



The Abdus Salam
International Centre for Theoretical Physics



SMR.1744 - 7

SCHOOL ON ION BEAM ANALYSIS AND ACCELERATOR APPLICATIONS

13 - 24 March 2006

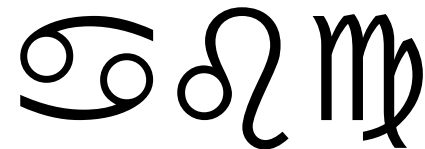
Broadbeam PIXE - Concepts and applications

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Proton Induced X-ray Emission

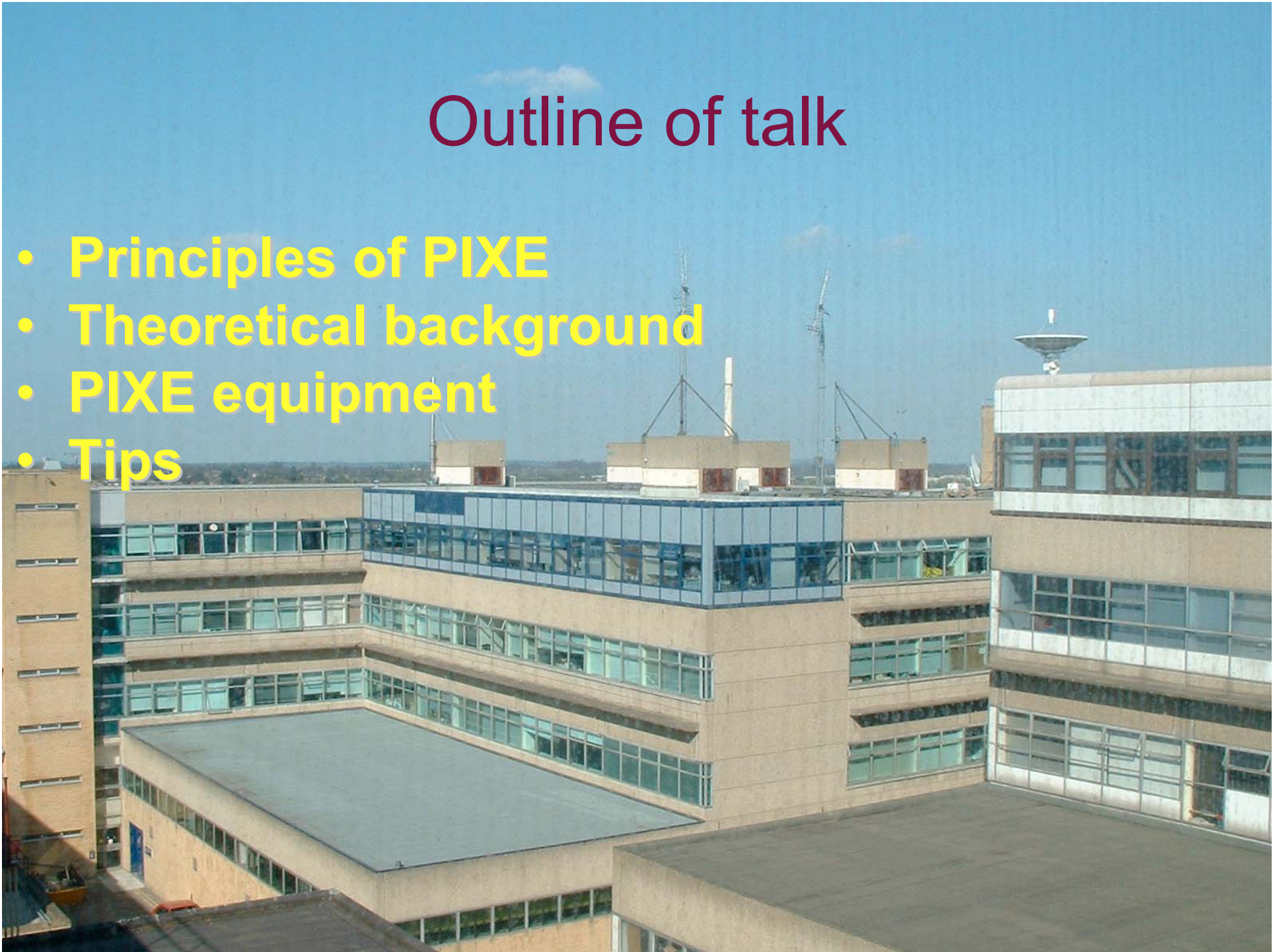
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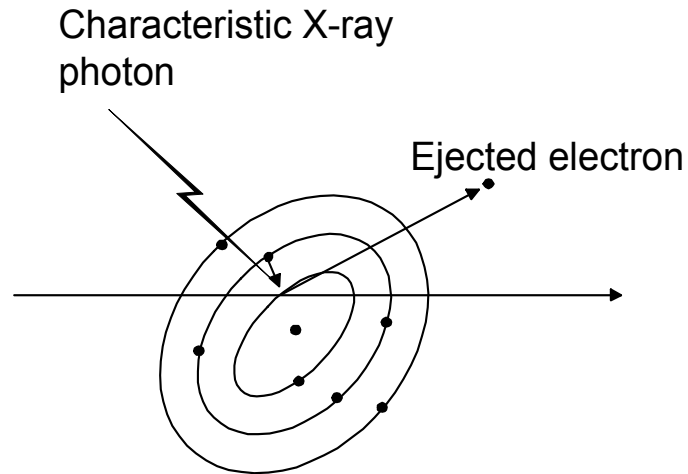


Outline of talk

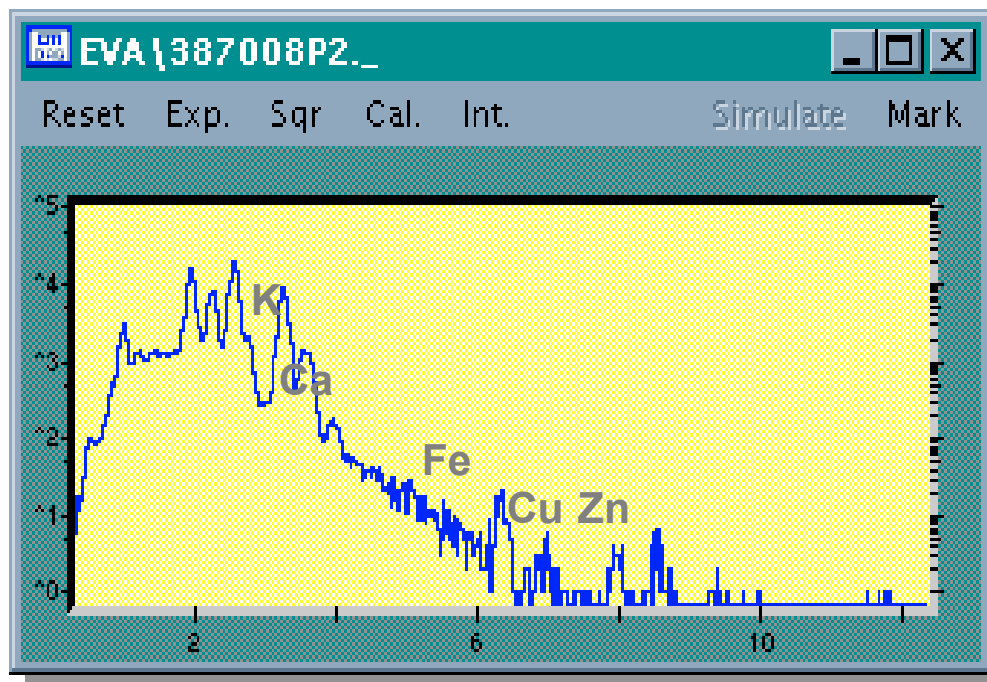
- Principles of PIXE
- Theoretical background
- PIXE equipment
- Tips



Proton Induced X-ray Emission



- Analogous to EDX using MeV protons
- No primary bremsstrahlung, so low detection limits (1-10ppm)
- Can be made quantitative



PIXE

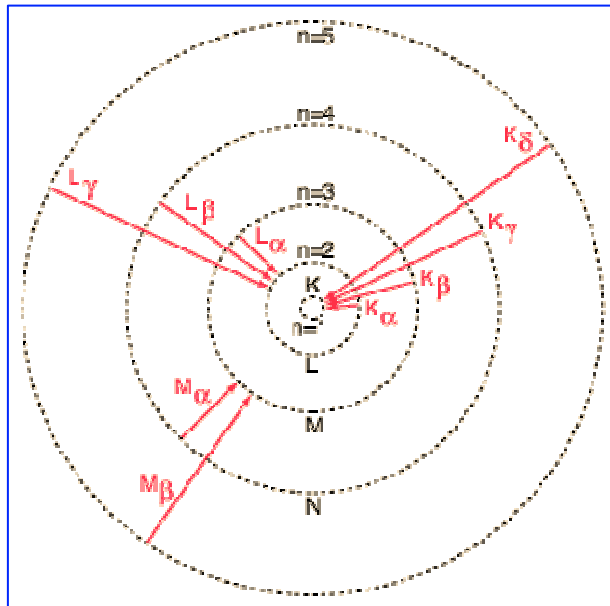
X-ray Emission Spectrometry (XRS)

- PIXE is one form of X-ray Emission Spectrometry
 - Create an inner shell vacancy by exciting the electron shells of the atom
 - Cascades from outer shells emit characteristic X-rays
 - Measure energy to determine atomic number and count photons to determine concentration
- **Ionisation methods**
 - **XRF**: X-ray fluorescence – use a beam of high energy x-rays
 - **EPMA**: Electron Probe Microanalysis – use a beam of electrons in a scanning electron microscope
 - **PIXE**: Use MeV protons or other ions (“P” can stand for “proton” or “particle”)
- **Detection methods**
 - **WD**: Wavelength dispersive – use a crystal spectrometer to measure the intensity at a single wavelength.
 - **ED(X)**: Energy dispersive – use a semiconductor detector to give a voltage pulse proportional to the energy of each photon

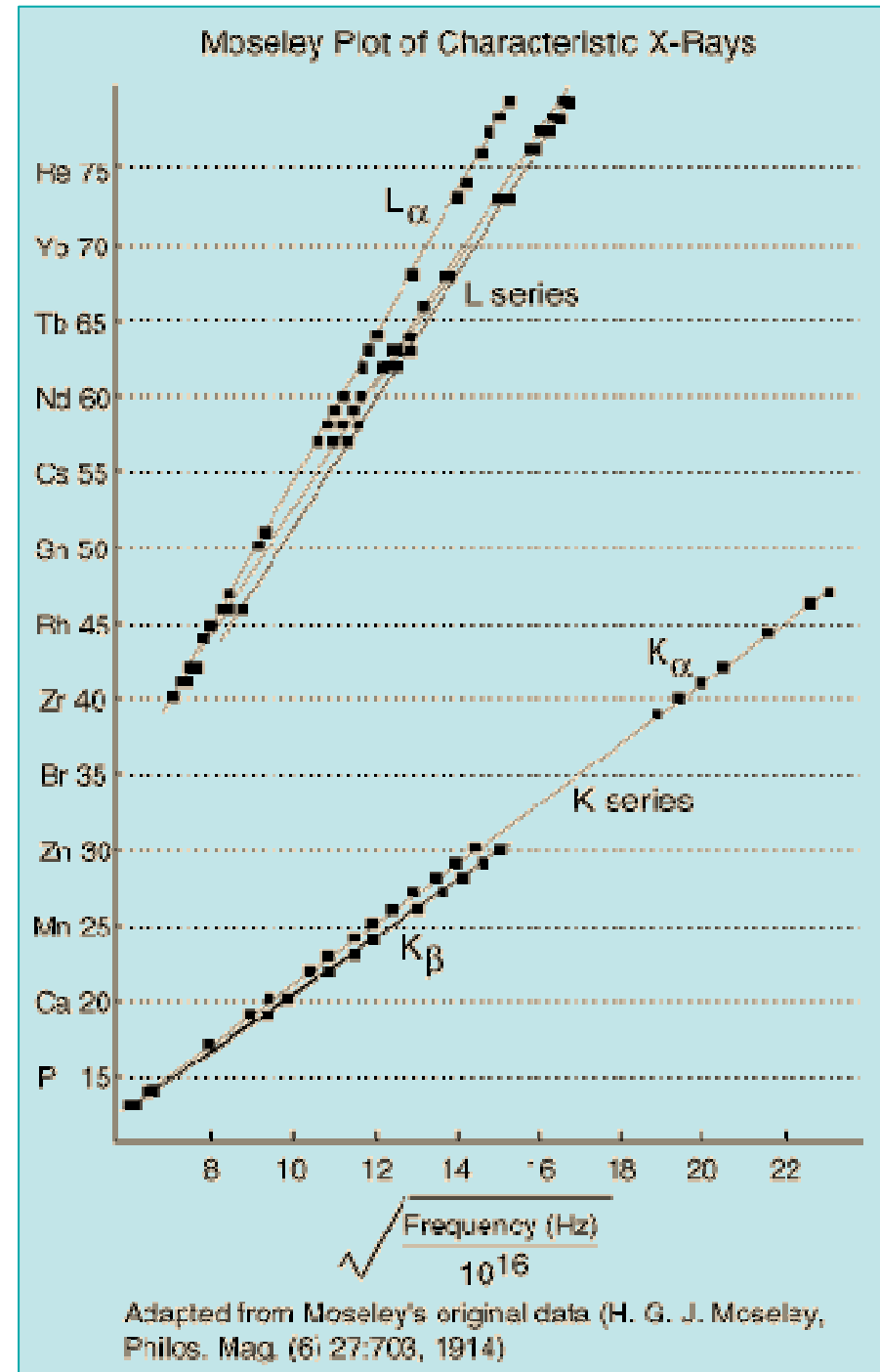
Energy of characteristic X-rays

The energy of the emitted x-rays is determined by the spacing of the energy levels of the electrons in the atom

