PIXE

PROF DAVID COHEN

Australian Nuclear Science and Technology Organisation

Lucas Heights, Sydney,

Australia

PIXE TALKS (I)

Morning Lectures will cover:-

PIXE Overview

- Ion - atom interactions
- Vacancy production
- ECPSSR K, L shell ionisation theory
- Ion transport

PIXE TALKS (II)

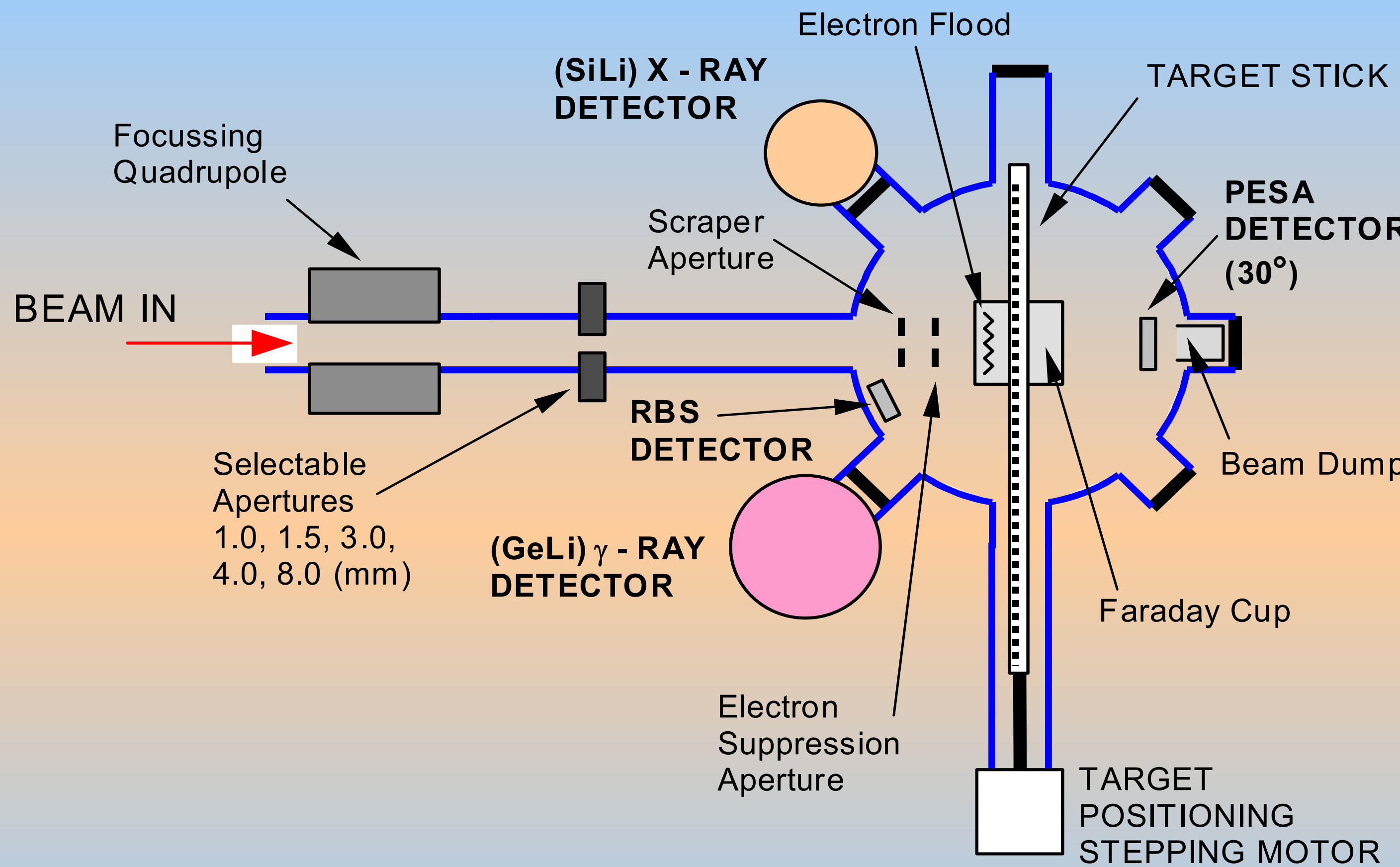
PIXE Systems

- PIXE end station designs
- Current measurement
- X-ray detection
- PIXE spectra, escape peaks
- PIXE electronics, pileup, sum peaks
- Filters and spectrum shaping
- Spectrum analysis, line shapes, backgrounds
- Peak areas to concentrations
- PIXE system calibrations
- X-ray detectors, efficiency

PIXE TALKS (III)

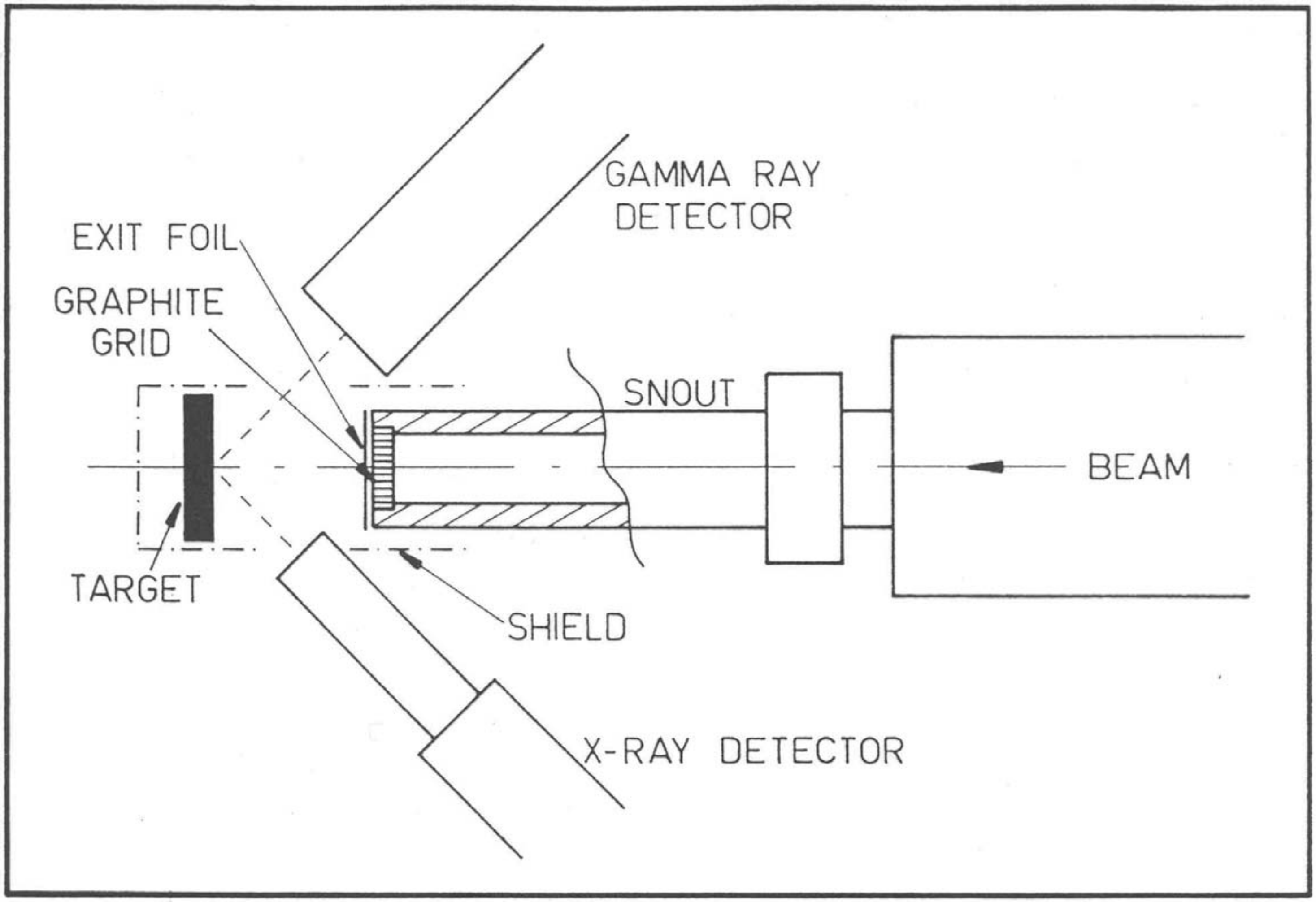
PIXE Analysis Methods

- DOPIXE Code,
- Peak areas,
- Elemental concentrations,
- Calibrations,
- For thin and thick samples.

