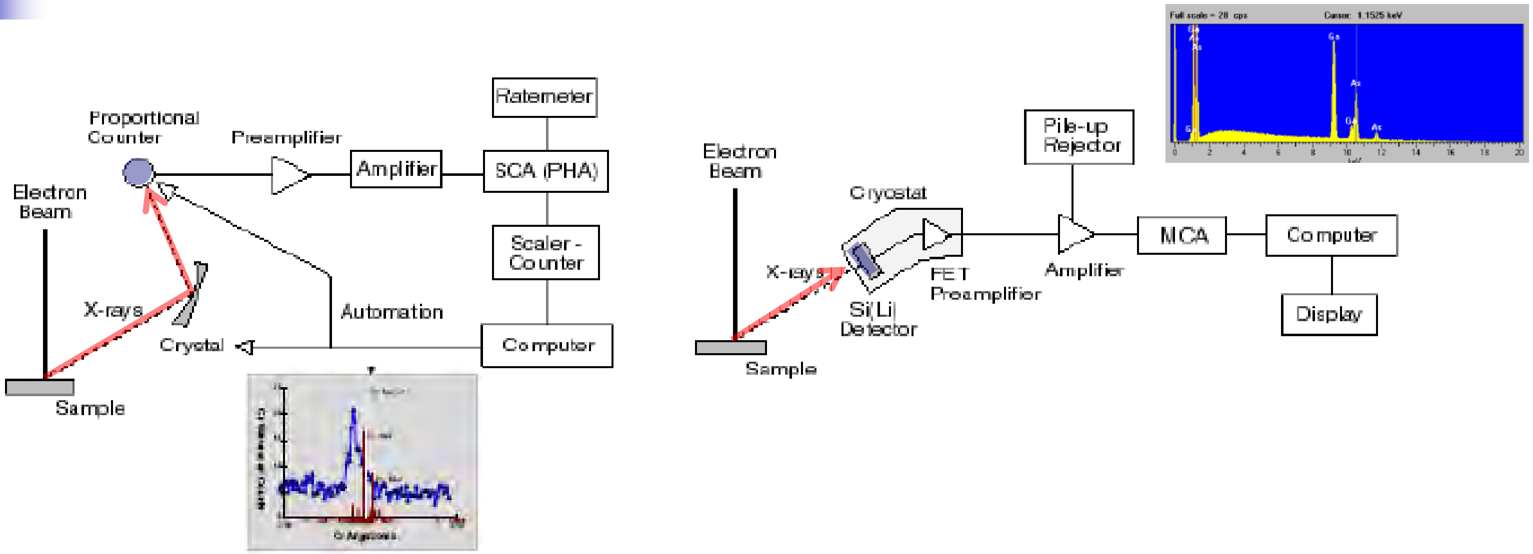
Curved Bkg

Peak shift



- Shifts in peak shape of certain elements can occur due to difference in chemical bonding, between different samples/standards.
- Examples are Al Ka and S ka, as well as P ka, and the “light” element K lines.

WDS vs. EDS



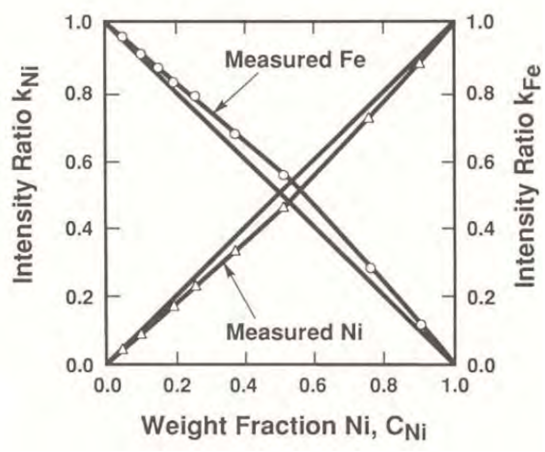
- Spectral resolution (2-6 eV WDS, 130-155 eV)
- Detector efficiency (<0.2% WDS, 2% EDS)
- The EDS detector located close to the sample, receives many stray X-rays and electrons and suffers peak distortion, peak broadening, escape peaks, absorption, and internal Si fluorescence