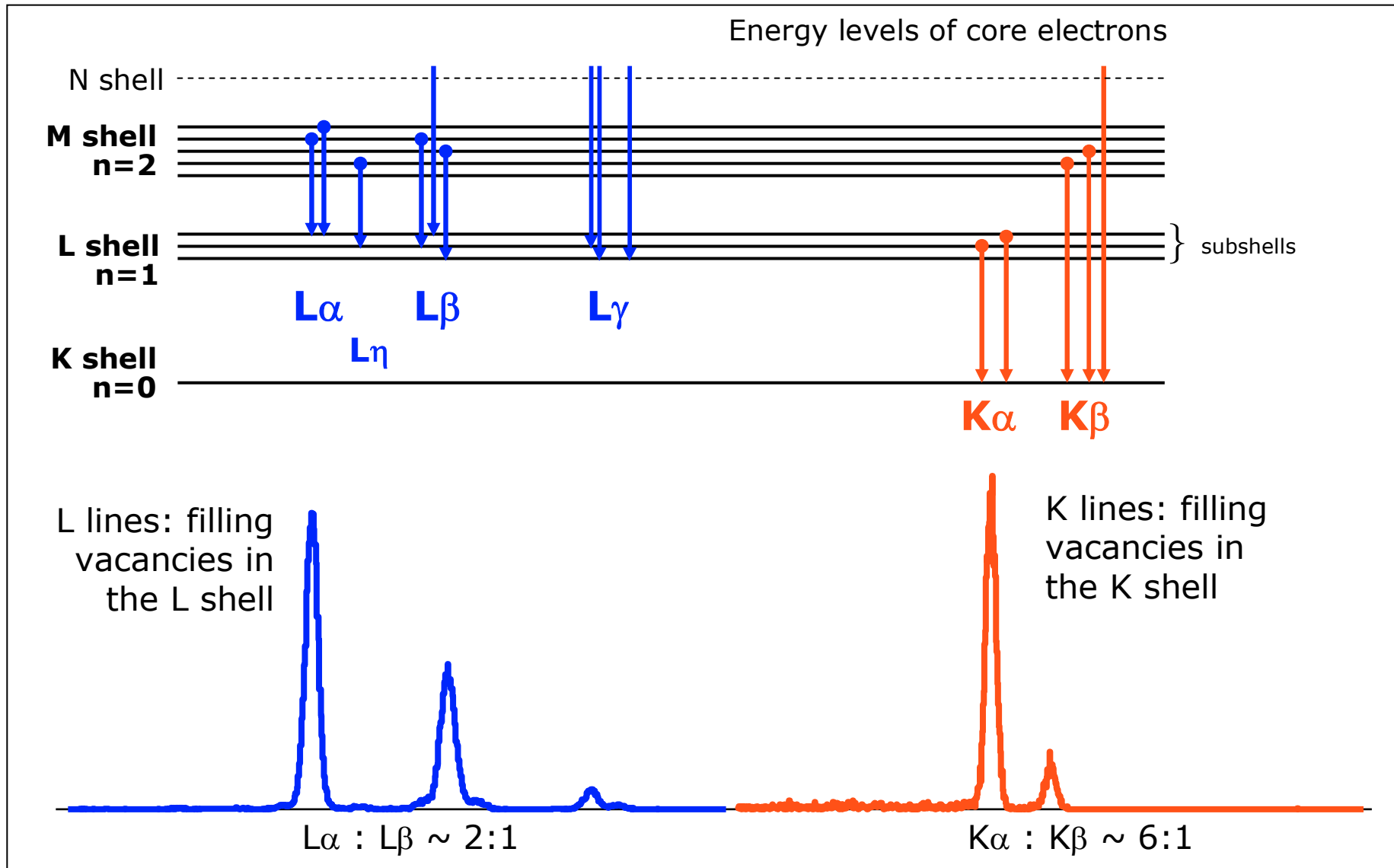
This gives rise to a number of **series** (K, L, M, etc.) depending on the final shell.



The Bohr model of the atom allowed these energies to be predicted and this was confirmed experimentally by Moseley in 1914.



Energy of characteristic X-rays



Transitions to the M shell give a series of M lines

Energy depends on Z. Useful ranges:

K:	F - Ag
L:	Cu - U
M:	Pt - U

Energy of characteristic X-rays

Element	K _α energy	L _α energy	M energy
Li	<i>0.052</i>		
O	<i>0.523</i>		
Na	1.041		
Si	1.740		
Ca	3.691	<i>0.341</i>	
Fe	6.403	<i>0.704</i>	
As	10.534	1.282	
Zr	15.774	2.042	<i>0.350</i>
Ag	22.162	2.984	<i>0.568</i>
Ba	32.191	4.467	<i>0.972</i>
W	<i>59.310</i>	8.396	1.774
Pb	<i>74.957</i>	10.549	2.342
Pu	<i>103.653</i>	14.297	3.350

Selected X-ray emission energies

- Values in *italic* can **not** be detected using conventional ED detectors.
- Note the possibility of overlaps, e.g. between As K_α and Pb L_α and Si K_α and W M_α
- Tables of Xray energy can be found in reference books (e.g. Mayer and Rimini) or for a searchable database look on the US National Institute of Science and Technology website (link below)

<http://physics.nist.gov/PhysRefData/XrayTrans/html>

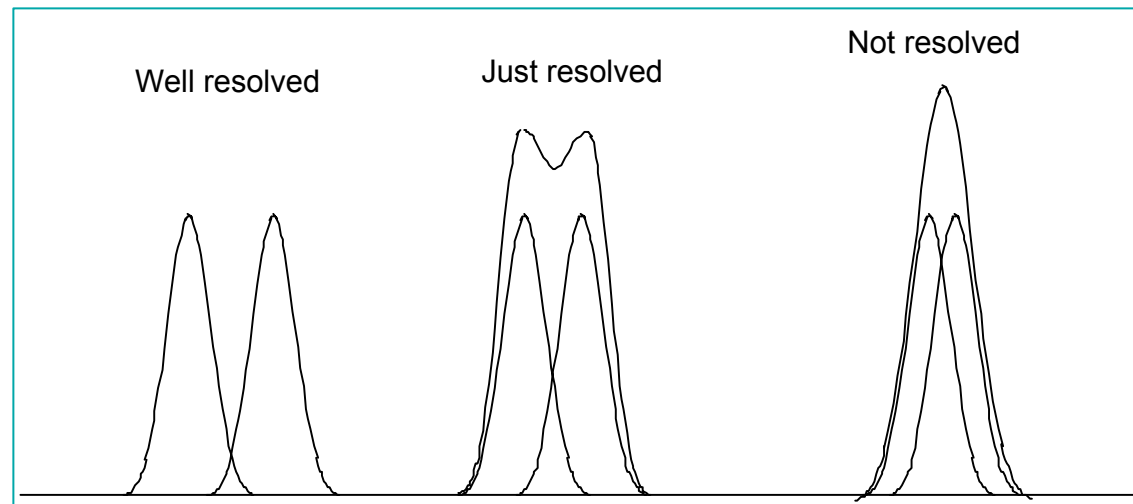
X-ray energy resolution

Energy resolution

This is the ability of the detector to separate closely spaced X-ray peaks.

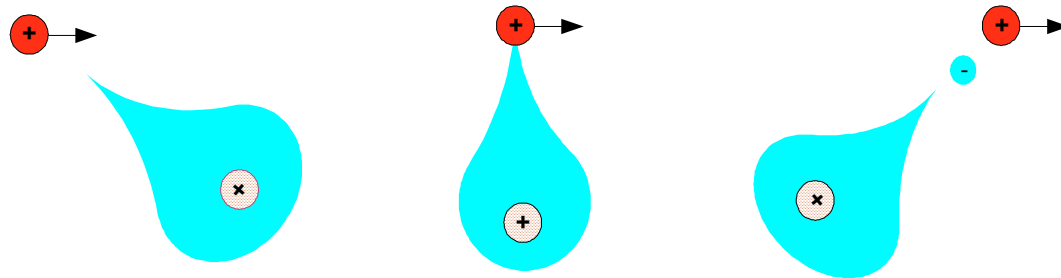
WD detectors have a very good resolution (~ 10 eV fwhm), but since they can only measure one wavelength at a time, this means that the analysis is slow (and is now used only for specialised applications).

ED detectors have a relatively poor resolution (typically ~ 150 eV fwhm) but they measure all energies simultaneously, so the analysis is very fast.



Efficiency of ionisation using protons:

Charged particles create vacancies by perturbing the electron clouds around the atom through their Coulomb interaction



For efficient ionisation we must satisfy two conditions:

1. The particle energy must be greater than the ionisation potential (binding energy) of the electron
2. The velocity of the particle must match the velocity of the electron in its orbit.

(The full explanation of this is quantum mechanical, but you can imagine that if the velocities are the same the interaction time is maximised)

Efficiency of ionisation:

The orbital velocity of inner shell electrons is typically 1 - 10% of the speed of light (e.g. for sulphur with a K shell ionisation energy of 2.47 keV, $v \approx 3.5 \times 10^7 \text{ m s}^{-1}$).

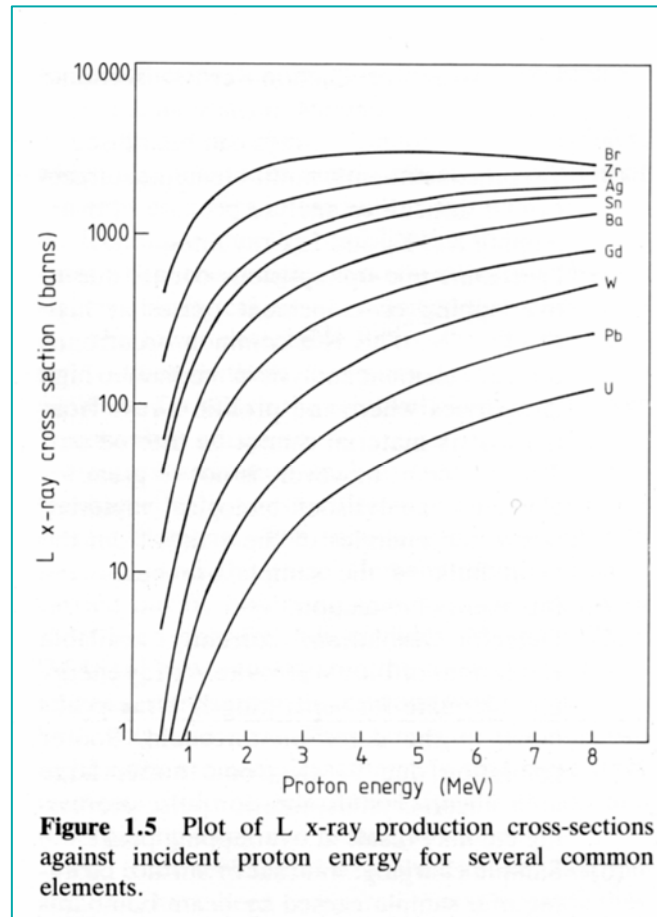
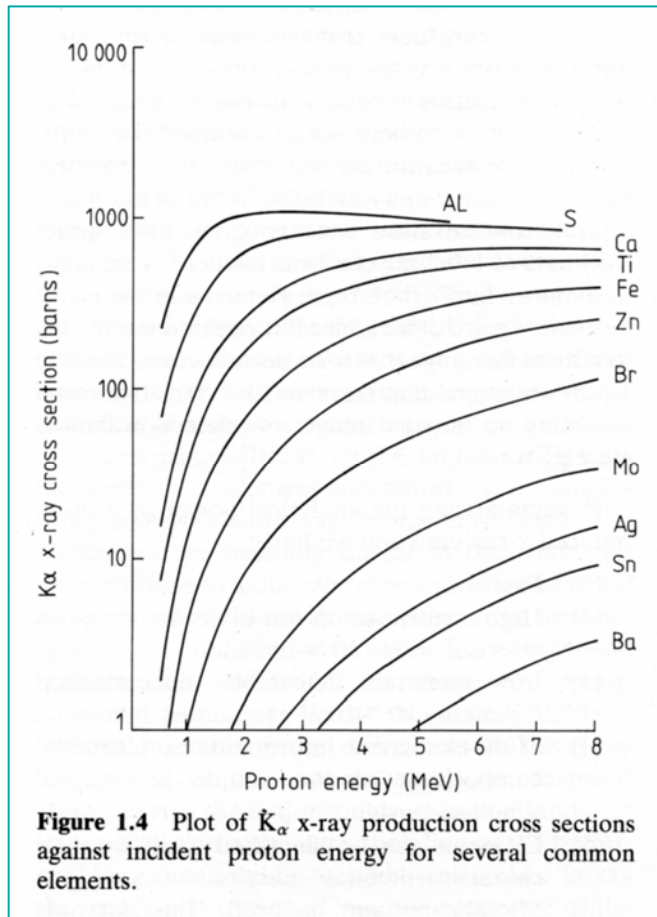
In order to reach this velocity with electrons, protons or alpha particles, they would need to have the following energy:

electron	2.5 keV
proton	4 MeV
alpha	16 MeV

This shows that both keV electrons and MeV protons from small accelerators have velocities close to the optimum. Excitation with alpha particles (and any heavier ions) requires much higher energies.

X-ray production cross sections:

The efficiency of X-ray production is normally measured by the **x-ray production cross-section**. This is the fictitious effective area that a single atom exposes to the beam assuming that each time a particle enters that area an x-ray is produced. Units are **barns** (1 barn = 10^{-24} cm²).



Note that typical RBS cross sections are measured in barns and nuclear reaction cross sections are measured in millibarns.

PIXE is a very high yield technique

Yield of PIXE:1

We can now calculate the total yield of X-rays generated in a PIXE experiment.

We will assume:

1. the sample is a very thin layer with N_T target atoms per cm^2 .
2. the beam has a flux of N_B protons per second (i.e. current, $I = N_B e$ ampere)
3. we are irradiating uniformly an area of $A \text{ cm}^2$ for a time t seconds (we will see that the irradiated area cancels out).

The total effective x-ray production cross section in the irradiated area is then

$$AN_T\sigma_X(E)\times 10^{-24} \text{ cm}^2 \quad \text{where } \sigma_X \text{ is the value of the x-ray cross section in barns}$$

The number of beam particles per cm^2 is $N_B t/A$, so the total number of photons created is

$$N_X = N_T N_B t \sigma_X(E) \times 10^{-24}$$

or

$$N_X = N_T I t \sigma_X(E) \times 10^{-24} / e$$

or

$$N_X = N_T Q \sigma_X(E) \times 10^{-24} / e$$

Where Q is the total beam charge in C and e is the electronic charge, $1.6 \times 10^{-19} \text{ C}$

Yield of PIXE:2

Assuming that the X-rays are emitted isotropically and that the detector has a solid angle of Ω sr and an intrinsic efficiency of $\varepsilon(E_x)$, the total number of detected X-rays is

$$N_X = N_T Q \sigma_X(E) \Omega \varepsilon(E_x) \times 10^{-19} / 4\pi e$$

This can be written in terms of the areal density of the target atoms, $m \mu\text{g cm}^{-2}$ as follows:

$$N_X = m Q Y(E) \Omega \varepsilon(E_x)$$

where

$$Y(E) = \frac{\sigma_X(E) \times 10^{-24}}{4\pi e A m_p} \approx 3 \times 10^5 \frac{\sigma_X(E)}{A} \text{ counts}/\mu\text{C}/\mu\text{gcm}^{-2}/\text{sr}$$

where $A m_p$ is the mass of the target atom.