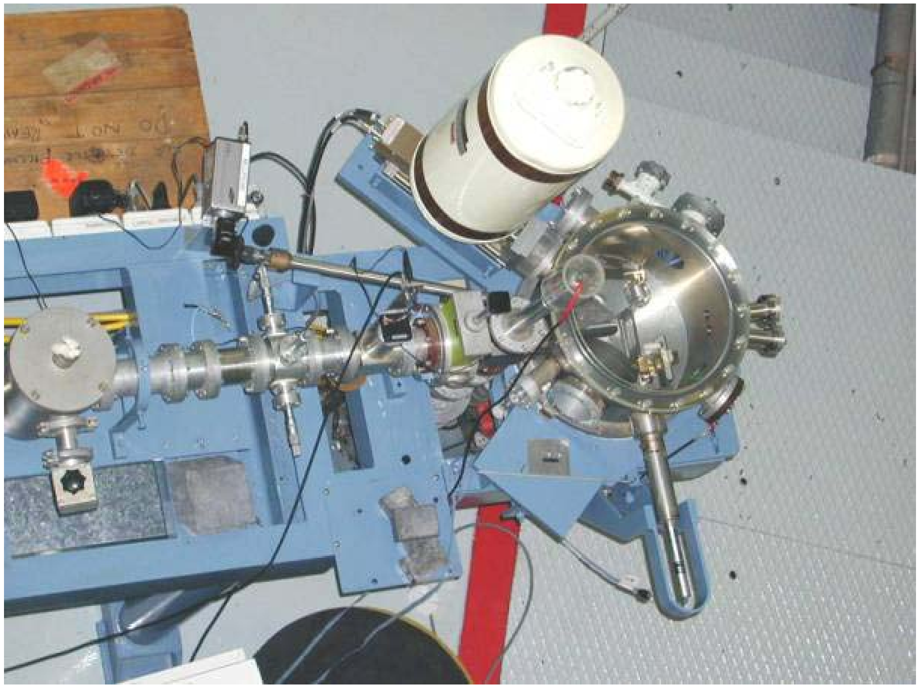


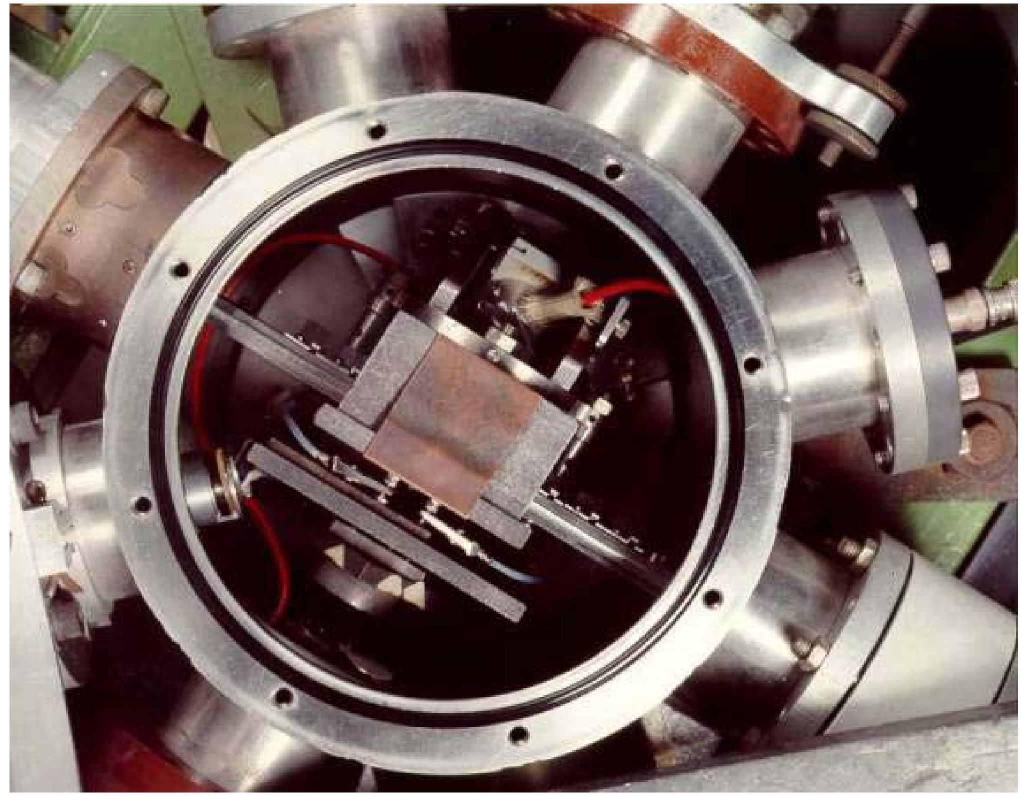
Layout of the SR2 Light Ion Analysis Station

PIXE, PIGE, RBS and PESA target chamber at ANSTO



External Beam Facility





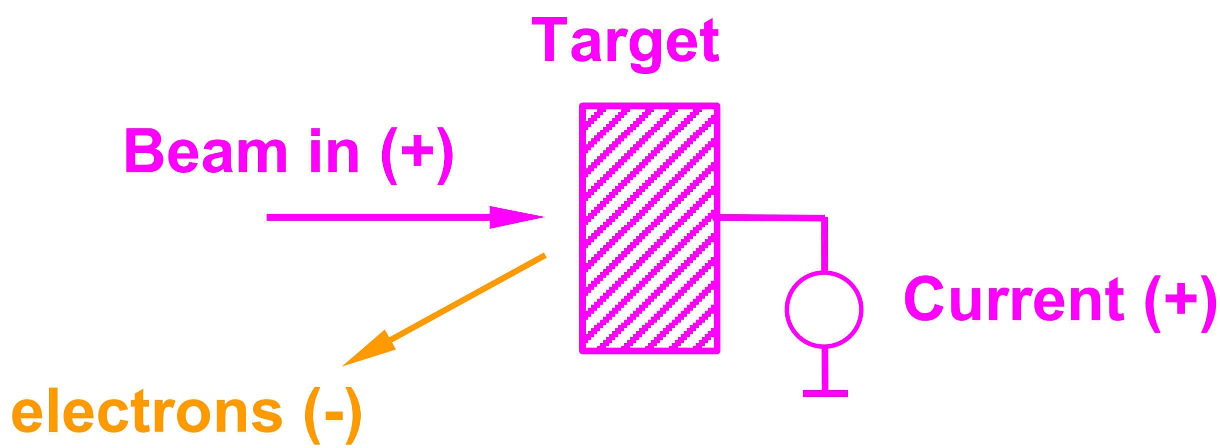
Typical IBA and PIXE end stations and chamber

Target Current Measurement

To obtain quantitative elemental analyses using ion beam techniques you need to measure the total charge hitting the target. This is performed by integrating the current,

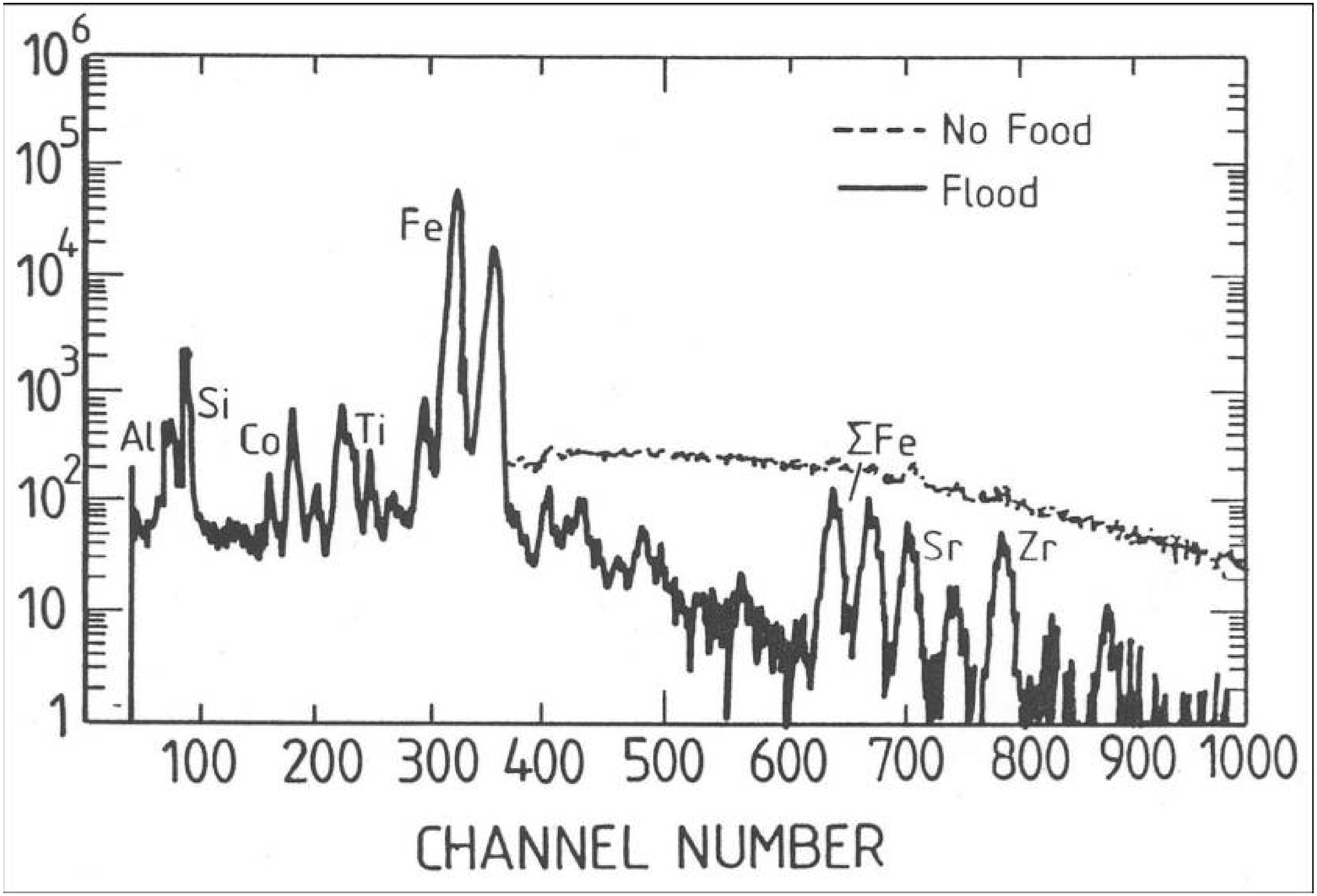
Charge = Current * Time, $Q = I*t$

To do this the target should be conducting and well insulated from ground (>> 100 MΩ).