Quantification (ZAF correction)

No interaction between elements

$$C^{A}_{unk} = C^{A}_{std}\left(\frac{I^{A}_{unk}}{I^{A}_{std}}\right)$$

$$C = C_{unk}\left(\frac{F_{unk}}{F_{std}}\right)$$



Z: backscattering and electron-stopping power

A: The absorption correction is a function of the take-off angle (length of path traversed by the X-rays), the distribution of X-ray generation, the wavelength of the emergent X-ray and the elements present.

F: The correction for fluorescence is a function of the elements present, their concentrations, their values of Ec and mass absorption coefficients, and the take-off angle.

Basic statistics

Mean $$x = \sum_{i=1}^{n} x_i / n$$

Standard deviation $$\sigma = \sqrt{\sum_{i=1}^{n} (\bar{x} - x_i)^2 / (n-1)}$$

Relative standard deviation $$\varepsilon = \frac{\sigma}{\bar{x}}$$

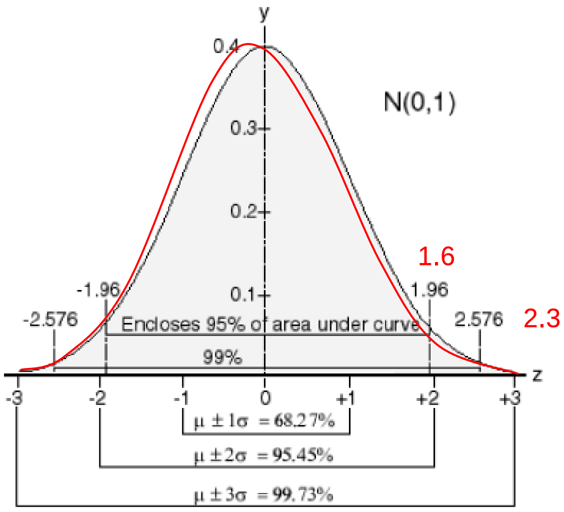
Standard error of the mean $$\sigma_x = \frac{\sigma}{\sqrt{n}}$$

Error propagation

C=A+B, C=A-B $$\sigma_C = \sqrt{\sigma_A^2 + \sigma_B^2}$$

C=A×B, C=A÷B $$\varepsilon_C = \sqrt{\varepsilon_A^2 + \varepsilon_B^2}$$

D=(A+B)/C



X-ray counts follow a Poisson distribution, which describes the counting of events that occur at random but at a definite average rate.
For a Poisson distribution, the standard deviation is the square root of the counts.

Accuracy and precision

- Incorrect standard values.
- Focus problems. Defocusing the beam on the sample results in imperfect spectrometer optics and reduced count rates.
- Specimen tilt, which produces systematic errors by changing the take-off angle.
- Irregularities in the sample surface, which are produced during polishing.
- Errors in matrix-correction factors. For example, F in apatite should be determined using a fluorapatite standard, while determining F in micas requires a F-rich mica.
- Variations in the thickness of the C-coat, which cause variable amounts of absorption for soft X-rays. For example, Na-Ka X-rays.
- Incorrect location of backgrounds.
- Large deadtimes.
- Peak shifts from standard to unknowns (e.g., S and F).
- Errors in nominal accelerating voltage.
- Electronic instability.