Y is the thin target PIXE yield. This is a function of the Z and A of the target atom, the type and energy of the incident ion and the measured X-ray transition.

Typical values (e.g. for Ca K α X-rays induced by 3MeV protons) are $\sim 10^6$ cts/ $\mu\text{C}/\mu\text{gcm}^{-2}/\text{sr}$

Thin and Thick target PIXE

X-rays are generated along the full length of the path of the particle, which can be up to 100 μm .

Absorption of deep X-rays can reduce the number of X-rays detected outside the sample. There are two situations we need to consider:

Thin target PIXE:

The sample is considered to be so thin that there is no absorption due to the matrix and the yield can be calculated as if the atoms were isolated.

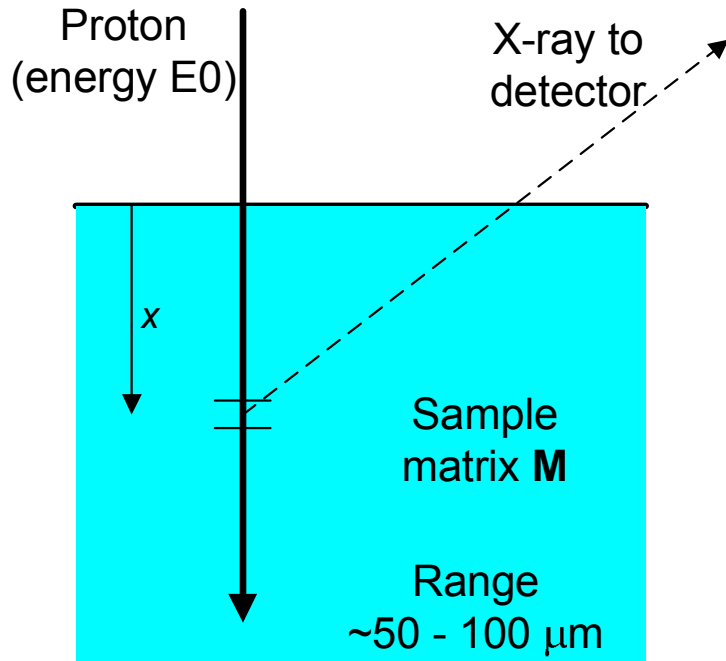
Thick target PIXE:

The sample matrix is assumed to have a major effect on the energy of the primary beam and the absorption of the emitted X-rays. Yield calculation is now a complex numerical integration requiring a knowledge of the major element composition of the matrix.

What is “thick”?

This depends on the energy of the emitted X-rays. Low energy X-rays (e.g. Al K with an energy of 1.4 keV) are completely absorbed in the top few microns of a sample, so most samples are thick. High energy X-rays (e.g. Ag at 22 keV) are not significantly absorbed, though we still have to consider the energy loss of the protons. If in doubt assume a thick target situation.

Quantification of Thick Target PIXE



Assume the sample is a flat homogenous slab

At depth x :

- Proton energy, $E(x)$ depends on E_0 , x and stopping power, **S**, of **M**
- X-ray production cross section, **σ** , depends on $E(x)$ and Z
- Absorption of emitted x-ray depends on the X-ray mass absorption coefficient, **μ** , of **M**, the energy of the xray and the angle of the detector

Integrate the yield to the end of the sample or the end of range to get the yield **Y** photons / ppm / μC

S, **σ** and **μ** are well parameterised

But we need to know **M** and the total number of protons hitting the sample (total charge, **Q**)

Mathematical break...

The variation of energy with depth is handled by noting that the depth, x , in the sample where the energy is E is given by

$$x = -\int_{E_p}^E \frac{1}{S(\mathbf{M}, E)} dE \quad (1) \quad \text{where } S \text{ is the stopping power of the matrix } \mathbf{M}$$

The yield of photons from an infinitesimal layer at depth x is given by:

$$dN_Z = KQc_Z\sigma_x(Z, E)\Omega\varepsilon(E_Z)\exp\left(-\mu(\mathbf{M}, E_Z)\frac{x}{\cos\theta}\right)dx$$

where c_Z is now the mass *fraction* of Z in the matrix. The exponential term reflects the X-ray absorption by overlying layers; $\mu(\mathbf{M}, E)$ is the mass absorption coefficient of X-rays of energy E in matrix \mathbf{M} , and θ is the angle between the sample normal and the detector direction.

The total X-ray yield is obtained by changing the depth variable from x to E using (1) and numerically integrating from the initial to the final proton energy, giving an expression for the concentration:

$$c_Z = \frac{N_Z}{KQ\Omega\varepsilon(E_Z)T_Z(\mathbf{M}, \sigma_x, S, \mu)}$$

where T_Z is the result of the integration involving the energy dependent parameters for unknown element Z .

The two new parameters of the matrix, S and μ , are also well measured and parameterised in the literature, so in principle, provided that we know \mathbf{M} and the sample thickness (or final energy) we can calculate the concentration directly from the number of detected photons and the charge.

Ways of determining charge and matrix

- **Charge**
 - Measure directly
 - Faraday cup / isolated sample stage
 - Chopper upstream of chamber
 - Isolated target chamber
 - Use an additional analysis technique such as RBS
 - Normalise to 100% if you can see x-rays from all the elements in sample
 - Use internal standard (e.g. yttrium)
 - Use ratios (charge not required)
- **Matrix**
 - Use known bulk composition (e.g. organics, minerals)
 - Iterate using derived PIXE concentrations as the matrix for the next iteration (maybe including ‘invisible elements’)
 - Use another simultaneous IBA technique (e.g. RBS, second PIXE detector)

Errors in charge and matrix determination may limit the accuracy of thick target PIXE

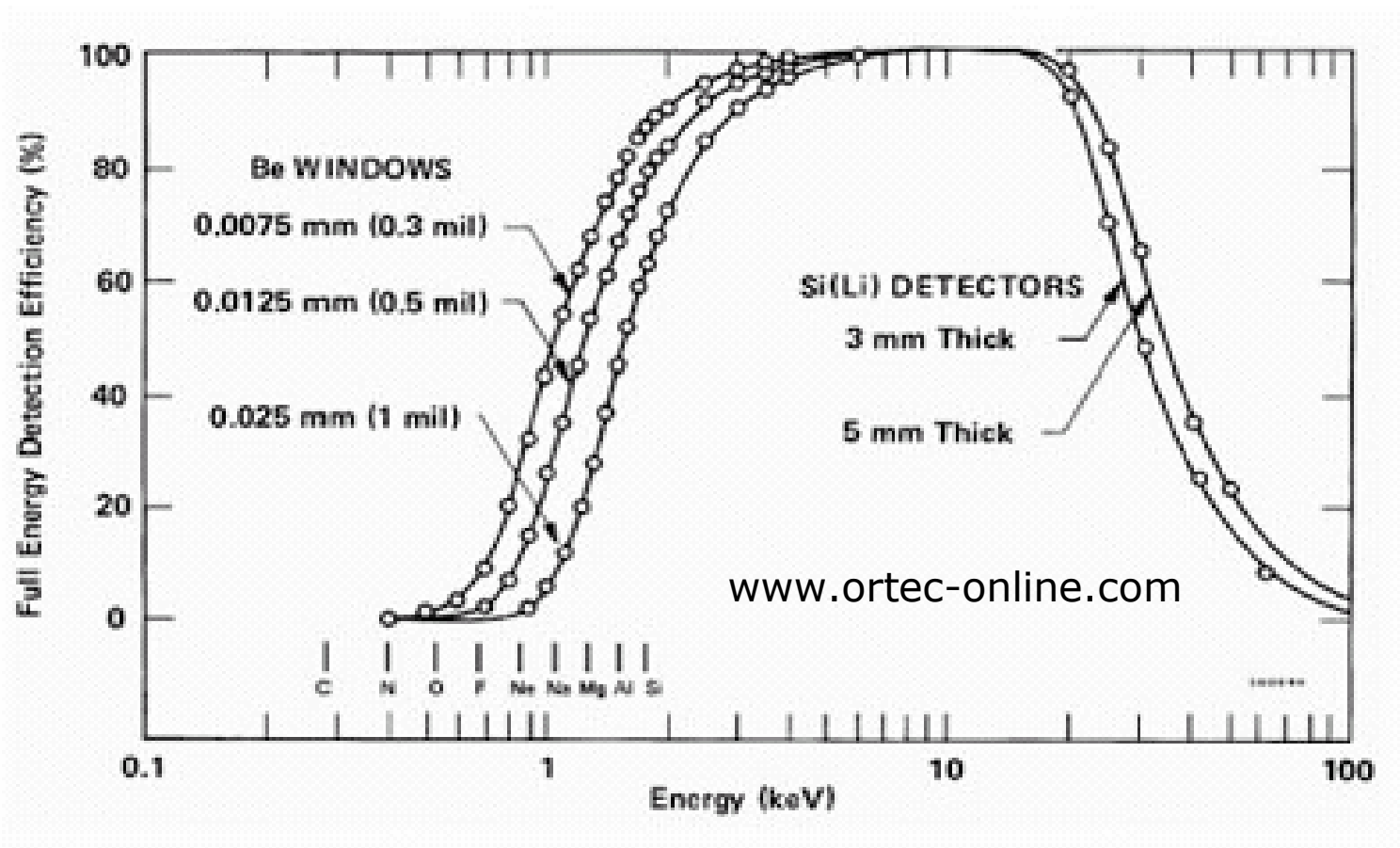
Other considerations for accurate PIXE

- **Secondary fluorescence**
 - High energy x-rays may cause fluorescence of lower energy x-rays from other atoms in the sample.
 - This reduces the yield of the high energy x-ray and enhances the yield of lower energy x-rays.
 - The magnitude of this effect may reach 10%.
 - Good PIXE software should correct for this based on the known concentrations
- **Surface roughness, sample non-uniformity etc.**
 - Any departure from the assumption that the sample is a flat homogenous slab will introduce errors in the calculated concentrations.
 - Take care with particulate samples – fractionation of phases into small grains may mean that the assumed average matrix is not applicable.
- **Samples of intermediate thickness**
 - PIXE is most accurate in the case of zero thickness (no correction) or very thick (final energy =0) samples
 - If the sample is of intermediate thickness (i.e. the beam passes through but there is enough mass to absorb x-rays), an additional measurement (RBS, STIM?) may be required to determine the local thickness or exit energy

The detector response: 1, Efficiency

- **Efficiency**

- The detector efficiency is determined by two effects:
 - At LOW energy, the efficiency falls because of absorption of X-rays in the detector window, contact layers etc.
 - At HIGH energy the efficiency falls because the depletion layer is not thick enough to absorb all the energy of the incident photons.



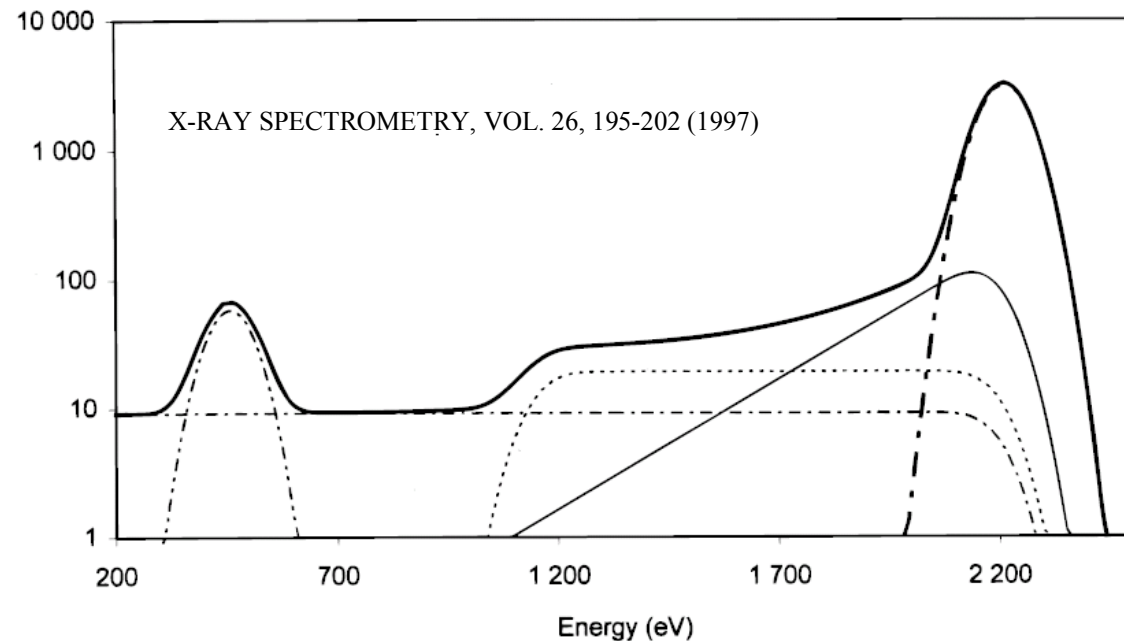
The detector response: 2, Peak shape

- **Peak shape**

- A detailed knowledge of the peak shape is necessary in order to extract the maximum amount of information from the spectra.

Peak shape models can be complex involving:

- Gaussian/Lorentzian main peak
- ‘Long’ low energy tail going to zero energy
- ‘Short’ low energy tail
- Exponential tail
- Escape peak
- etc.



Detector models require a number of parameters to be determined experimentally or varied as part of a spectrum fitting procedure

How to find parameters relevant to PIXE

Stopping power

<http://www.srim.org>

X-ray production cross sections

Various tabulations e.g.