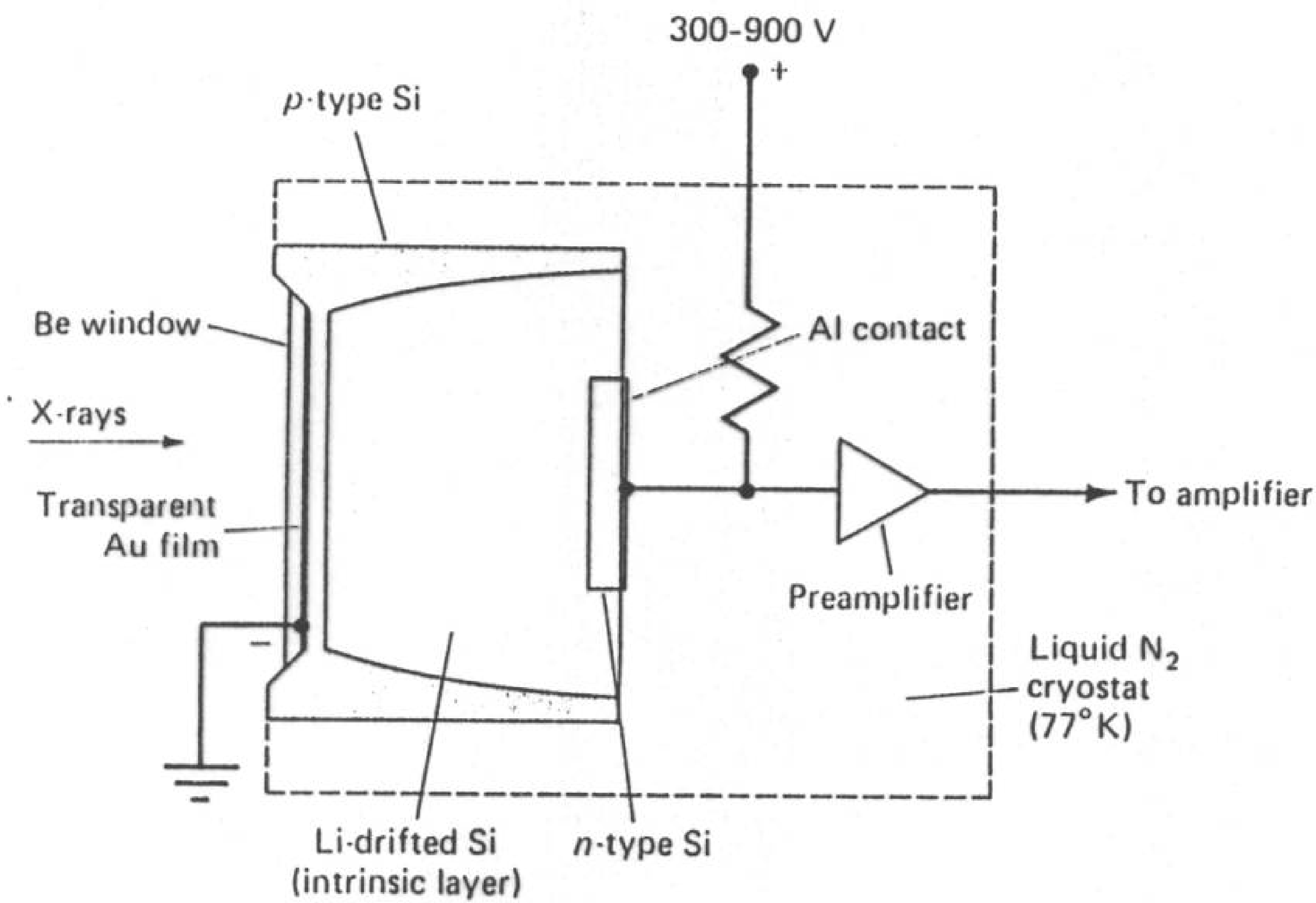


Electron flood, Coat with carbon, Bias the target

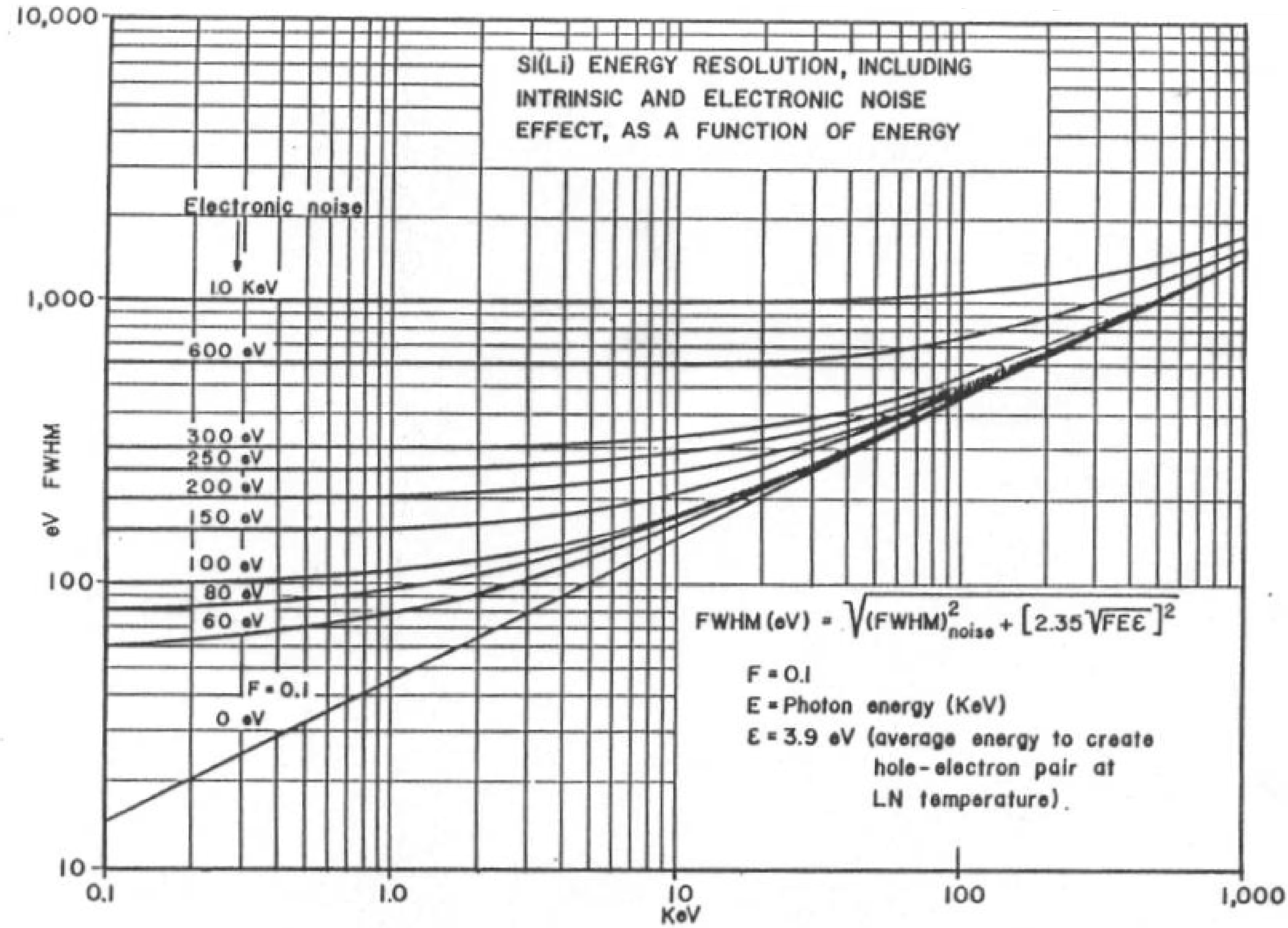
Electron Target Flood



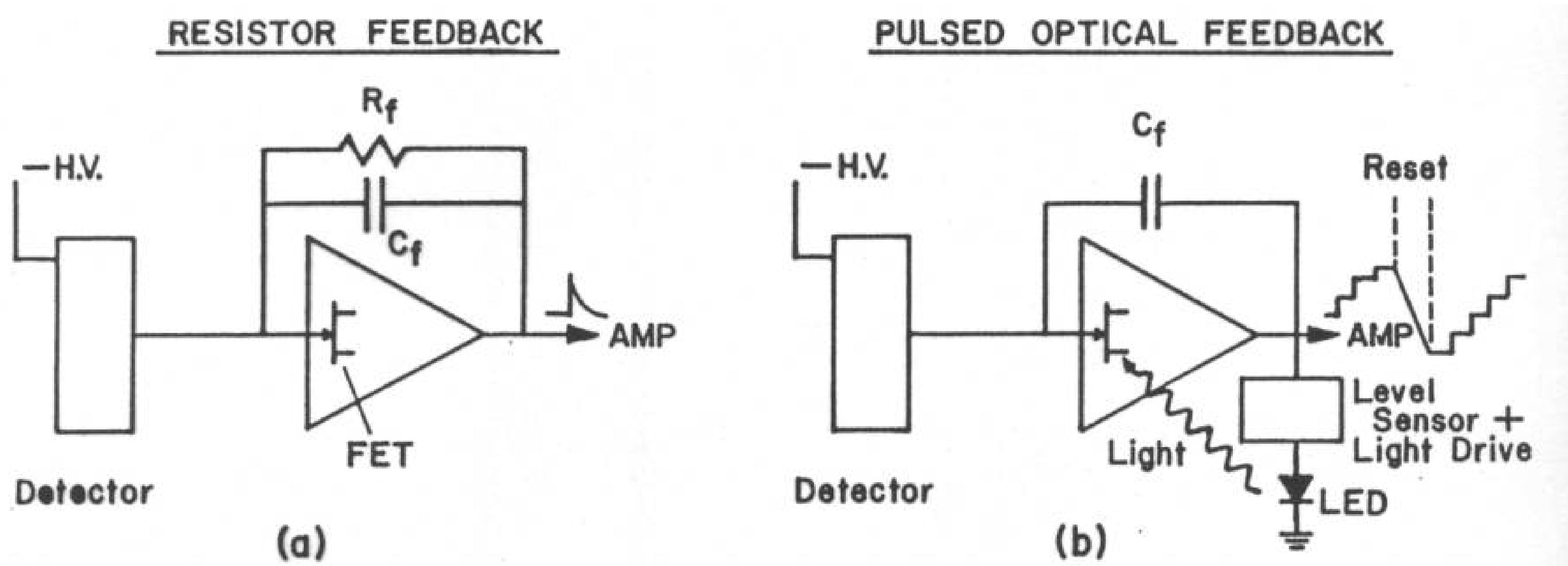
X-ray Detector



Si(Li) Detector Resolution

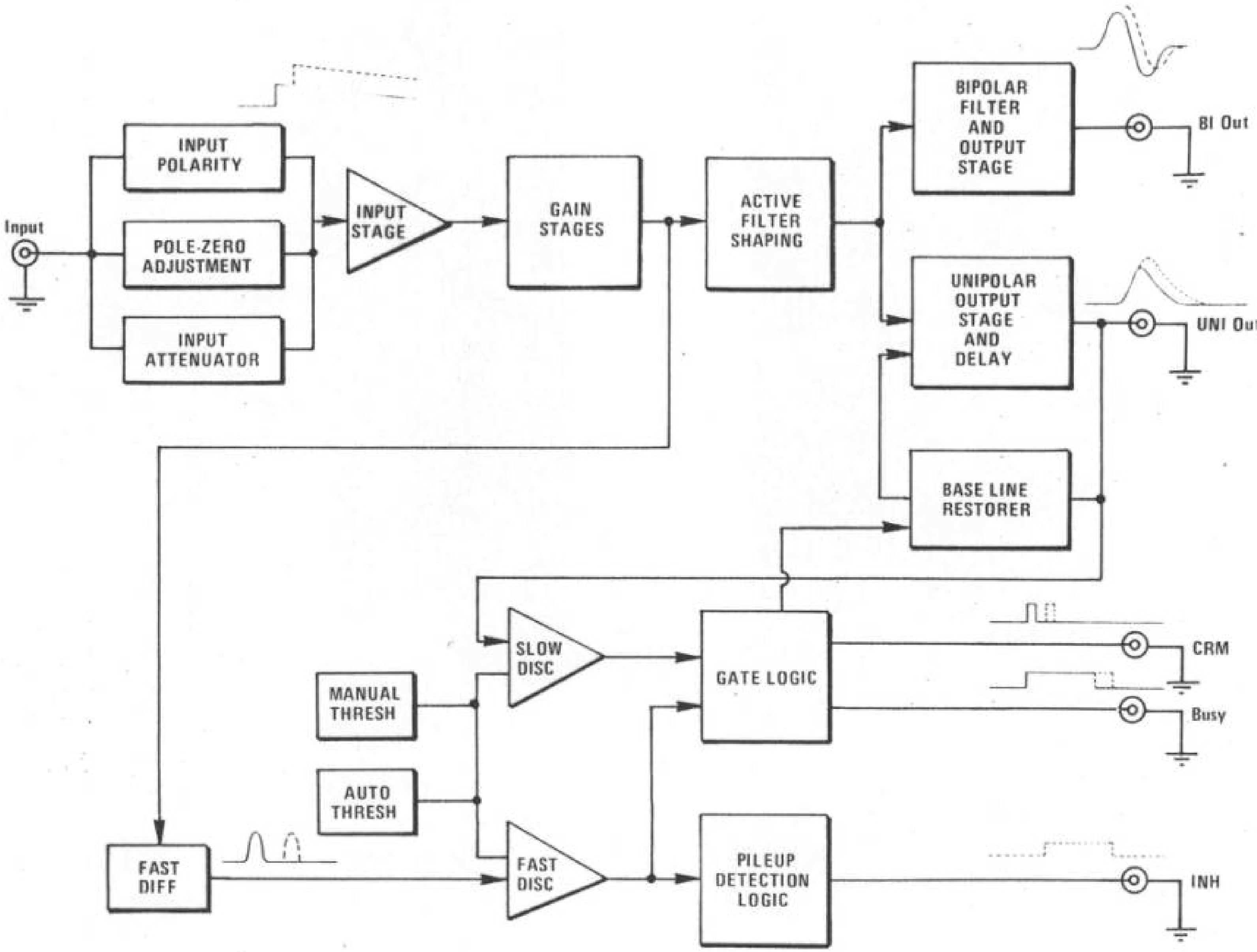