Detection Limits

$$C_{corr} = C_{pk} - C_{bkg},$$

$$\sigma_{pk} = \sqrt{C_{pk}} \text{ , and}$$

$$\sigma_{bkg} = \sqrt{C_{bkg}} \text{ .}$$

$$\sigma_{corr} = \sqrt{\sigma_{pk}^2 + \sigma_{bkg}^2} \text{ ,}$$

$$\text{so, } \sigma_{corr} = \sqrt{C_{pk} + C_{bkg}} \text{ .}$$

$$(C_{pk} - C_{bkg}) > z\, \sigma_{corr}$$

$$\text{D.L.} = z\, \sigma_{corr}$$

$$\text{D.L.} = z\, \sigma_{corr} = z \sqrt{2C_{bkg}}$$

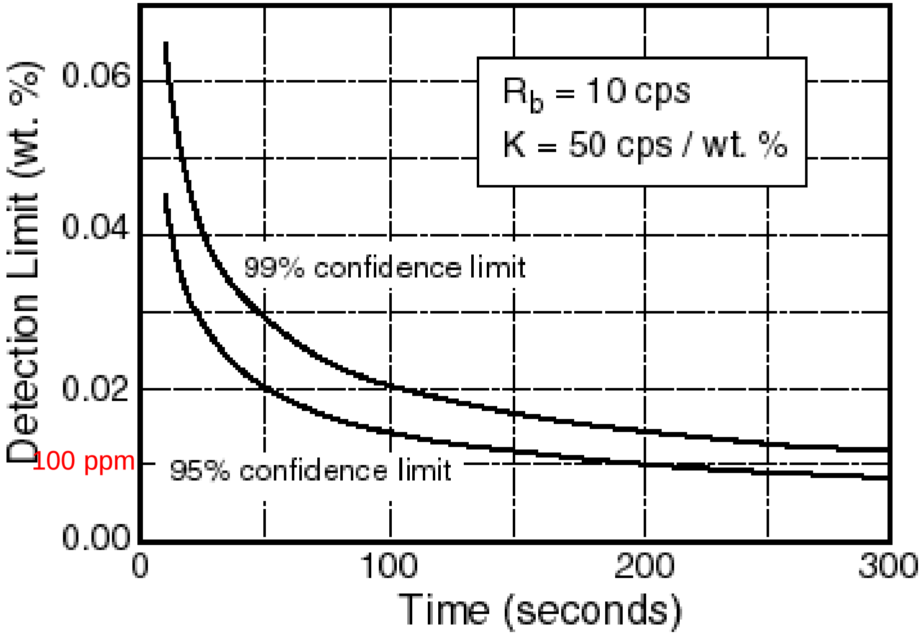
$$C_{bkg} = R_{bkg}\, T_{bkg}$$

$$\text{D.L.} = z \sqrt{2\,(R_{bkg} \times T)}$$

$$\text{D.L.} = \frac{z\sqrt{2\, R_{bkg} T_{bkg}}}{K\, T_{bkg}}$$

$$\text{D.L.} = \frac{z\sqrt{2\, R_{bkg}}}{K\sqrt{T_{bkg}}}$$

Z = confidence level factor
K = count per second/concentration
R_{bkg}=count rates of background
T_{bkg}=counting time of background



DL = f(counting time, accelerating voltage, beam current, background modeling)

Significant figures

- In any value, there is an unstated implication of an error of ± 1 in the last digit (0.054±0.001, 1.9 % error)
- 0's to the left of all non-zero digits ARE NOT significant (0.00054, 2 significant figures).
- 0's between non-zero digits ARE significant (0.05004, 4 significant figures).
- 0's to the right of the last non-zero digit and to the right of the decimal ARE significant (0.0550, 3 significant figures).
- 0's to the right of the last non-zero digit and to the left of an implied (not present) decimal are ambiguous. (5200, either 2, 3, or 4 significant figures. This ambiguity can be removed by writing the value in scientific notation: $5.2\text{x}10^3$ contains 2 significant figures, $5.20\text{x}10^3$ (5.20E3) contains 3 significant figures, and $5.200\text{x}10^3$ (5.200E3) contains 4 significant figures.

Propagating significant figures

Addition or subtraction

The result retains as many significant figures to the right of the decimal as there are in the number which contains the least number of significant figures to the right of the decimal (the number with the largest absolute error). For example,

14.72 + 1.4331 + 0.00235 = 16.16

Multiplication and division

The result retains as many significant figures as there are in the number which contains the least number of significant figures (the number with the highest relative error). For example,

2.35×1.2345×0.2214=0.642

Standard deviation

If the first significant figure in the standard deviation is 3, 4, 5, 6, 7, 8, or 9, the standard deviation is expressed using one significant figure

If the first significant figure in the standard deviation is 1 or 2, the standard deviation is expressed using two significant figures.