Chen and Crasemann, ADNDT 33, 217, 1985 (K and L)

Chen and Crasemann, ADNDT 41, 257, 1989 (M)

Campbell et al, Nucl. Instr. Meth. B170, 193-204 (2000)

X-ray mass attenuation coefficients

http://www-cxro.lbl.gov/optical_constants/filter2

Helper programs supplied with GUPIX

GUCSA: Access to the GUPIX data base

GUYLS: Calculation of PIXE yields for specific cases

GUCSA

GUYLS

Detection limit and background

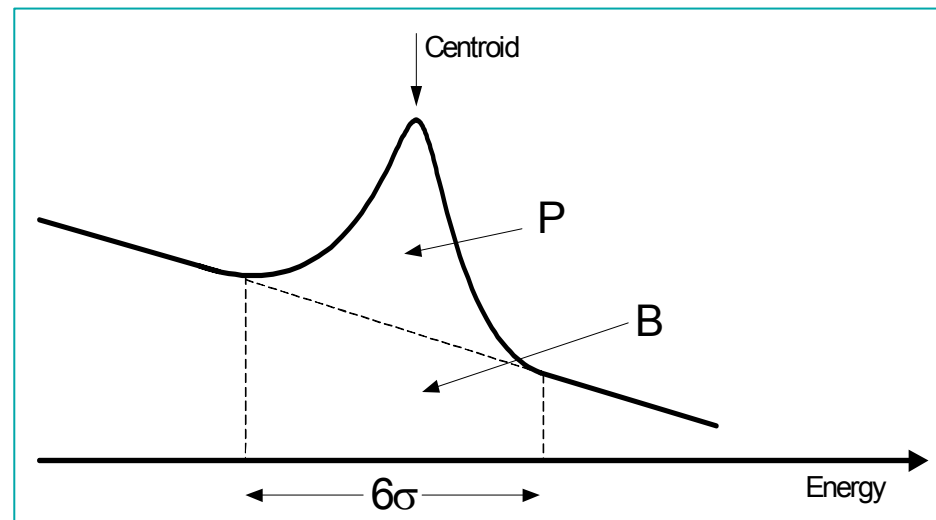
Sensitivity (Limit of Detection, LoD or Minimum Detectable Limit, MDL).

The smallest quantity of an element that can be detected. This depends on the ratio of the area of the characteristic peak to the non-specific background (noise) beneath the peak.

This depends on the excitation method – we need a high ionisation efficiency and a low background.

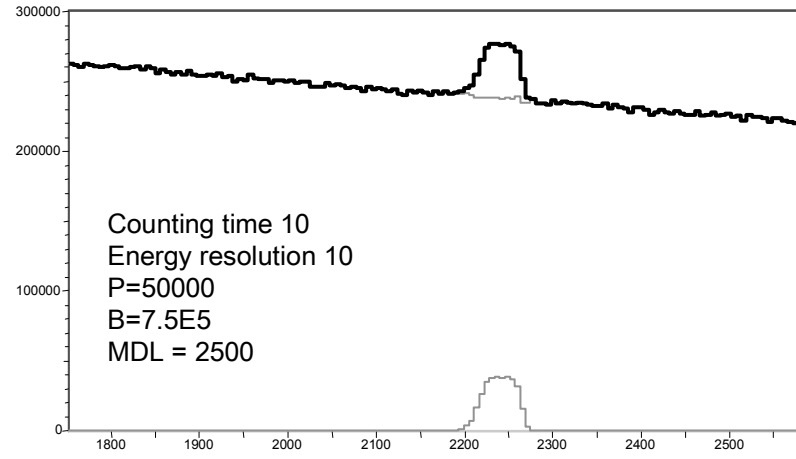
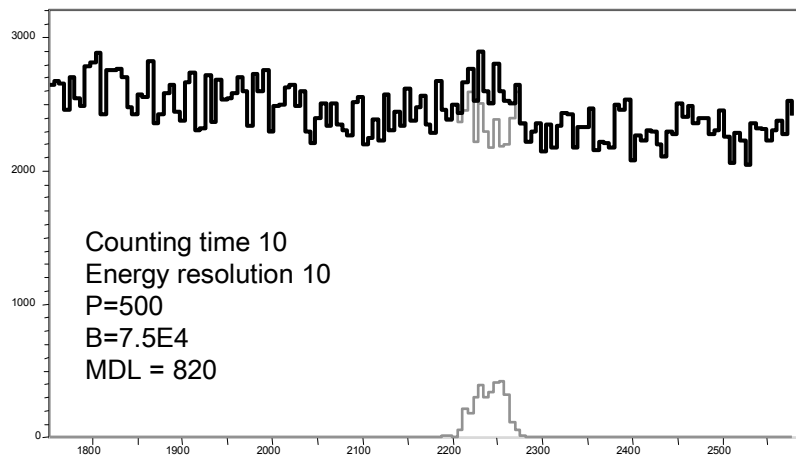
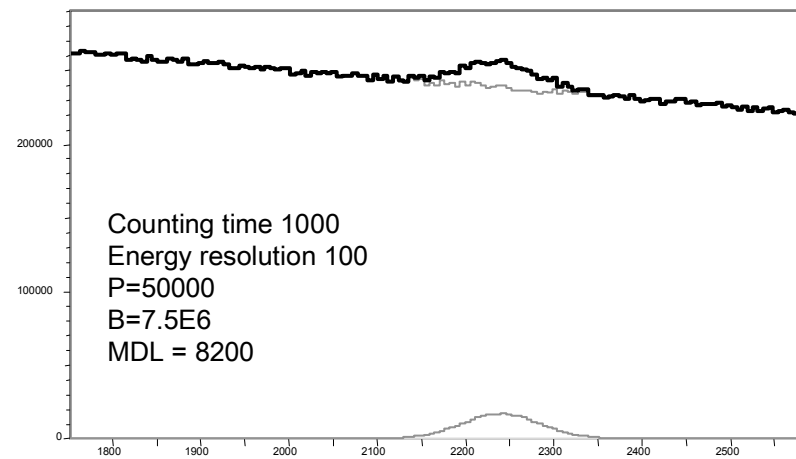
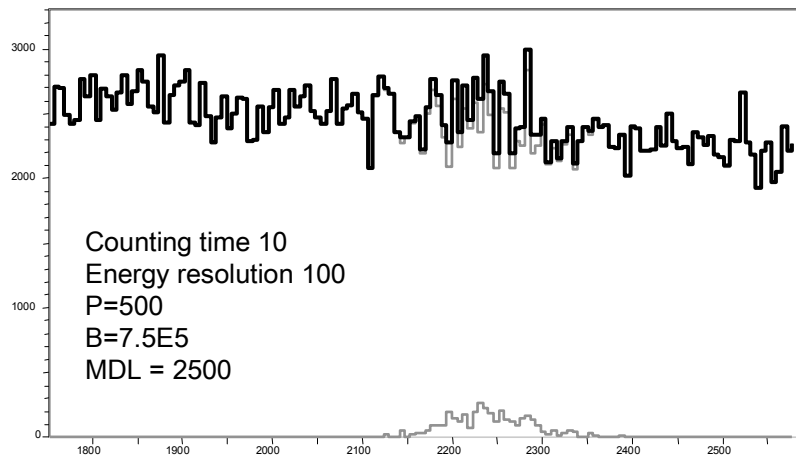
Various definitions of MDL, but usually something like

$$\text{MDL} = 3 \times \sqrt{(\text{background within } 6 \text{ s.d. of the centroid})}$$



Simulations showing the effects of counting statistics and resolution in determining sensitivity

The background under a peak depends on the total counting time and the resolution of the detector



Sources of background

For PIXE the possible sources of background are as follows:

1. Primary proton bremsstrahlung
2. Secondary electron bremsstrahlung and synchrotron radiation
3. Spurious responses in the detector
4. Sample charging

Sources of background: 1

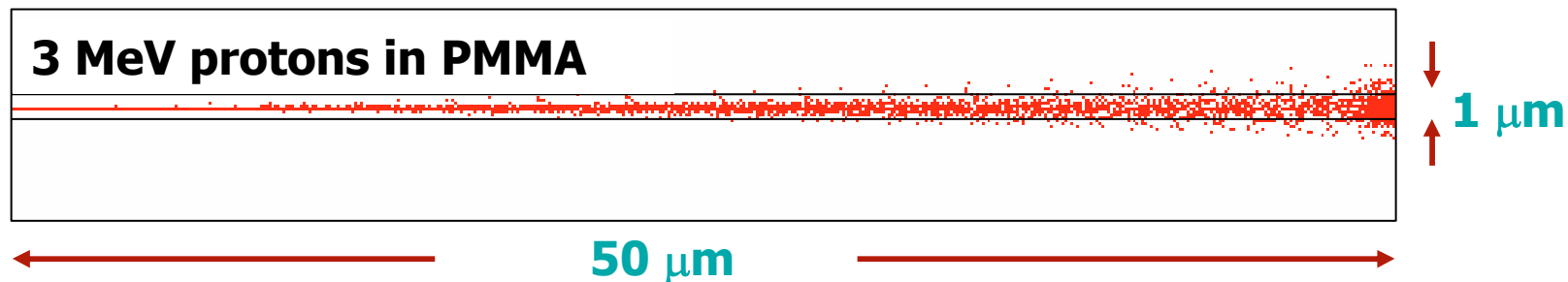
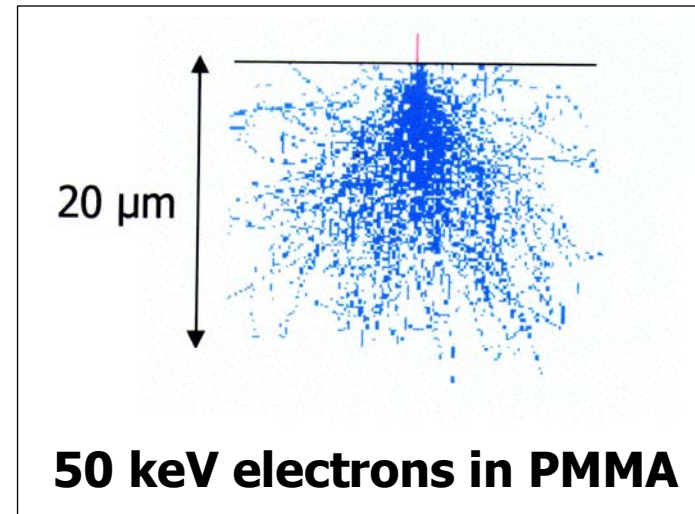
1. Primary proton bremsstrahlung

In ELECTRON induced X-ray emission, the primary electrons are strongly scattered by the electrons in the sample. Each deflection causes the primary electron to radiate broad-spectrum **bremsstrahlung** radiation with a maximum energy equal to the electron energy. This can be very intense and swamps weak characteristic lines

By contrast the high mass of protons means that they have very small deflection at each electron collision. This means that

primary bremsstrahlung is essentially absent.

This is the single piece of physics that makes PIXE worth doing!



Sources of background: 2

2. Secondary electron bremsstrahlung (SEB) and synchrotron radiation

The electron removed by ionisation may either collide with nearby electrons and eventually stop, or execute an orbit returning to its parent atom (synchrotron radiation). In each case bremsstrahlung is emitted.

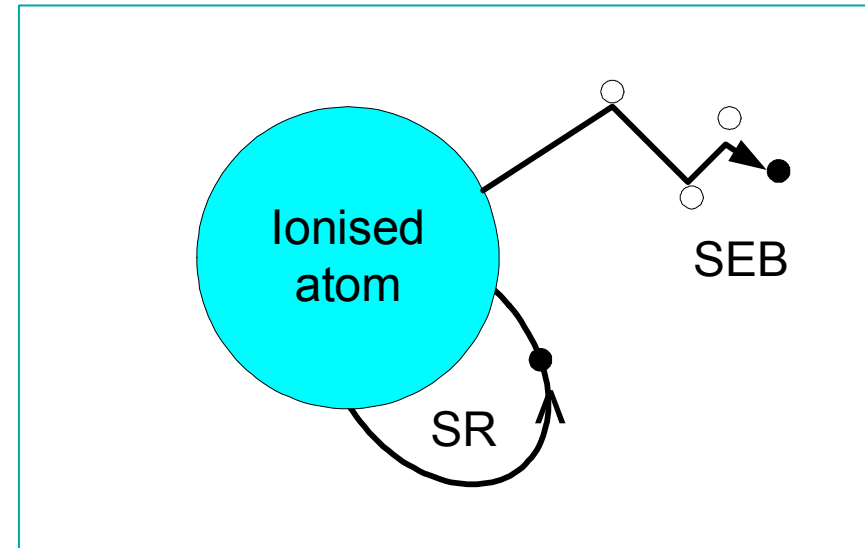
This is much less severe than the primary bremsstrahlung of electrons because:

1. The maximum energy that can be transferred to an electron in a proton-electron collision is

$$E_e = (4m_e / m_p) E_p$$

or about 6.5 keV for 3MeV protons. This means that SEB only affects the lower energy part of the spectrum.

2. SEB is a secondary process! The number of secondary electrons created is orders of magnitude lower than the number of primary particles



Note that secondary electrons created by X-ray fluorescence can have an energy comparable with the primary x-ray energy (> 30 keV), which contributes to a significant background in XRF

Sources of background: 3

3. Spurious responses in the detector

Semiconductor ED detectors can generate spurious peaks or background under high flux conditions. If these fall at the same energy as a small peak of interest then the detection limit will be degraded. The most important spurious responses are:

Pile-up. This occurs when the flux is so high that two photons are detected simultaneously, giving a spurious peak at the sum of their energies (e.g. two Ca $K\alpha$ photons will give a sum peak at the same energy as Ni $K\alpha$, so it can be difficult to measure Ni in bone).

Escape peaks. These are caused by the emission of silicon $K\alpha$ X-rays from the detector near-surface regions. This causes a peak with an energy 1.7 keV below the primary peak which can cause a problem if the primary peak is intense (e.g. the escape peak from Ca $K\alpha$ has the same energy as P $K\alpha$, again giving problems in bone)

Low energy tails. Various carrier trapping processes in the detector contribute to a long low energy tail on each peak.