Types of Si(Li) Detectors

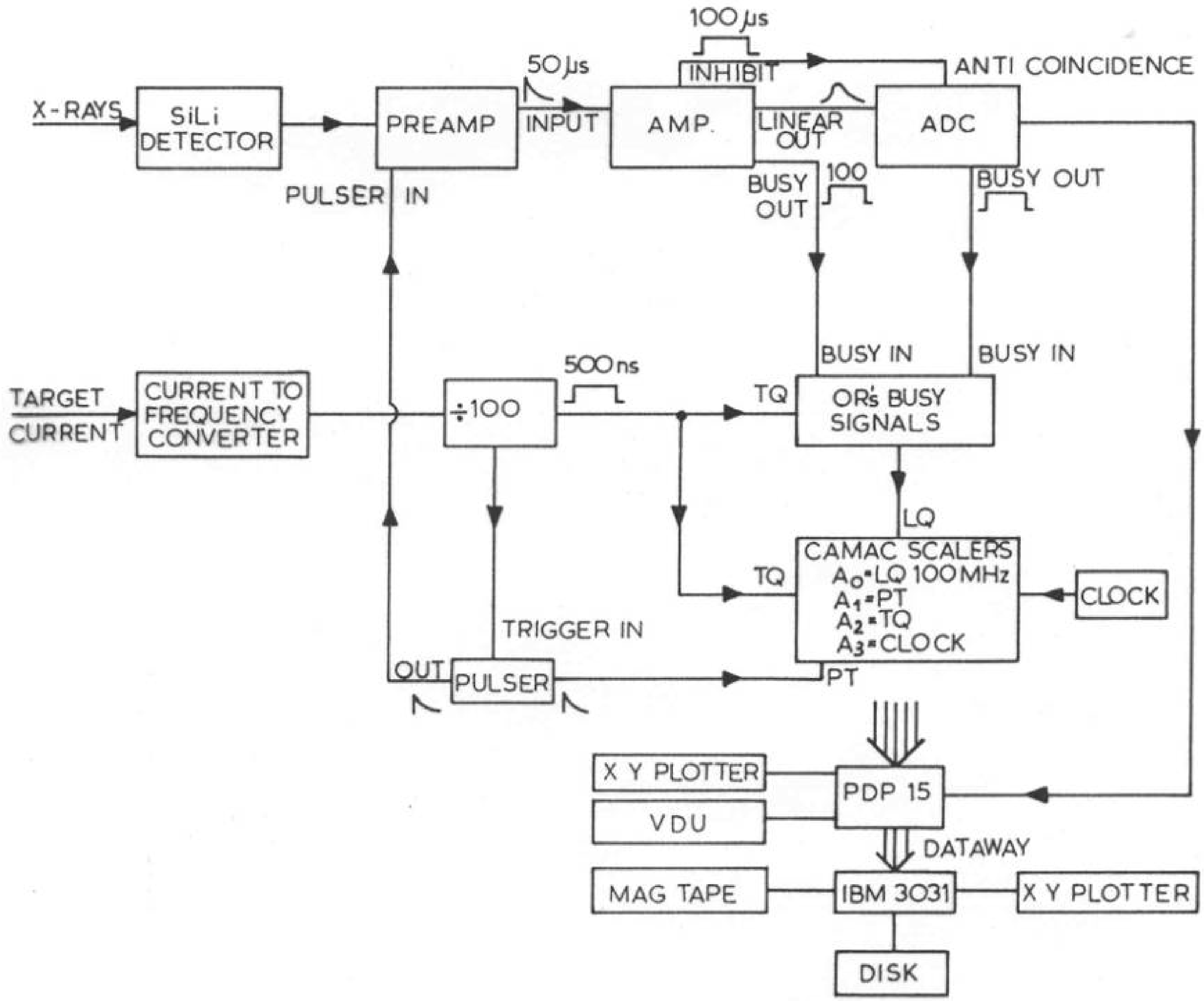


Schematic representation of a. "resistor" and b. "pulsed optical" preamplifier operation.

Amplifier Block Diagram



System Block Diagram



Dissection of PIXE Spectra

A typical PIXE spectrum is composed of:

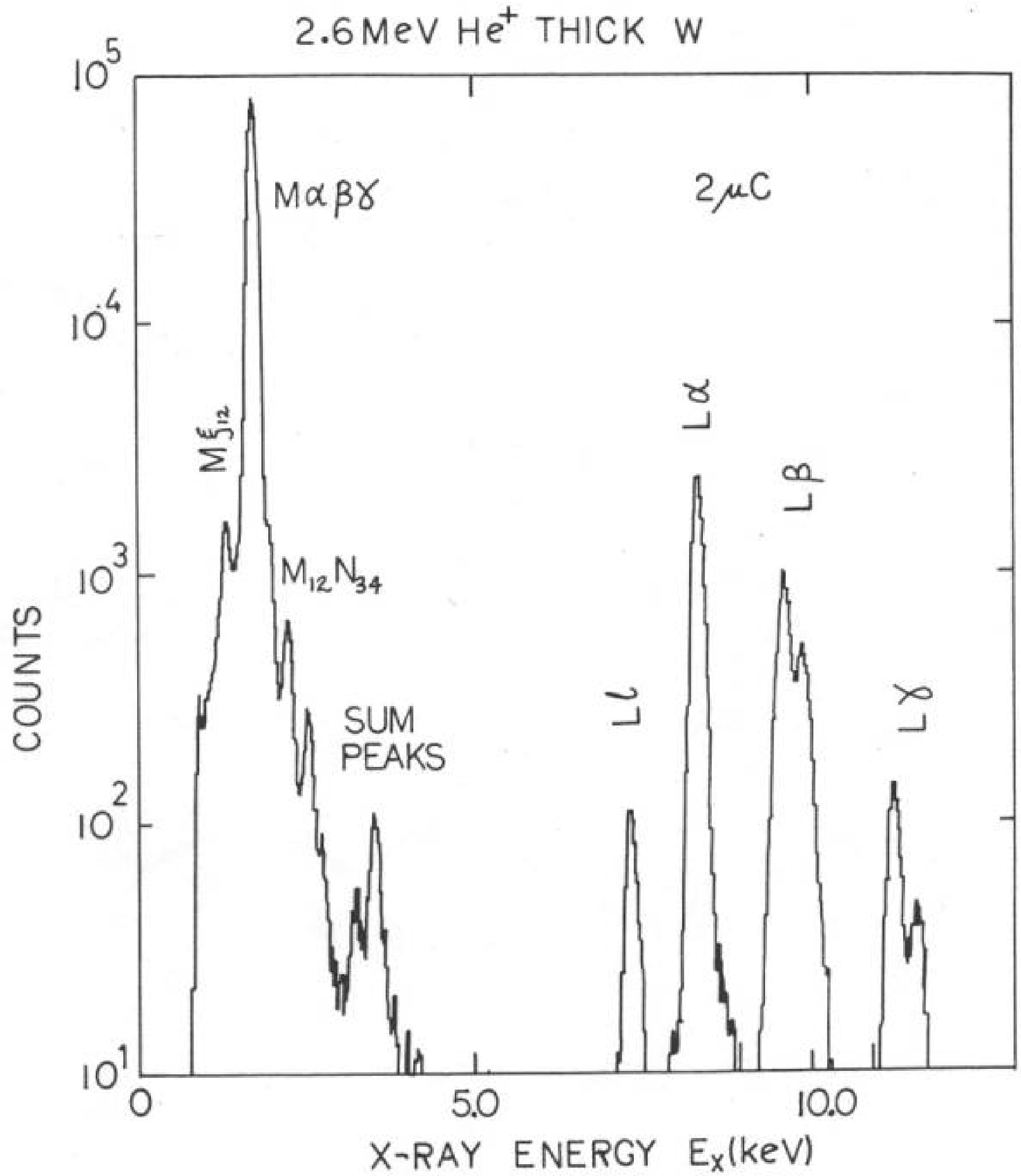
Characteristic X-ray lines

Background
- 2nd electron brem.
- amplifier noise
- gamma ray background

Spectrum artifacts
- sum peaks
- escape peaks
- tailing

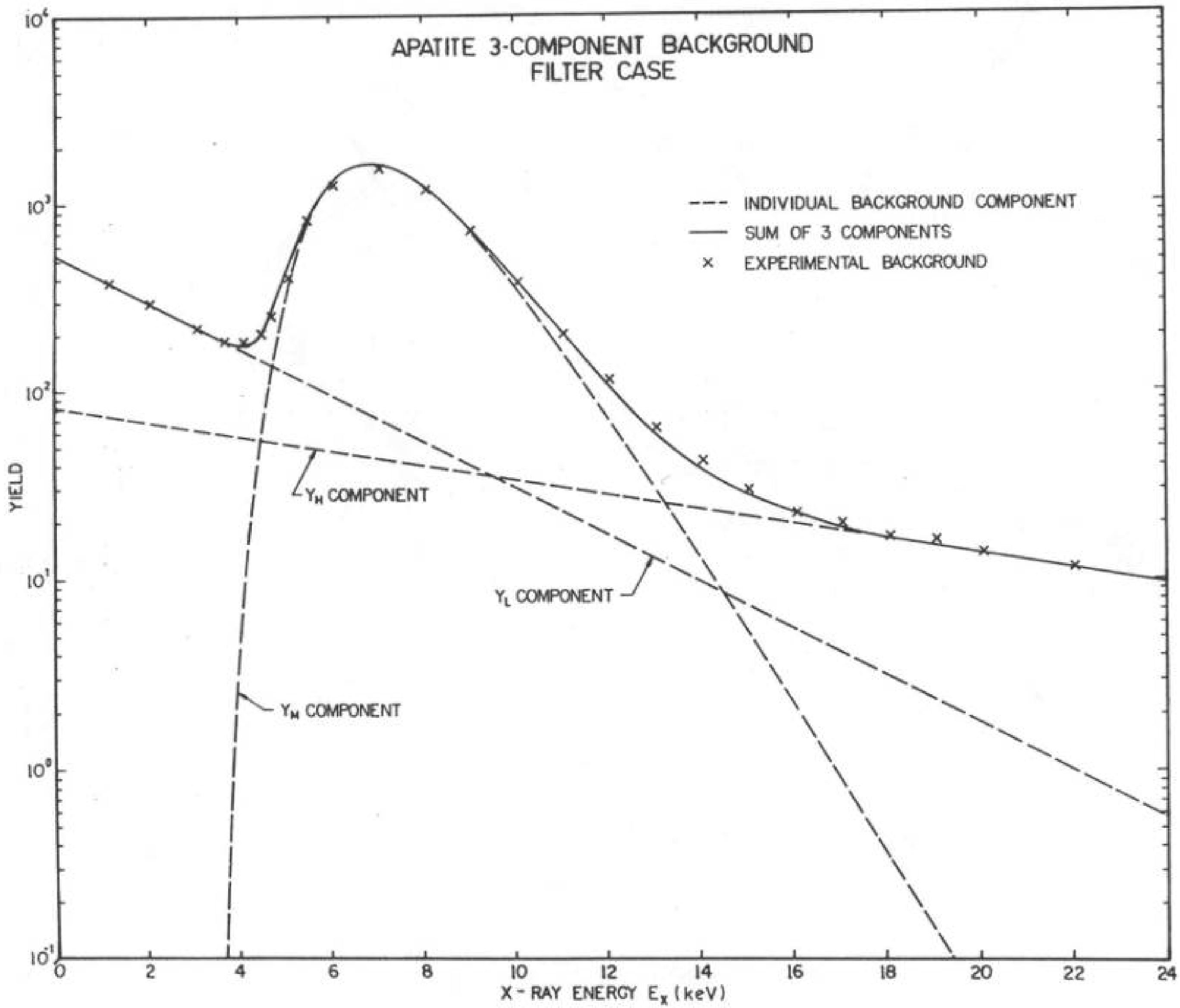
Filters and Spectrum shaping.

Characteristic X-ray Lines

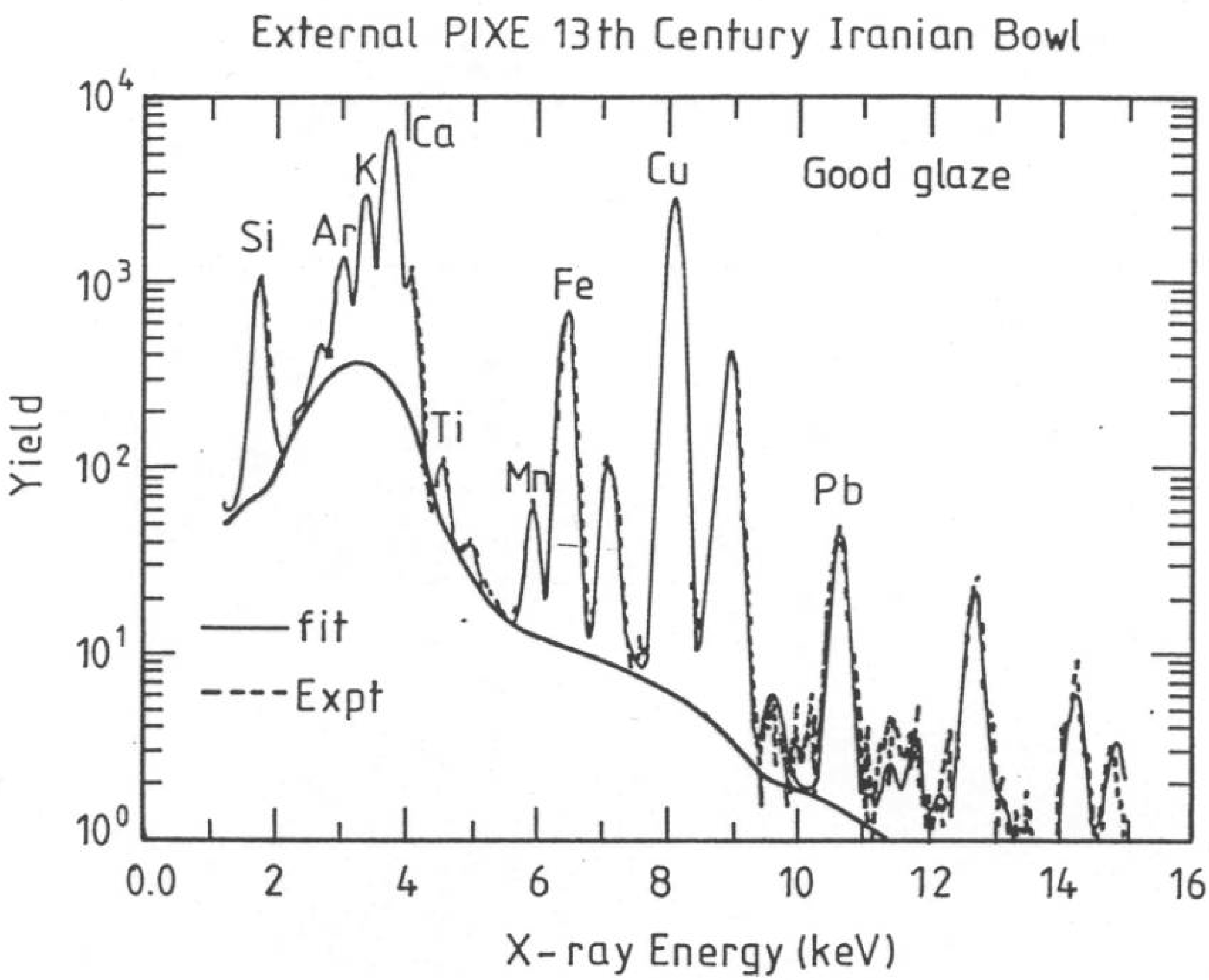


2.6 MeV He$^+$ on thick W

PIXE Background Components



Typical PIXE Spectrum



Taken in air - note argon peak.