Example: 0.10, 0.15, 0.20, 0.29, 0.3, 0.5, and 0.9. Represent 3 to 33% errors.

Or always use two significant figures: 0.10, 0.15, 0.20, 0.29, 0.30, 0.50, and 0.90. Represent 1 to 10% errors.

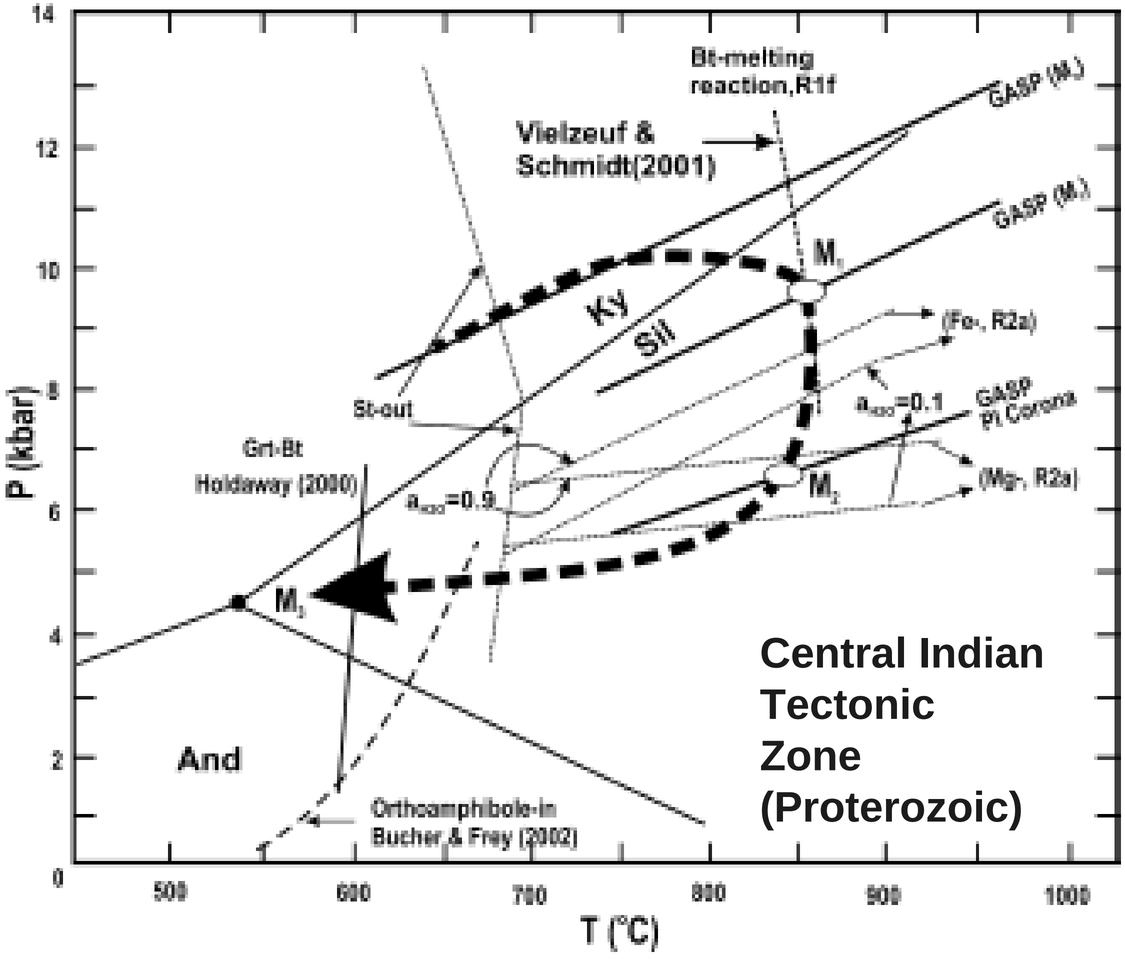
Rounding

Rounding: >5 round up, >5 round down, odd number round up, even number round down.