These problems are most significant at high count rates, and so it is crucial to ensure that intense peaks are attenuated using suitable absorbers

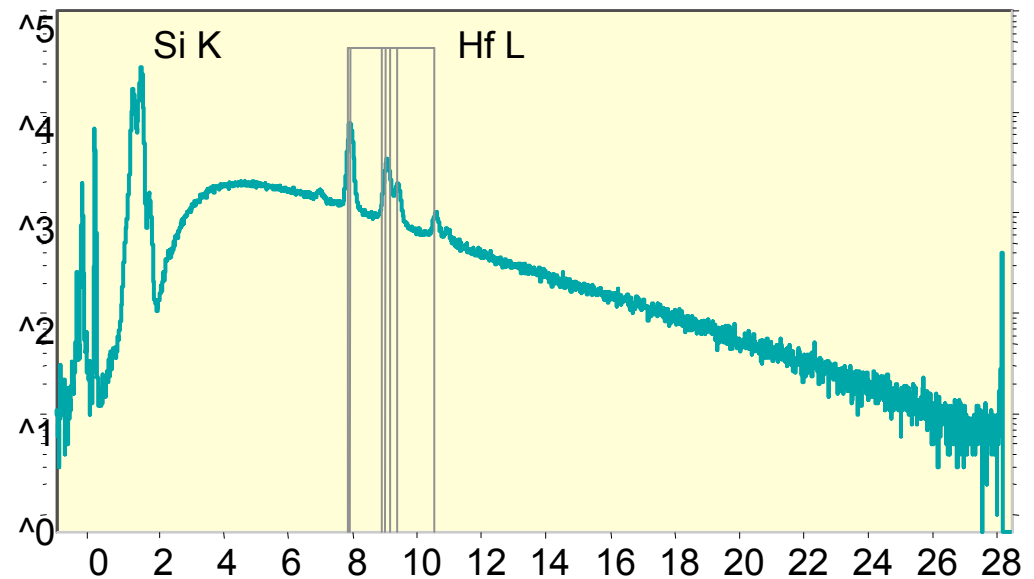
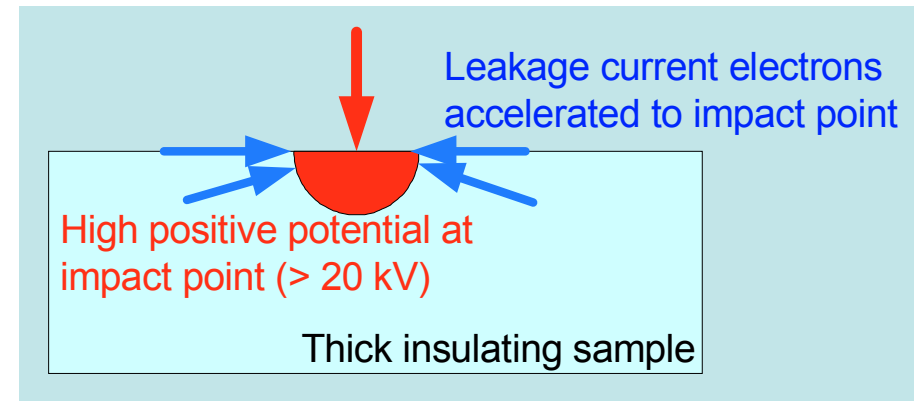
Sources of background: 4

4. Sample charging

Thick insulating samples may charge up to a very high potential (tens of kV) under the beam. Electrons carrying leakage current across the surface or through the volume are accelerated to this potential and emit high energy, high flux bremsstrahlung.

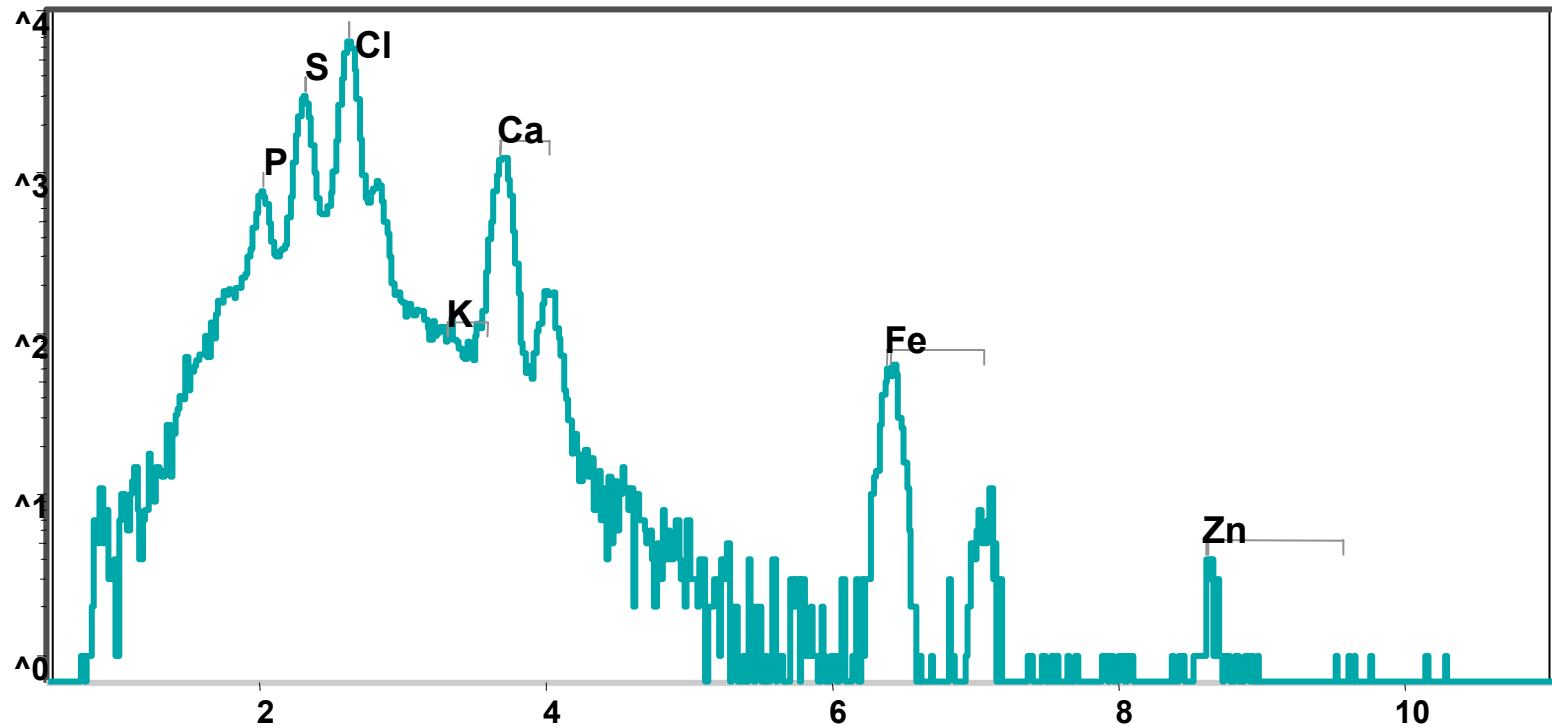
This can be a serious problem in materials with high resistivity such as glass, rock, bone, dry wood.

The problem can be improved by coating the sample surface with a thin layer of conducting material such as carbon (or analysing in air).



PIXE spectrum of a HfO coated glass laser mirror showing intense bremsstrahlung background due to charging. Surface coating was not possible for this sample

“Normal” PIXE spectrum



PIXE spectrum of a thin protein sample acquired using 2.5 MeV protons. This shows clear well-resolved peaks, a low energy bremsstrahlung peak with a cut-off energy of around 5.5 keV (the theoretical value for 2.5MeV protons) and a negligible background above this.

PIXE is capable of achieving detection limits around **1 part per million (w/w)**

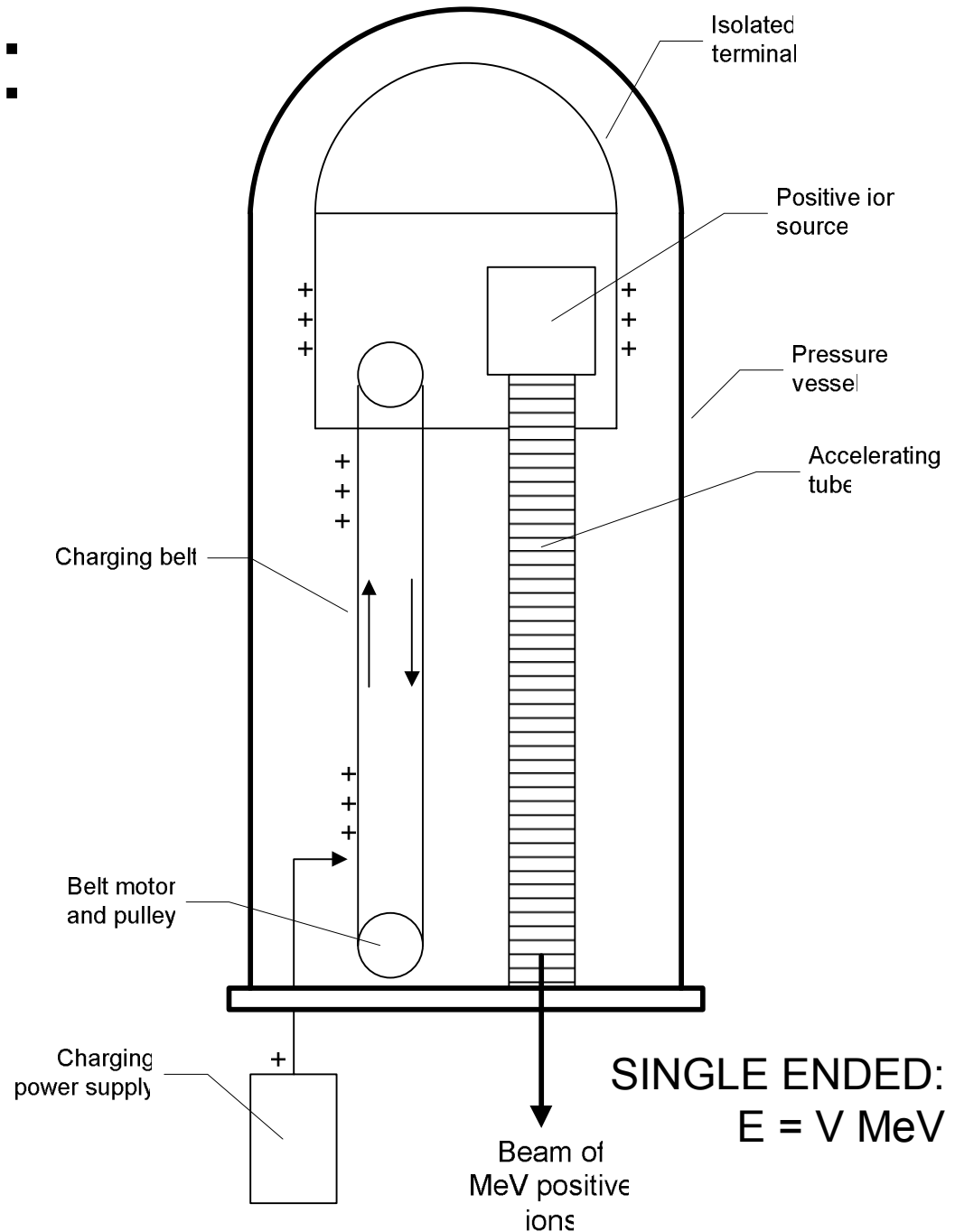
Using a microbeam (sampling volume $1 \mu\text{m}^3$) this corresponds to an absolute detection limit of around **10^{-18}g (1 attogram, or around 10^6 atoms)**

Practical aspects of PIXE

Accelerators:

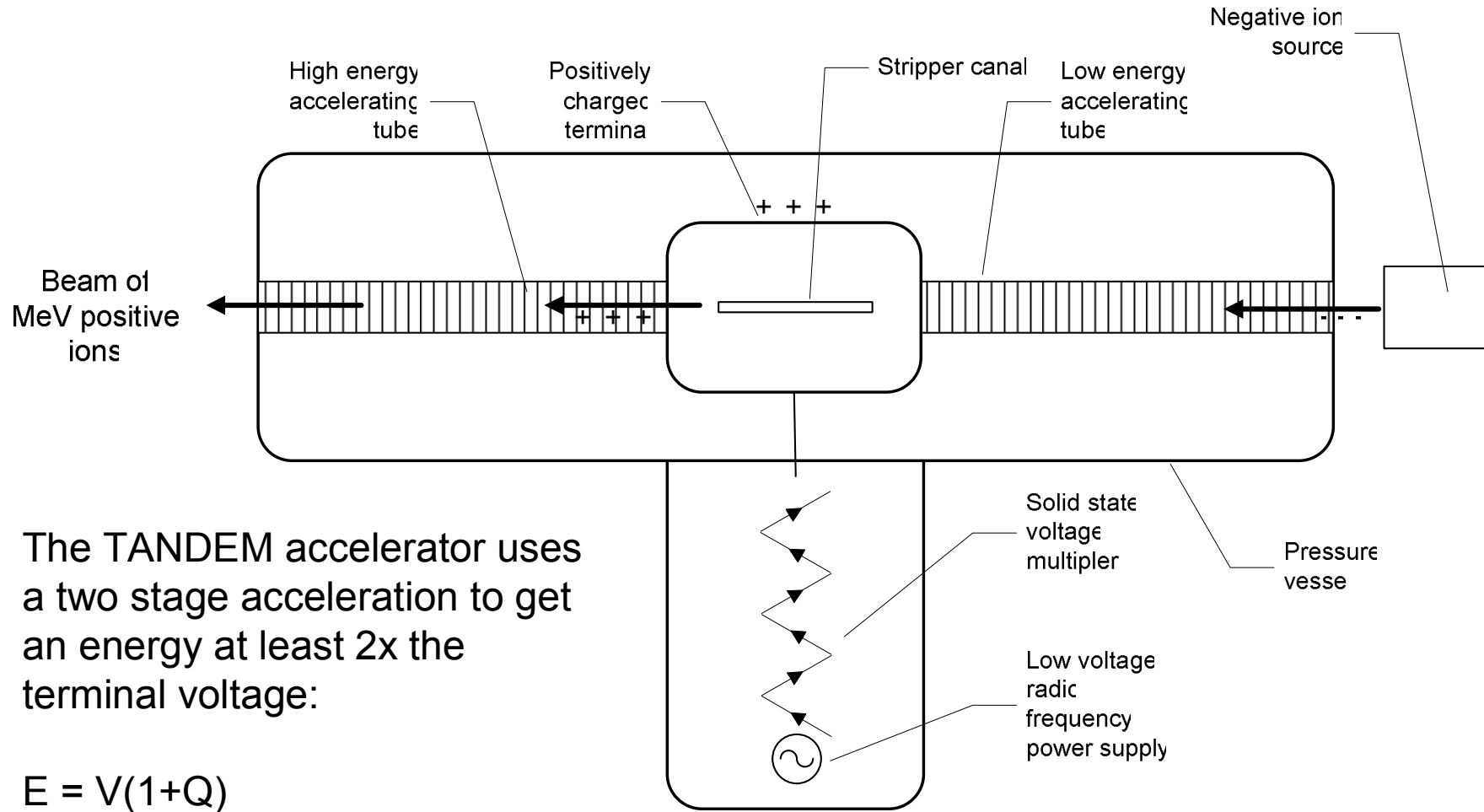
- Most PIXE analysis uses electrostatic accelerators

The diagram shows a Van de Graaff type accelerator where the high terminal voltage is generated by a moving belt. Typical small Van de Graaffs can reach up to 4MV.