Electronic Pulse Shaping

An electronic pulse is received from the detector preamp and shaped in the amplifier.

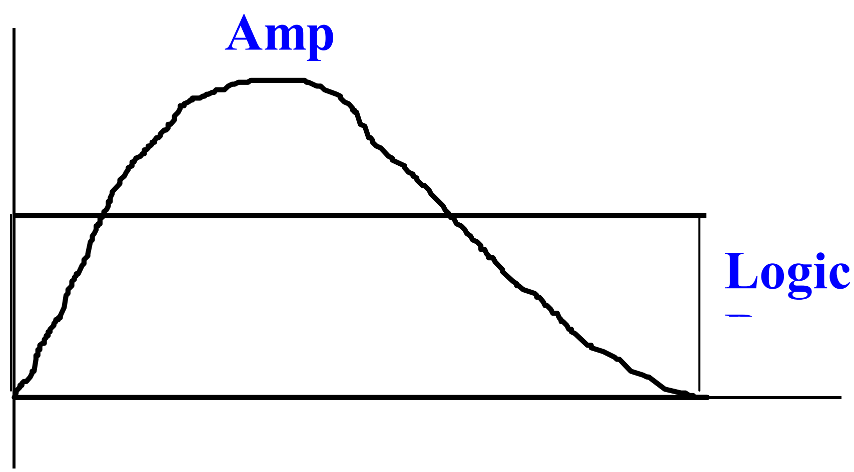
For a shaping constant of τ μsecs the time to peak is usually 2.2τ and the time to base 6τ.

Generally τ is selectable from 0.5 μs to 10 μs.

The electronics is generally dead for at least the time it takes to measure the time to peak, 2.2τ.

Most systems generate a logic busy signal which is 6τ long and is extended if another pulse arrives within this time period.

Count Rates/ Deadtime



10^3 Hz $\Rightarrow$ $10^3 \times 6\tau$ sec/ sec deadtime

$\Rightarrow$ 6% deadtime, $\tau = 10\mu s$

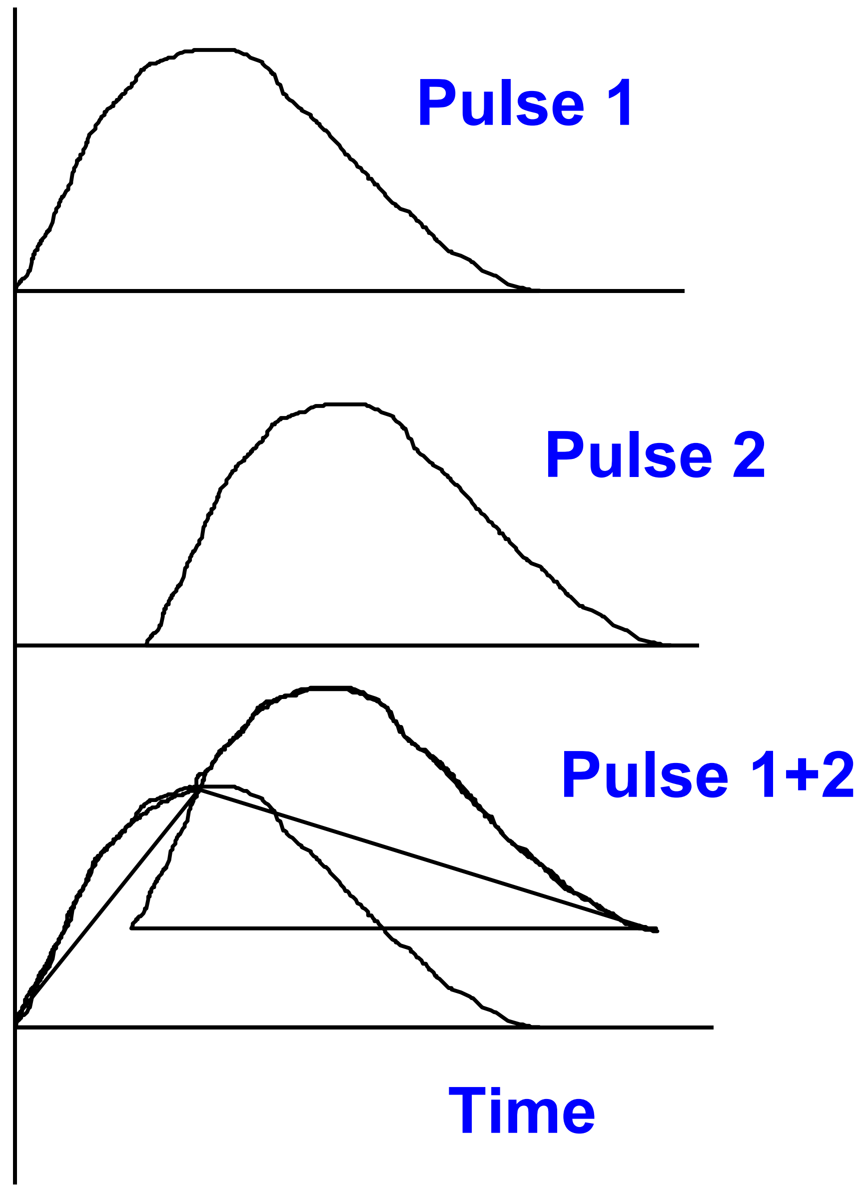
10^4 Hz $\Rightarrow$ $10^4 \times 6\tau$ sec/ sec deadtime

$\Rightarrow$ 36% deadtime, $\tau = 6\mu s$

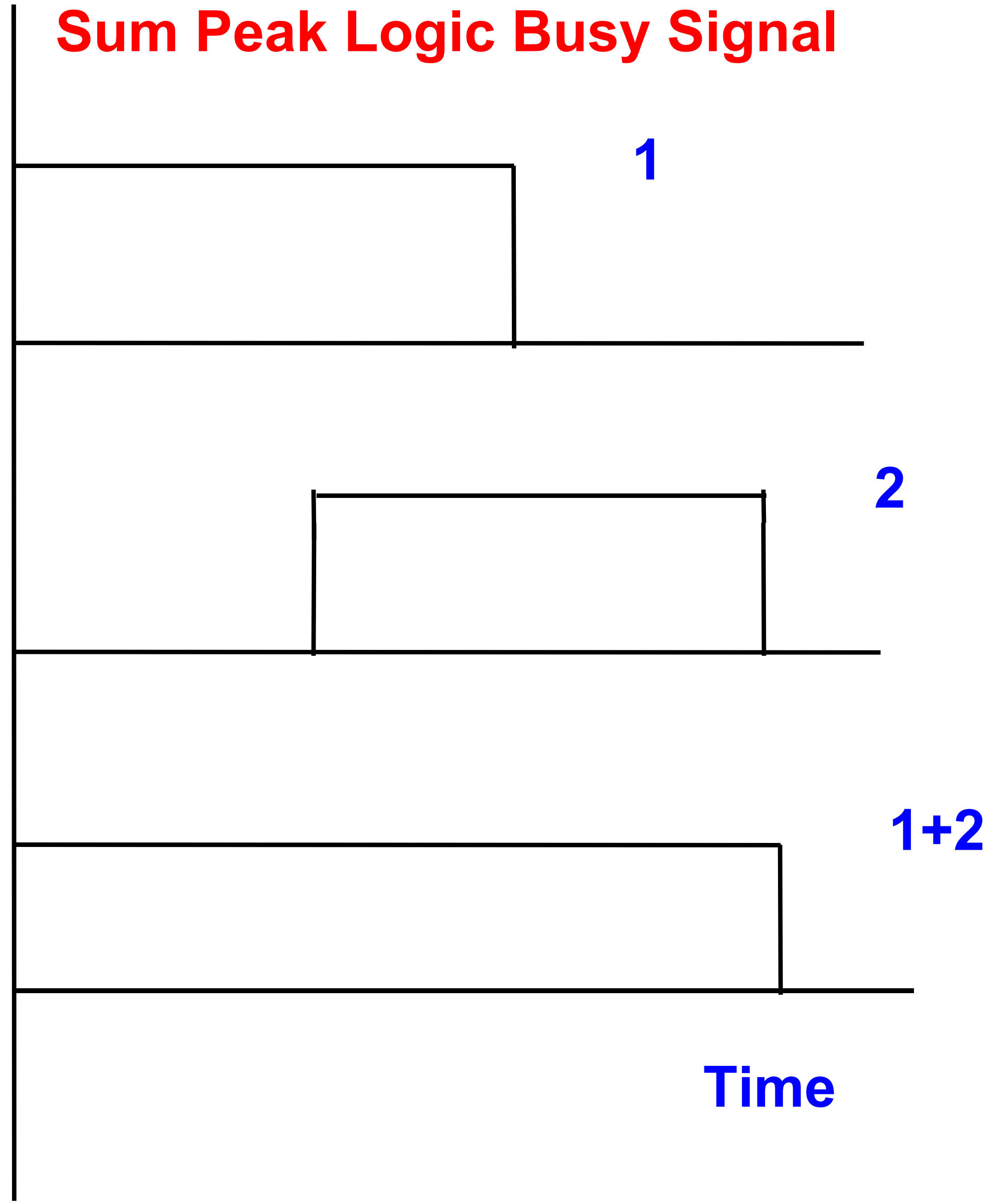
Typically count rates between a few Hz and 10 kHz are used for most applications.