Applications of electron microprobe

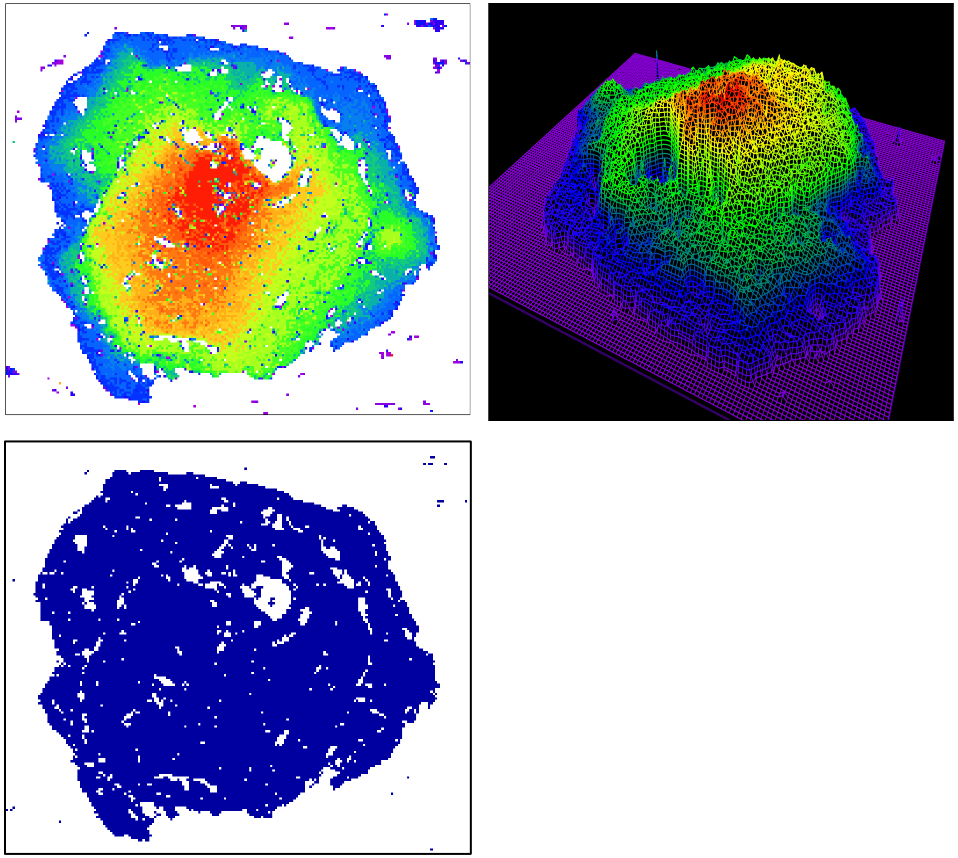
- Geoscience research: mineral identification, descriptive petrology, geothermometry and geobarometry, experimental petrology, cosmochemistry, zoning in minerals, diffusion studies, and particle analysis
- Material science: metals and alloys, thin films, semiconductors, electronics and photonics, ceramics and composites, glass, optical fibers, fuel cells and batteries
- Medical science: teeth and bones
- Environmental science
- Forensic science
- Archaeology

Applications in P-T-t reconstruction



Central Indian
Tectonic
Zone
(Proterozoic)