Accelerators

A more modern method of generating the high voltage is a high frequency diode-capacitor voltage multiplier stack (“Tandetron”)



The TANDEM accelerator uses a two stage acceleration to get an energy at least 2x the terminal voltage:

$$E = V(1+Q)$$

2MV Tandemron accelerator at University of Surrey



Detectors

The detector most often used for PIXE is the lithium drifted silicon detector, or **Si-Li**.

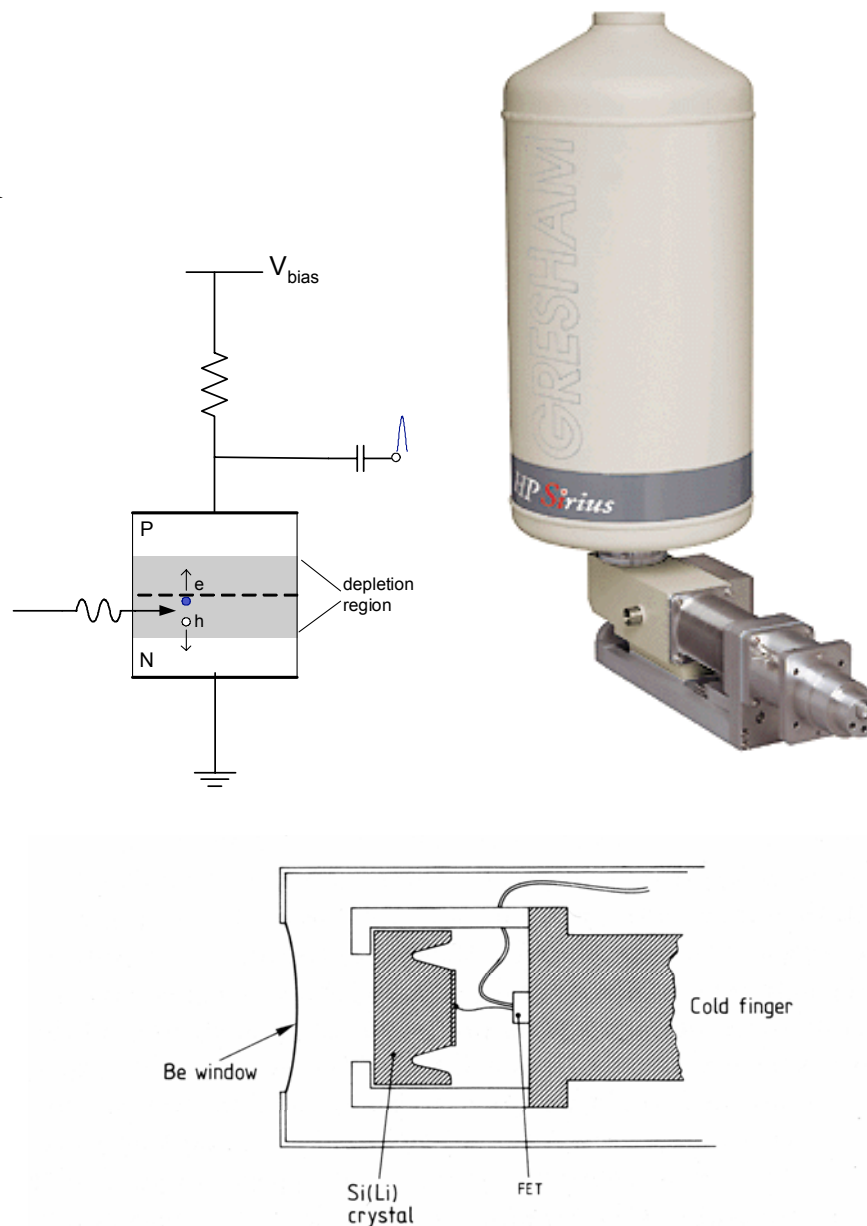
This is a reverse biased P-N silicon diode which generates a pulse of charge proportional to the energy of incident X-ray photons.

The detector must be operated at the temperature of liquid nitrogen to reduce the leakage current (and hence noise). This requires a large insulated container to hold the LN2 and a 'cold finger' to mount the crystal. The first transistor of the signal amplifier is also mounted on the cold stage.

The area around the crystal is kept under vacuum to avoid condensation. X-rays are admitted through a thin window (typically 12 μm beryllium to reduce absorption).

Detectors based on materials such as cadmium zinc telluride (CZT) are under development which may eventually eliminate the requirement for LN2.

The development of the Si-Li detector in the late 1960s opened the way to PIXE analysis



Si-Li detectors are fragile and expensive (~£15k)

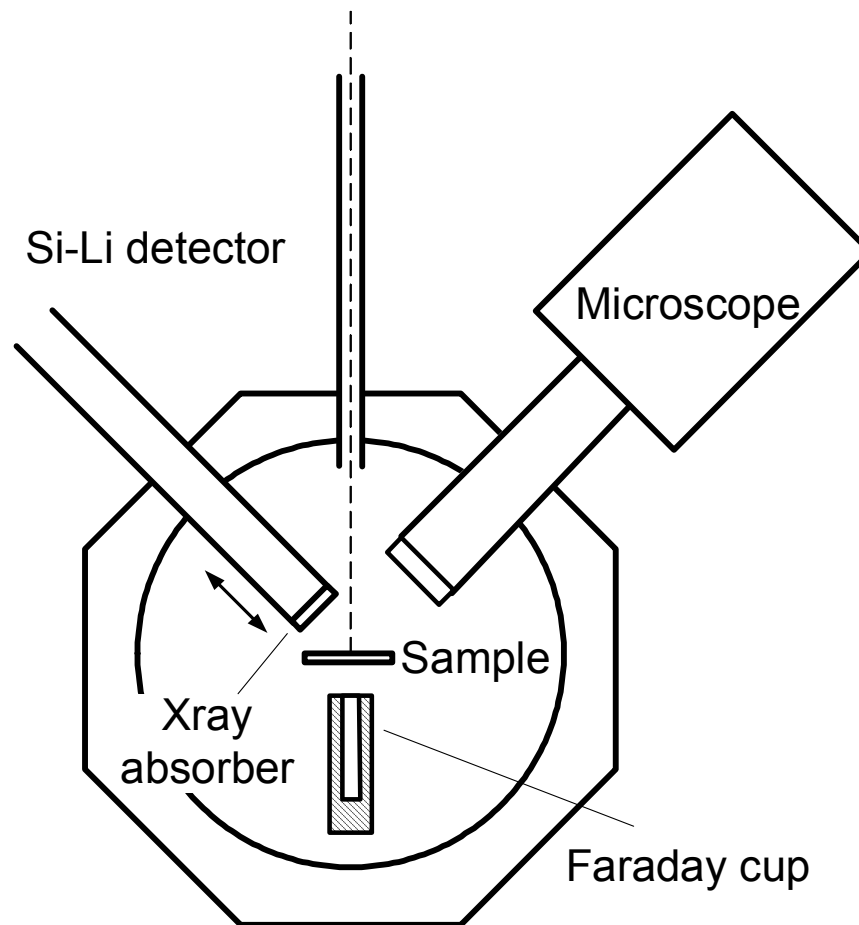
Handle with care!!

Target Chamber

Target chambers

A typical PIXE facility may contain the following components

- Si-Li detector with facility to fit X-ray absorber. Detector may be retractable to allow the count rate to be controlled
- Microscope for sample viewing
- Sample mounted on adjustable stage (may allow mounting many samples)
- Faraday cup to measure the incident beam current with thin samples
- Evacuated sample chamber connected to beamline



The use of absorbers

The “dynamic range” of PIXE analysis is very large: the same spectrum may have significant peaks with 10 counts and 10 million counts (this is why PIXE spectra are normally displayed on a log scale). Intense peaks are usually not interesting (e.g. Si in rocks and glass, Ca in bone) and can cause severe problems with spurious peaks and background.

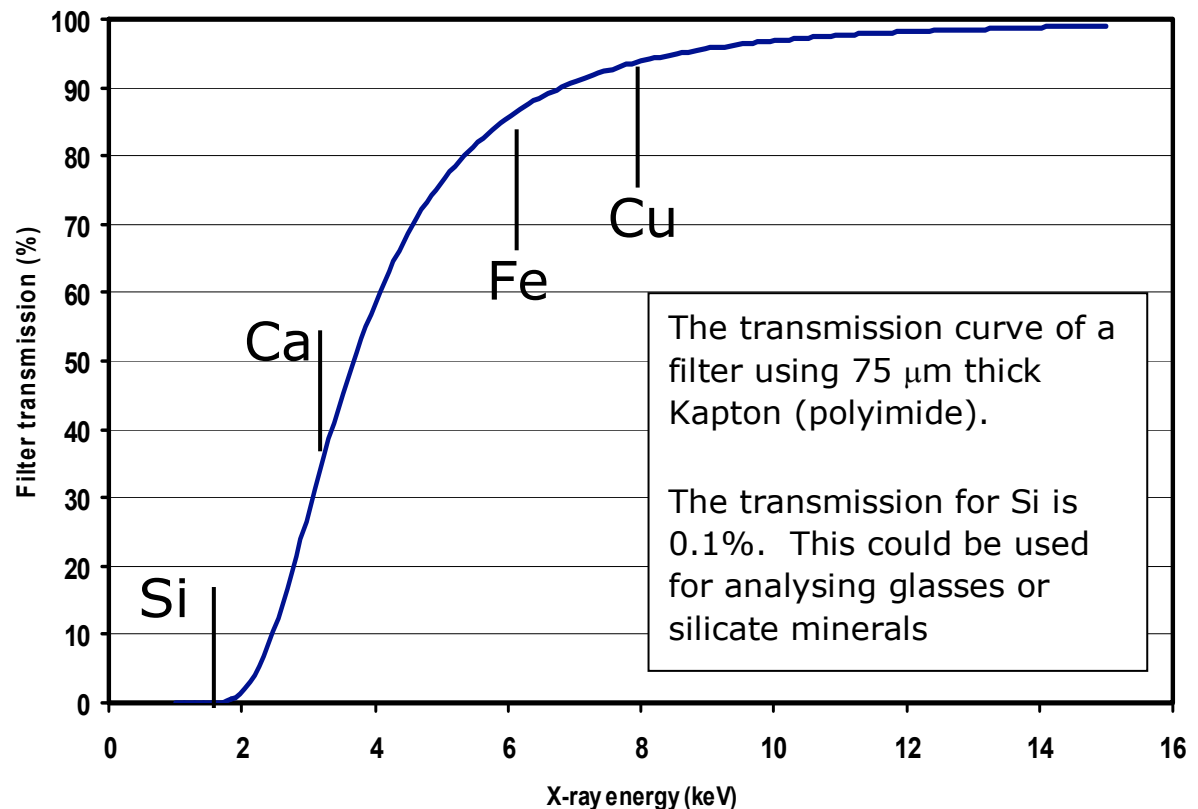
Their effect can be minimised by fitting an x-ray absorber which selectively attenuates the low energy region of the spectrum and transmits the high energy peaks from the trace elements of interest.

Filters can also be used to stop protons entering the detector and degrading the signal processing

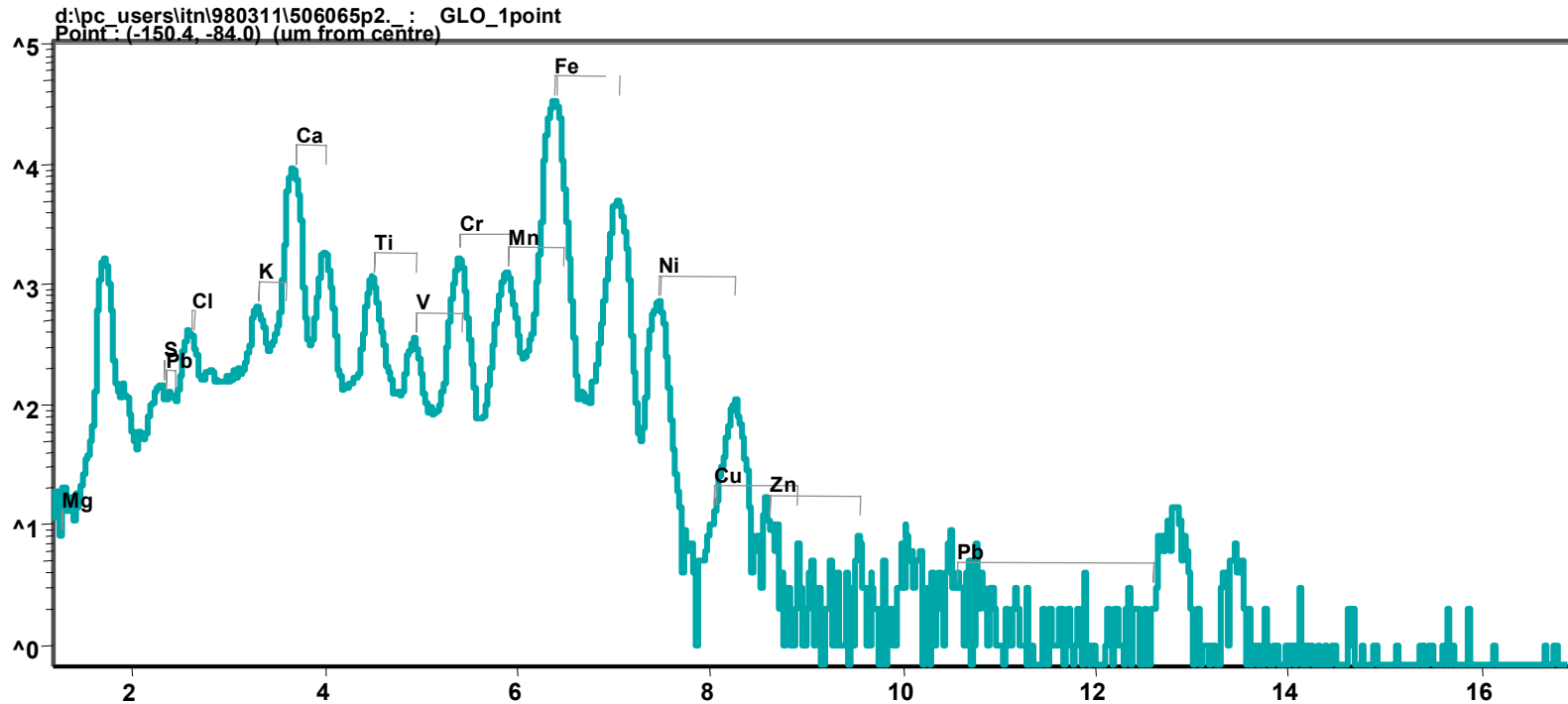
Absorber foils are made from a variety of materials, but usually polymers or low Z metals (to avoid spurious fluorescence peaks).