The run lengths are usually increased to allow for this system deadtime.

Sum Peaks

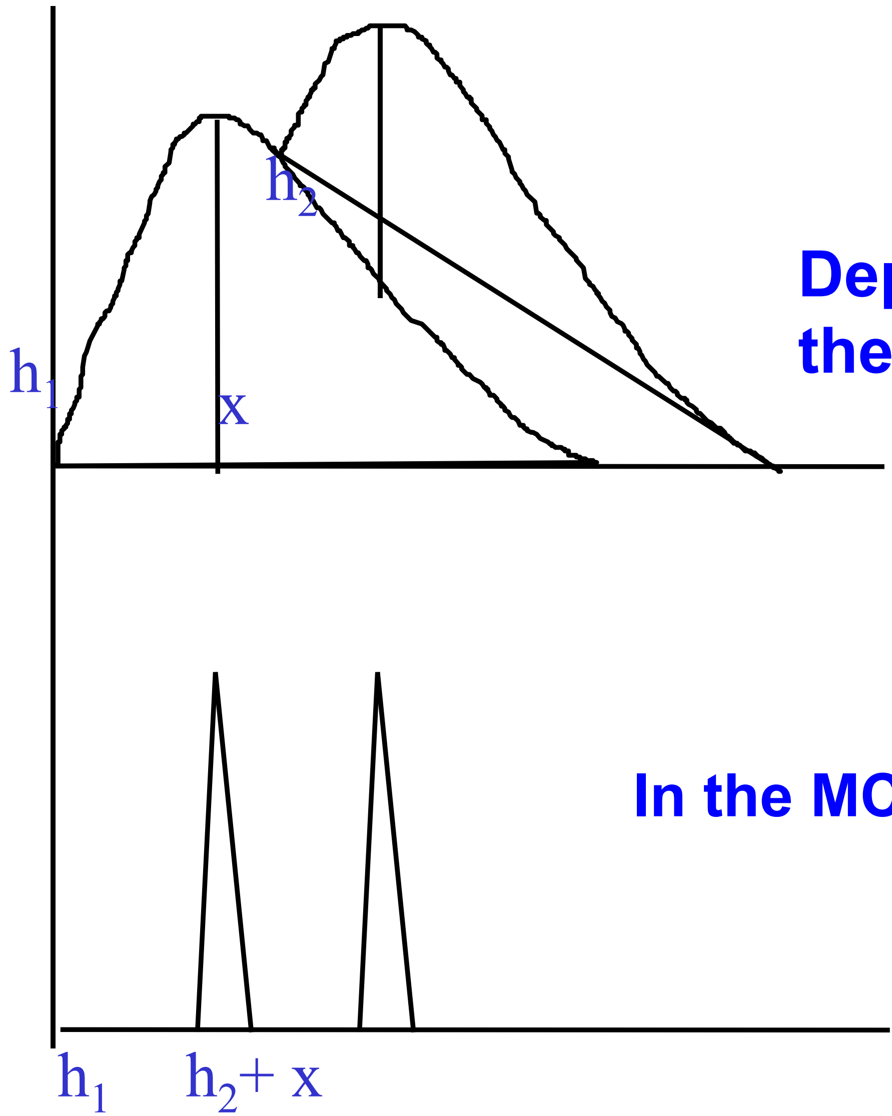


Sum Peak Logic Busy Signal



What is Pileup ?

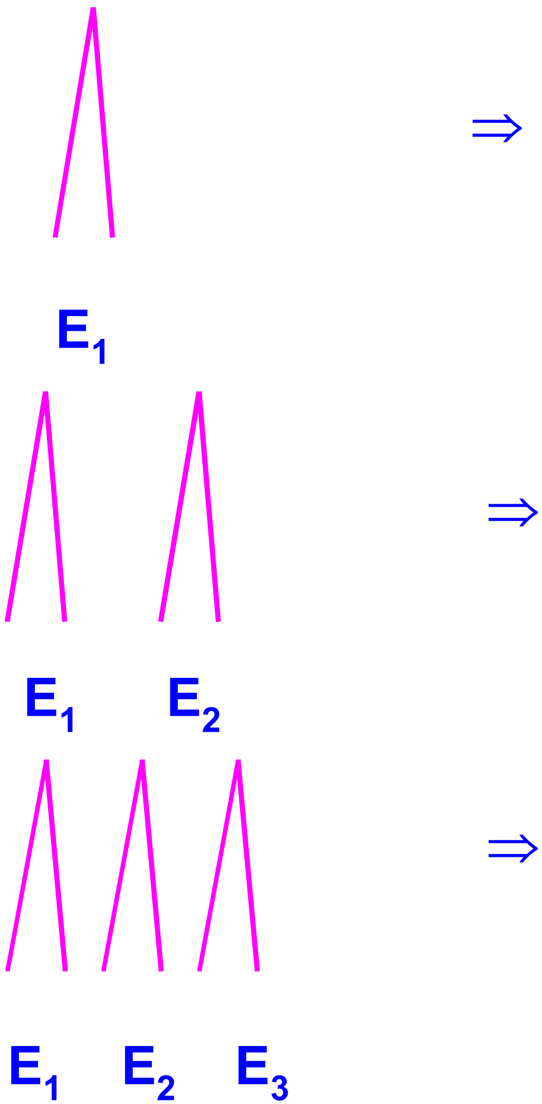
In the amplifier



Depends on the count rate.

In the MCA

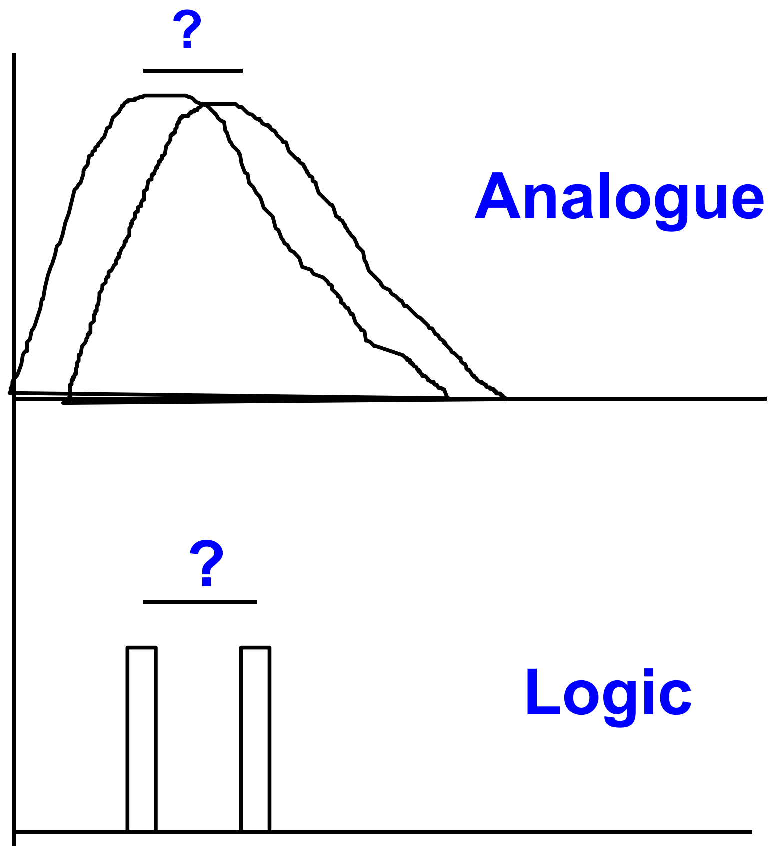
How Many Sum Peaks ?



Every peak can sum with itself, every other peak and the background

Pulse Pair Resolution

If two pulses arrive very close together (much less than the time to peak) and are not clearly resolved by the electronic logic then the second one could be lost.



Resolution typically 0.5 μs for X-ray work.

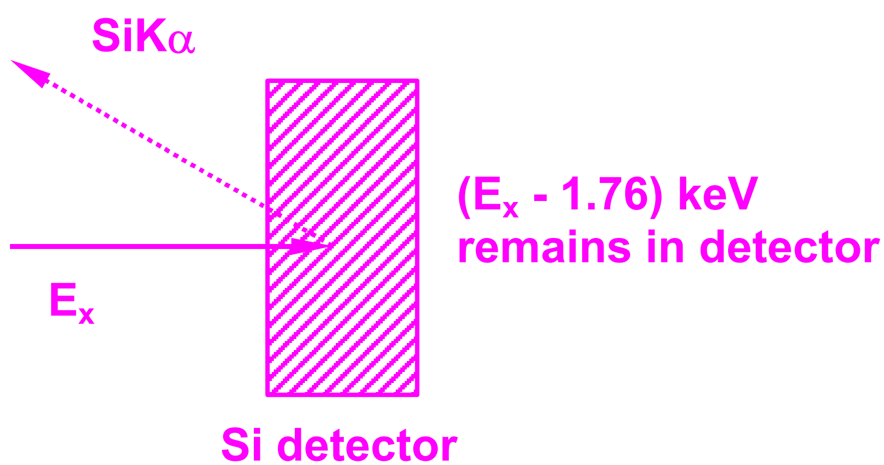
Escape Peaks

A photon of energy E_x entering the silicon detector may interact with a silicon atom, producing a characteristic silicon Kα x-ray of energy 1.76 keV.