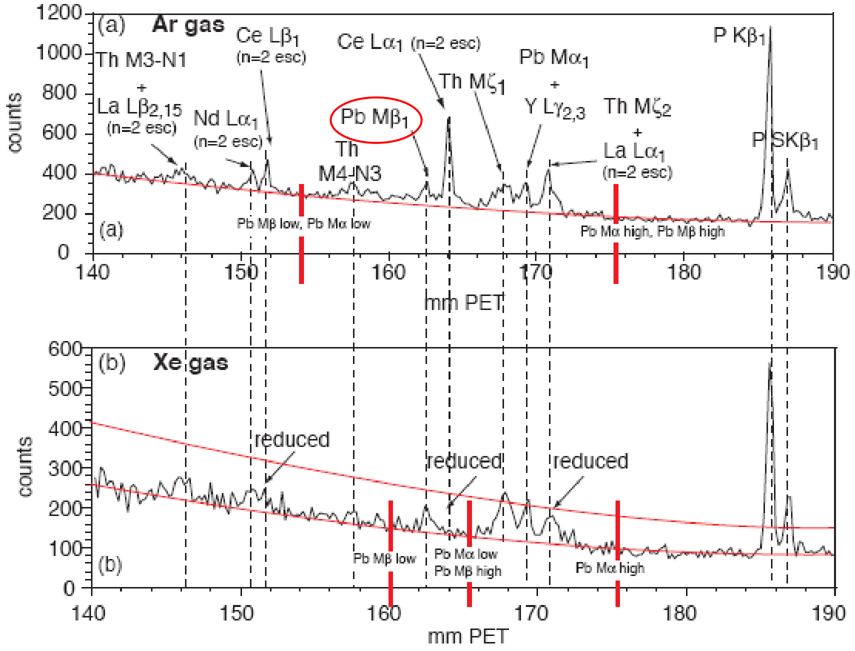
Application of X-ray mapping

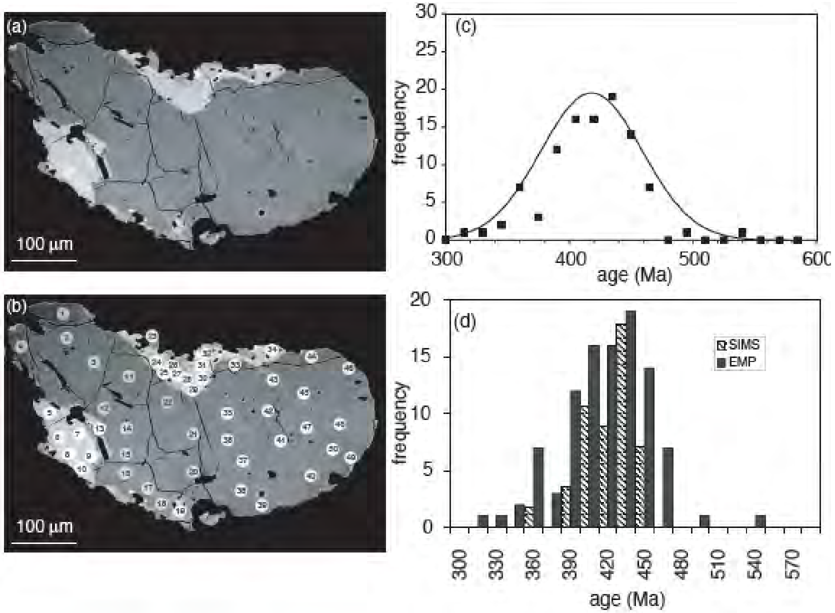


- Accomplished by rastering the beam over the sample surface. Used for many of the same types of studies described before. Particularly useful for:
- Location and distribution of mineral phases
- Quick location and identification of trace particles
- Subtle zoning patterns in mineral samples
- Examination of the interfaces between phases

Geochronology: chemical dating of monazite

$$Pb = Th/232\left[e^{\lambda^{232}\tau}-1\right]208+(U/238.04)0.9928\ \mathrm{x}\left[e^{\lambda^{238}\tau}-1\right]206+(U/238.04)0.0072\ \mathrm{x}\left[e^{\lambda^{235}\tau}-1\right]207$$





Suggested reading

- James H. Wittke's (Northern Arizona University) lecture note on http://www4.nau.edu/microanalysis/Microprobe/Probe.html
- Reed, S. J. B., 1997. Electron Microprobe Analysis. Cambridge University Press; 2nd edition. 344 pages