Some tricks that are used include:
Absorption edge filtering: Using a foil with a Z just below the element you are trying to filter.

Magic filters: Filters with a small hole to allow a small fraction of the low energy lines to come through.



Spectrum processing



This is a typical PIXE spectrum from a metal sample (in fact a reactor vessel alloy). Note the sequence of overlaps: $K K_{\beta} - Ca K_{\alpha}$; $Ti K_{\beta} - V K_{\alpha}$; $V K_{\beta} - Cr K_{\alpha}$; $Cr K_{\beta} - Mn K_{\alpha}$; $Mn K_{\beta} - Fe K_{\alpha}$ etc. There is a set of pile-up peaks from Fe starting at 12.8 keV. The Si escape peak from $Fe K_{\alpha}$ is at an energy of $6.4 - 1.7 = 4.7$ keV which is very close to the $Ti K_{\alpha}$ at 4.4 keV. There is a suggestion of a group of peaks around 10 keV which could be pile-up, but may also be traces of $Pb L_{\alpha}$. The lower energy part of the spectrum is sitting on the SEB background.

How can we deal with this sort of complexity?

Spectrum processing software

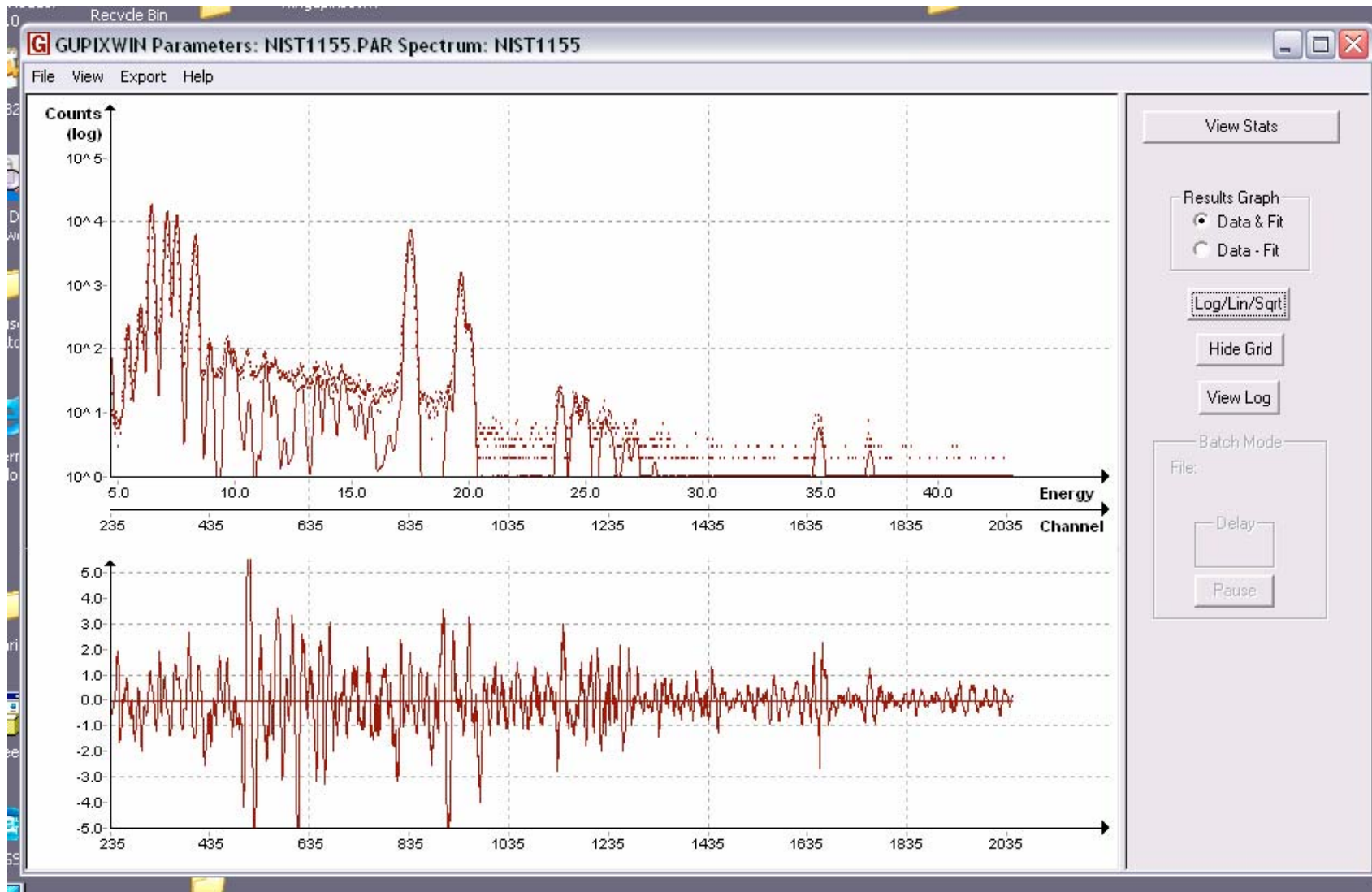
This is a three stage process:

1. Remove the slowly varying background using a technique such as numerical smoothing, digital filtering, or fitting a smooth function. This leaves a spectrum consisting only of characteristic peaks
2. For each element in the sample, create a theoretical model of the full characteristic spectrum, including detector responses. This requires a knowledge of the physics of the radiation emission, the matrix composition and the detector response function (including the spurious responses).
3. Using an optimisation algorithm, vary the relative concentrations of the elements (rather than peak areas now), to simulate the whole spectrum in a single operation and obtain a good fit to the measured data. This automatically deals with peak overlaps and spurious responses and yields as a final answer the concentration values that we are really interested in.

This type of software is still being developed.

There are several software packages to handle this operation, e.g.
AXIL, GEOPIXE II, PIXYKLM, GUPIX/Dan32

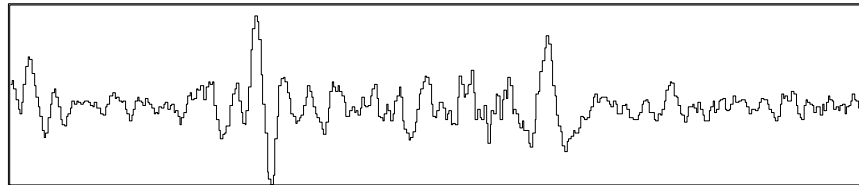
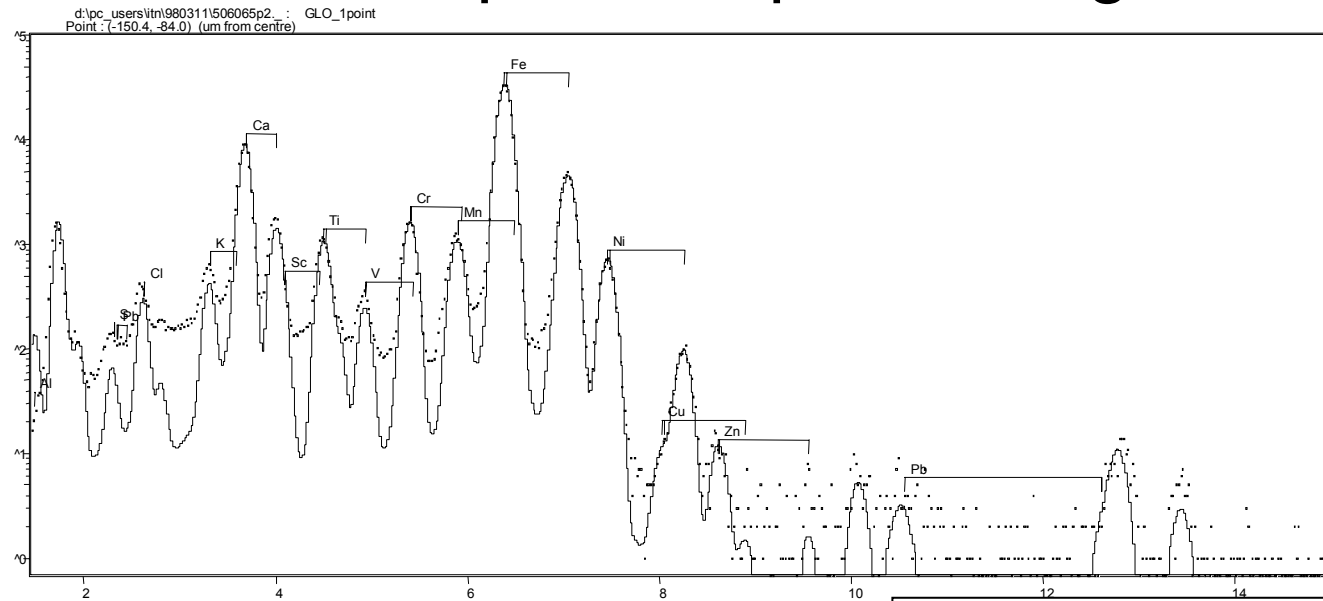
Spectrum processing software: WinGUPIX



We will use this for the practical class

<http://pixe.physics.uoguelph.ca/gupix/download/>

Spectrum processing: Results!



Matrix composition :
1. 2.00 um 1.051g/cm3 210.200ug/cm2: Fe8Al7.07Si6.05Ca1.02
Fe 52.65%; Al 22.47%; Si 20.04%; Ca 4.84%;

Trace Elements :

Al K	1	21.198%	(28987)	+8%
Si K	1	18.904%	(1875)	+1%
S K	1	521.80	(192)	+20%
Cl K	1	2043.10	(132)	+4%
K K	1	1941.40	(125)	+4%
Ca K	1	4.557%	(50)	+0%
Sc K	1	931.90	(355)	+19%
Ti K	1	6795.90	(118)	+2%
V K	1	787.00	(193)	+11%
Cr K	1	1.487%	(83)	+1%
Mn K	1	1.084%	(368)	+2%
Fe K	1	49.645%	(464)	+0%
Ni K	1	1.665%	(114)	+1%
Cu K	1	287.90	(110)	+29%
Zn K	1	471.50	(92)	+15%
Pb LA	1	923.00	(442)	+38%
P K	1	<	(847)	
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A PIXE checklist

(Things you should always check when you are collecting PIXE data)

Peaks

- Can you identify **every** peak in the spectrum?
- Are there any spurious peaks (pile-up, escapes) which will affect weak elements that you are interested in?
- Have you considered all the element overlaps (e.g. Ti $K\alpha$ /Ba $L\alpha$, As $K\alpha$ /Pb $L\alpha$)?
- Are all the elements expected?! (if not check that you are hitting the sample and not the mounting!)
- Does the shape of the peaks look right? Deformed peaks can indicate detector problems or high count rate or protons entering the detector

Background

- Does the low energy background cut off at around 5 or 6 keV?
- Is there any significant high energy background (if so, check for sample charging or high count rate)

Count rate (for Si-Li detectors, count rate should be $< \sim 2000$ counts/sec)

- Is the count rate high enough to give you enough counts in the weakest peak of interest in a reasonable time (remember that statistical accuracy of a peak is $1/\sqrt{N}$)?
- Is the count rate so high that the spectrum is full of spurious peaks and background?
- Is the high count rate due to a few low energy peaks? If so consider fitting an absorber.

Summary of PIXE

- High yield (rapid!) trace element analysis
- Detects all elements simultaneously
 - Element range set by detector response: typically Na – U
- Very low background (no primary bremsstrahlung), so ppm detection limits
- Yield can be calculated from fundamental physics, so you can get good accuracy with a minimal dependence on standard reference materials.

Applications of broad beam PIXE

- The use of PIXE for routine high volume elemental analysis has been largely superseded by techniques such as ICP-MS or AAS
- PIXE still has advantages in certain areas:
 - Little sample preparation required (e.g., aerosol filters)
 - Fast
 - Multielemental, so can detect “unexpected” elements
 - No strong dependence on standards
 - Can analyse in air
- Current active areas of application:
 - Aerosol filter analysis
 - Monitoring of industrial processes (looking for contamination)
 - Identification of “totally unknown” samples
 - Cultural heritage applications
- **PIXE becomes much more exciting when used with microbeams!**

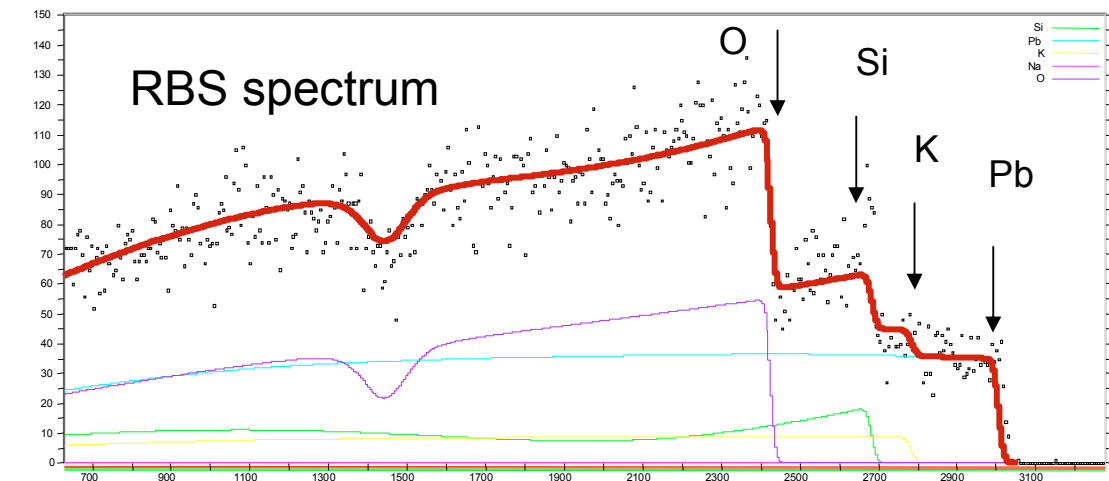
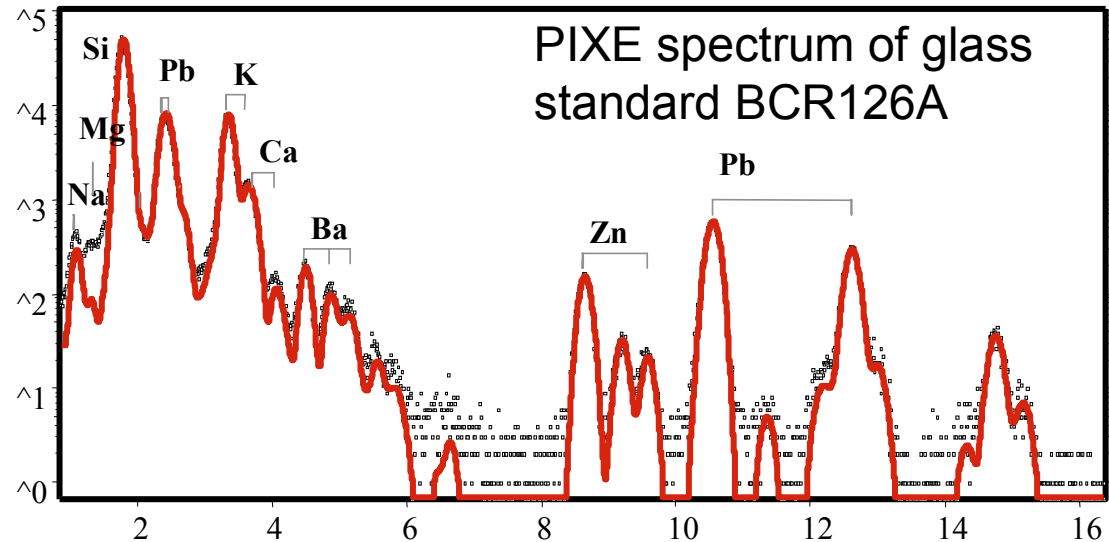
Further reading on PIXE

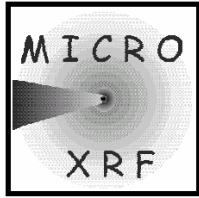
- Johansson, S.A.E. & Campbell, J.L. (1988). *PIXE, A novel technique for elemental analysis*. J.Wiley: Chichester.
- S.A.E. Johansson, J.L. Campbell, K.G. Malmqvist, “Particle-induced X-ray Emission Spectrometry” (1995) John Wiley & Sons
- F Watt G W Grime (eds.), “Principles and Applications of High Energy Ion Microbeams” (1987) Publisher: Hilger; ISBN: 0852745176 (rather dated by now)
- Proceedings of the International Conferences on Particle Induced X-ray Emission and its Applications (last one in 2004, Portoroz, Slovenia, <http://pixe2004.ijs.si/proceedings>)
- Grime, G.W. (1999). High Energy Ion Beam Analysis Methods (and Background). In *Encyclopedia of Spectroscopy and Spectrometry* (Lindon, J.C., Tranter, G.E. & Holmes, J.L., eds.). pp. 750-760, Academic Press: Chichester.

Quantitative analysis using PIXE and RBS

- Simultaneous RBS and PIXE analysis of a certified reference material (lead glass)
- RBS provides
 - Total beam charge
 - Sample matrix compositionso that PIXE yield can be calculated accurately

The “Q-factor method”





WP6

Reproducibility



UniS

Typical results from 5 sequential analyses at the same spot

	Certified wt %	1	2	3	4	5	Average Conc.	Rel s.d. (%)	PIXE/RBS
Na	2.66	2.685	2.703	2.817	2.769	2.800	2.755	2.1	
Si	26.97	27.219	27.551	27.270	27.636	28.141	27.563	1.3	
K	8.3	8.368	8.483	8.432	8.530	8.676	8.498	1.4	
Pb (L)	22.26	22.718	22.682	22.697	22.864	23.334	22.859	1.2	
Mg	0.31	0.227	0.273	0.273	0.201	0.206	0.236	14.9	
Al	0.07	0.087	0.131	0.115			0.111	19.7	
Ca	0.74	0.741	0.750	0.737	0.773	0.790	0.758	3.0	
Zn	0.82	0.844	0.837	0.852	0.857	0.856	0.849	1.0	
Ba	0.93	0.942	0.976	0.904	0.942	0.964	0.946	2.9	

20 point (100 analyses) gives a mean relative s.d. of 3.0% (without Mg and Al)

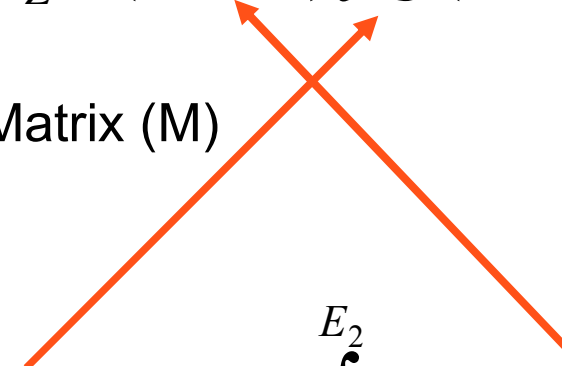
PIXE and RBS yields

PIXE

$$N_x = \Omega_P \varepsilon(E_x) c_Z Y(Z, M) fQ(1 - \Delta_x)$$

Unknowns: charge (fQ), Matrix (M)

RBS

$$N_b = \int_{E_1}^{E_2} S(E) dE = \Omega_b fQ(1 - \Delta_b) \int_{E_1}^{E_2} R(E, M) dE$$


Q factor method

Assuming detector solid angles etc. are well known -

fQ is determined by ratio of areas of fitted and measured RBS spectra.

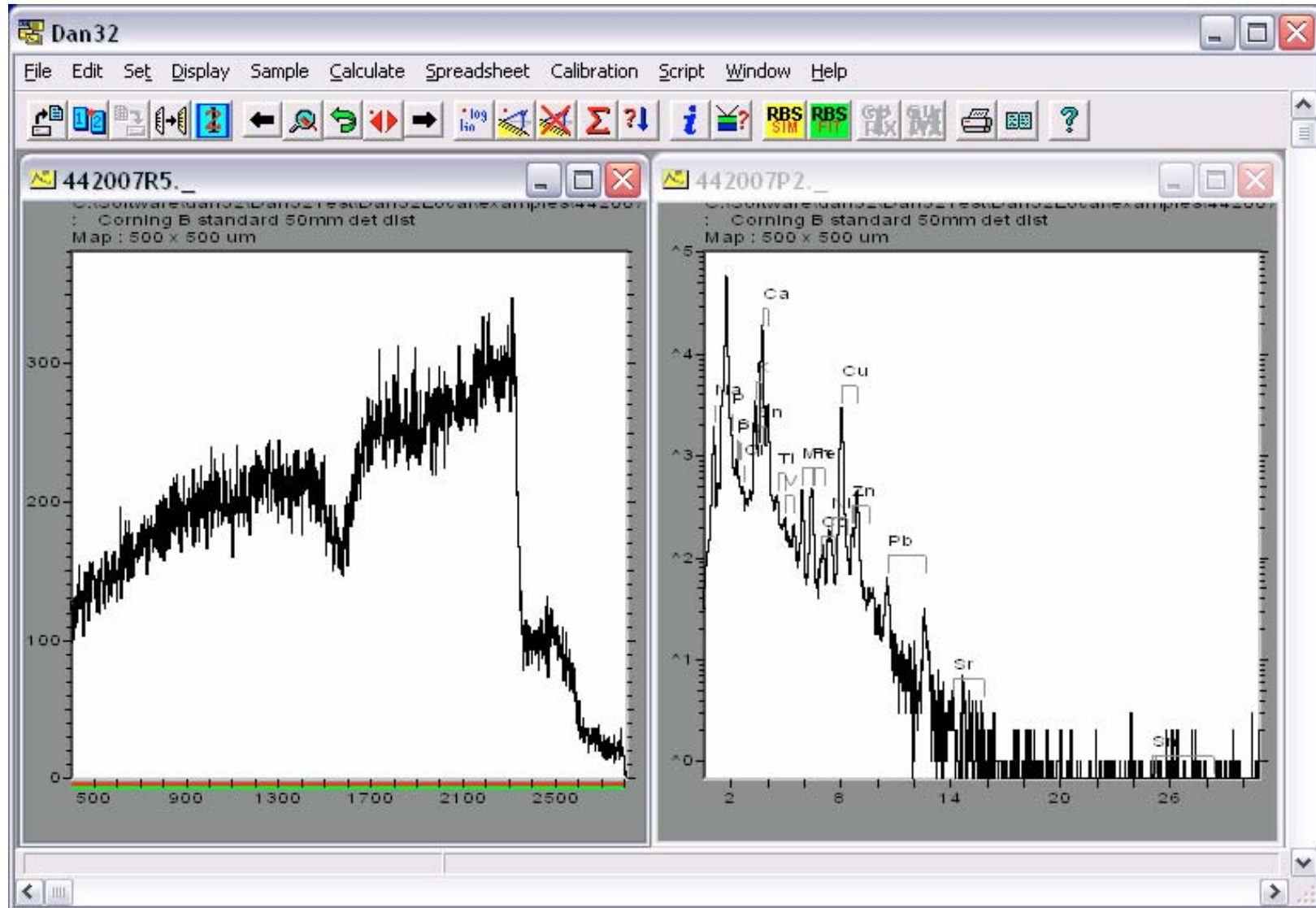
This also determines the local sample matrix

Limitations: RBS fit must be good - requires good cross sections and a target with simple structure.

(See G.W. Grime, "The "Q factor" method: Quantitative microPIXE analysis using RBS normalisation", Nucl. Instr. and Meths. B109 (1996) 170-174)

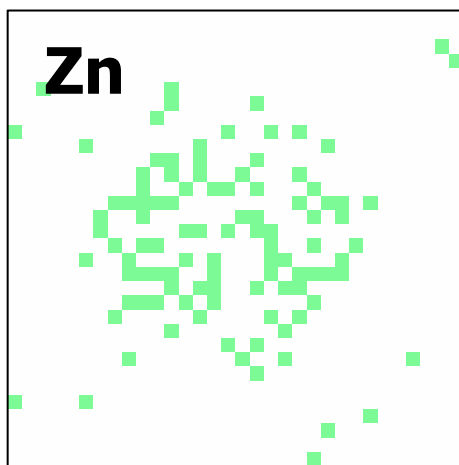
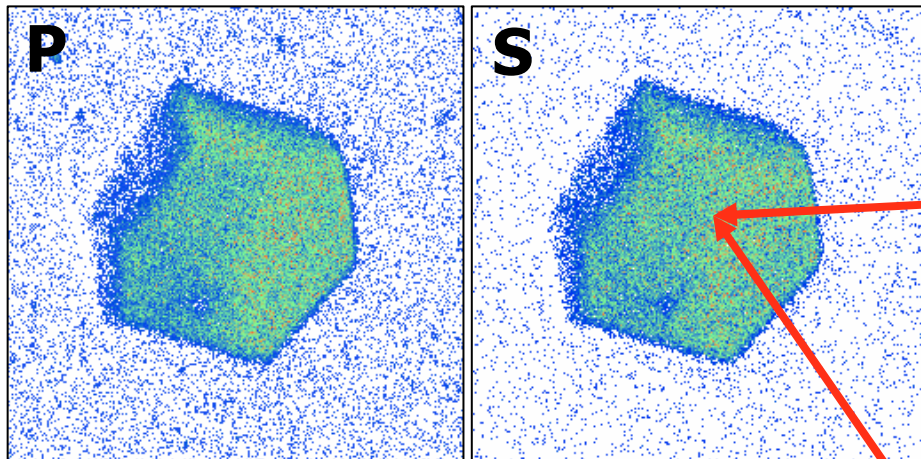
Spectrum processing software Dan32

Implements the Q-factor method and processes RBS and PIXE spectra simultaneously

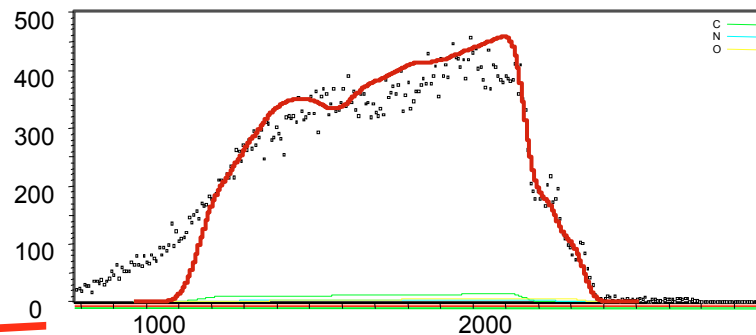


<http://www.microbeams.co.uk/downloads>

Crystal of Blue-tongue virus

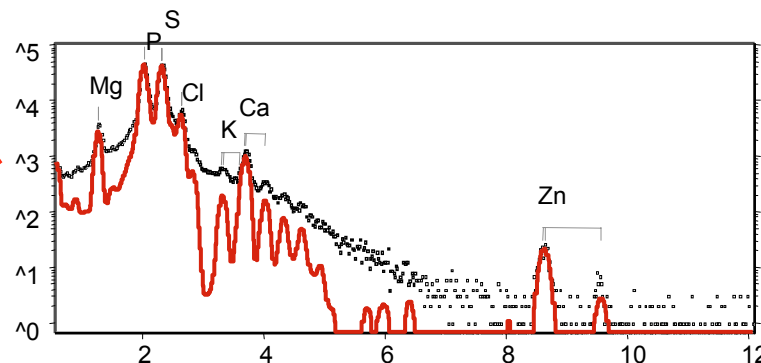


200 μm



RBS fit:

$\text{C}_4\text{N}_{1.25}\text{O}_{1.43}$ 20.7 μm



PIXE results:

P	1.49%	Ca:S	0.02:1 atoms
S	1.17%	Zn:S	0.004:1 atoms
Ca	350ppm	P:S	1:1 atoms
Zn	90ppm		