If this photon is near the crystal surface the

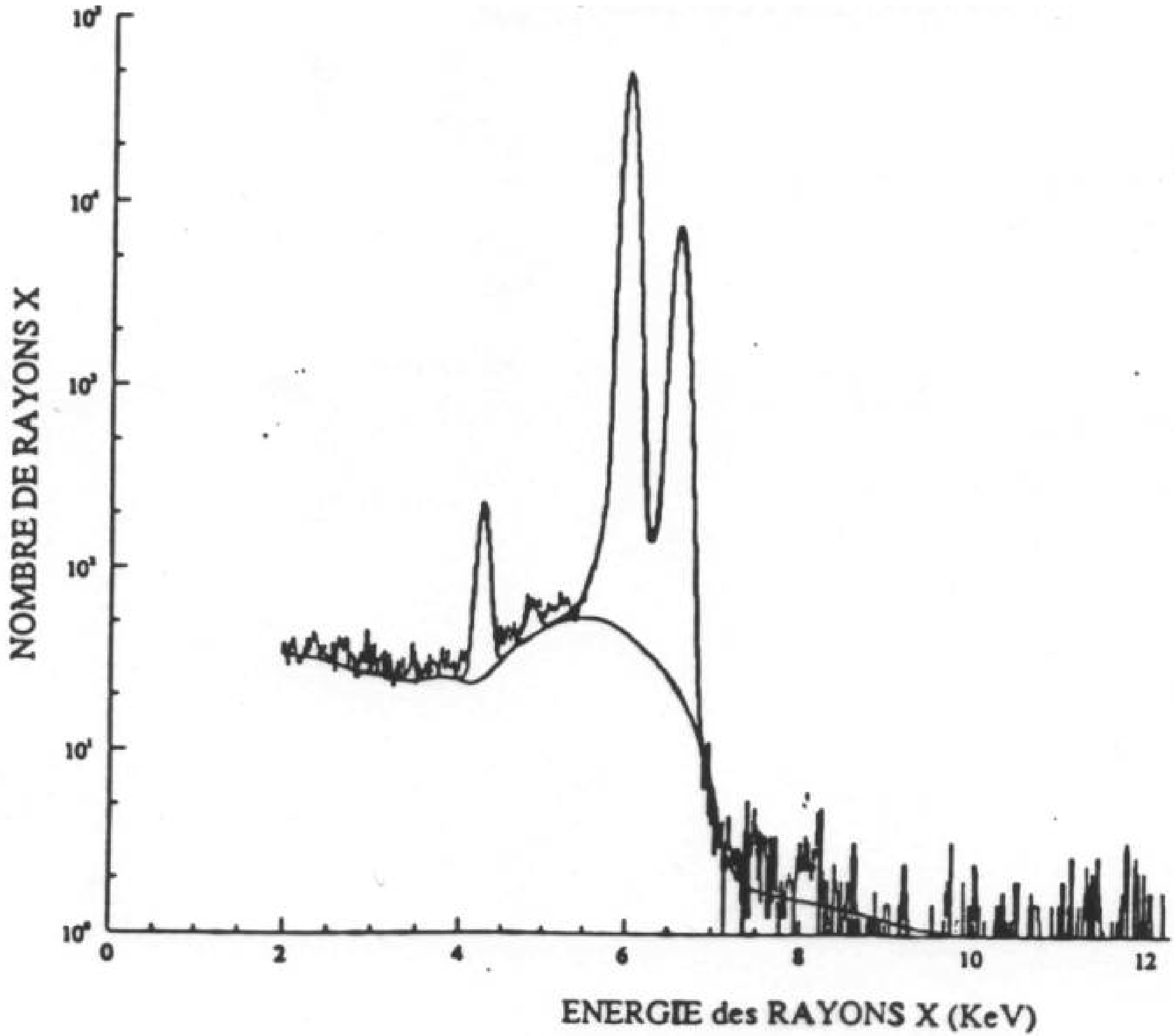
Si Kα x-ray may escape leaving an energy of (E_x - 1.76) keV in the detector.

This is known as the silicon escape peak.



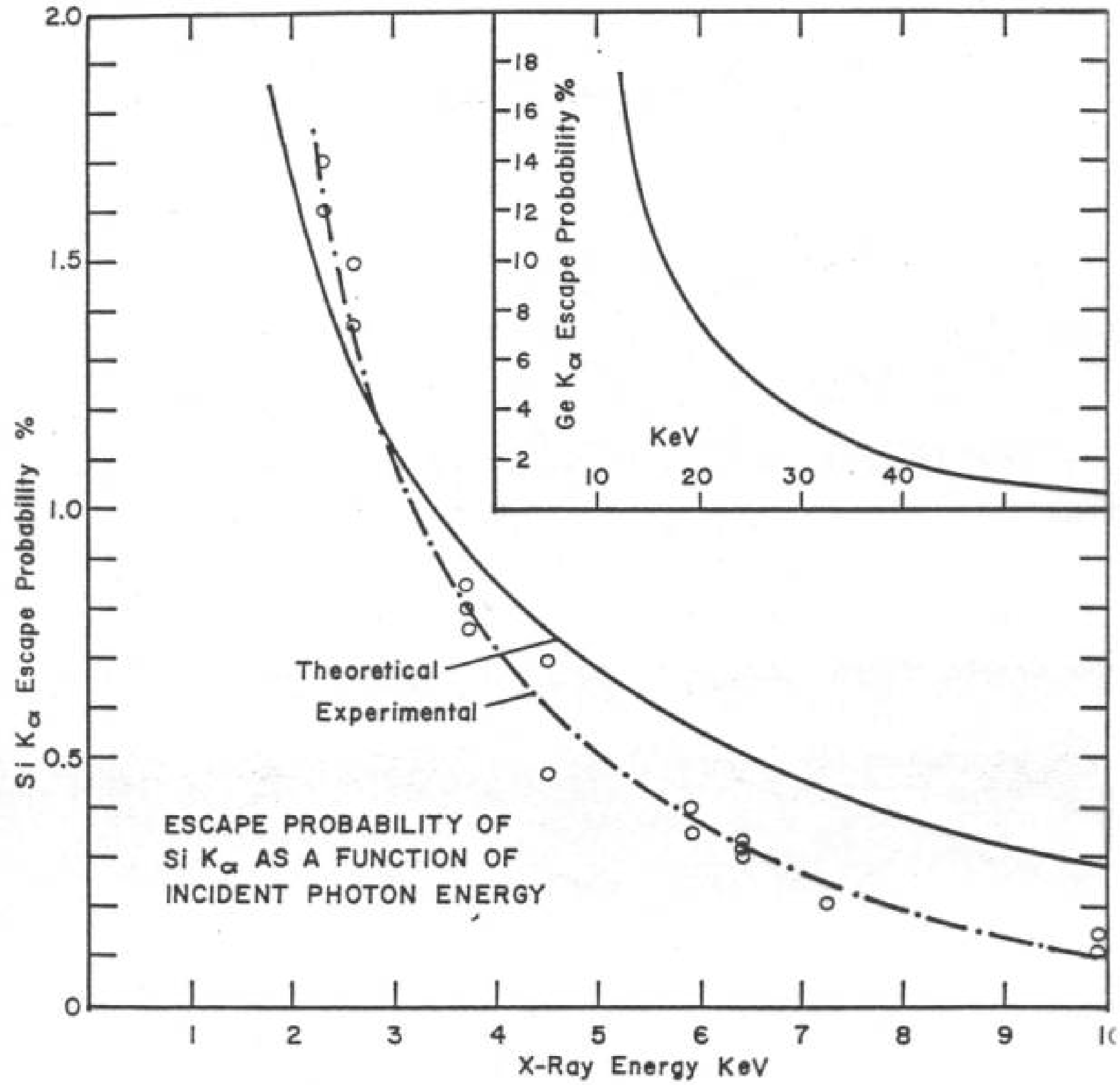
Escape peak probabilities decrease with E_x.

Escape Peaks



Mn silicon escape peaks

Escape Peak Probabilities



Silicon and Germanium escape peak probabilities

Filters and Spectrum Shaping.

Typical PIXE spectrum cover the X-ray energy range from 0 to 40 keV. The production rate for X-rays varies by several orders of magnitude over this range.

This produces large differences in count rates into different parts of the spectrum and can limit the target currents that may be used for analysis.

This can be achieved by the used of selected thin filters placed between the target and the detector to absorb low energy photons relative to high energy photons.

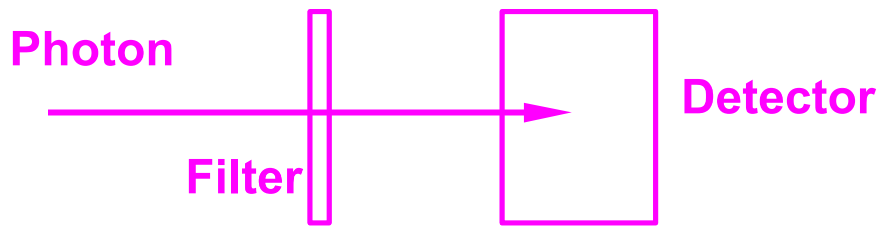
For metals these thin filters may be only a few microns thick.

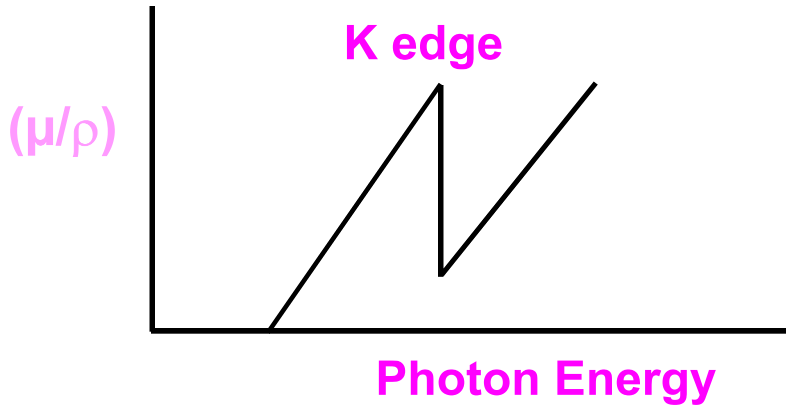
For polycarbonate films such as Mylar or Perspex they can be anything up to several millimetres thick.

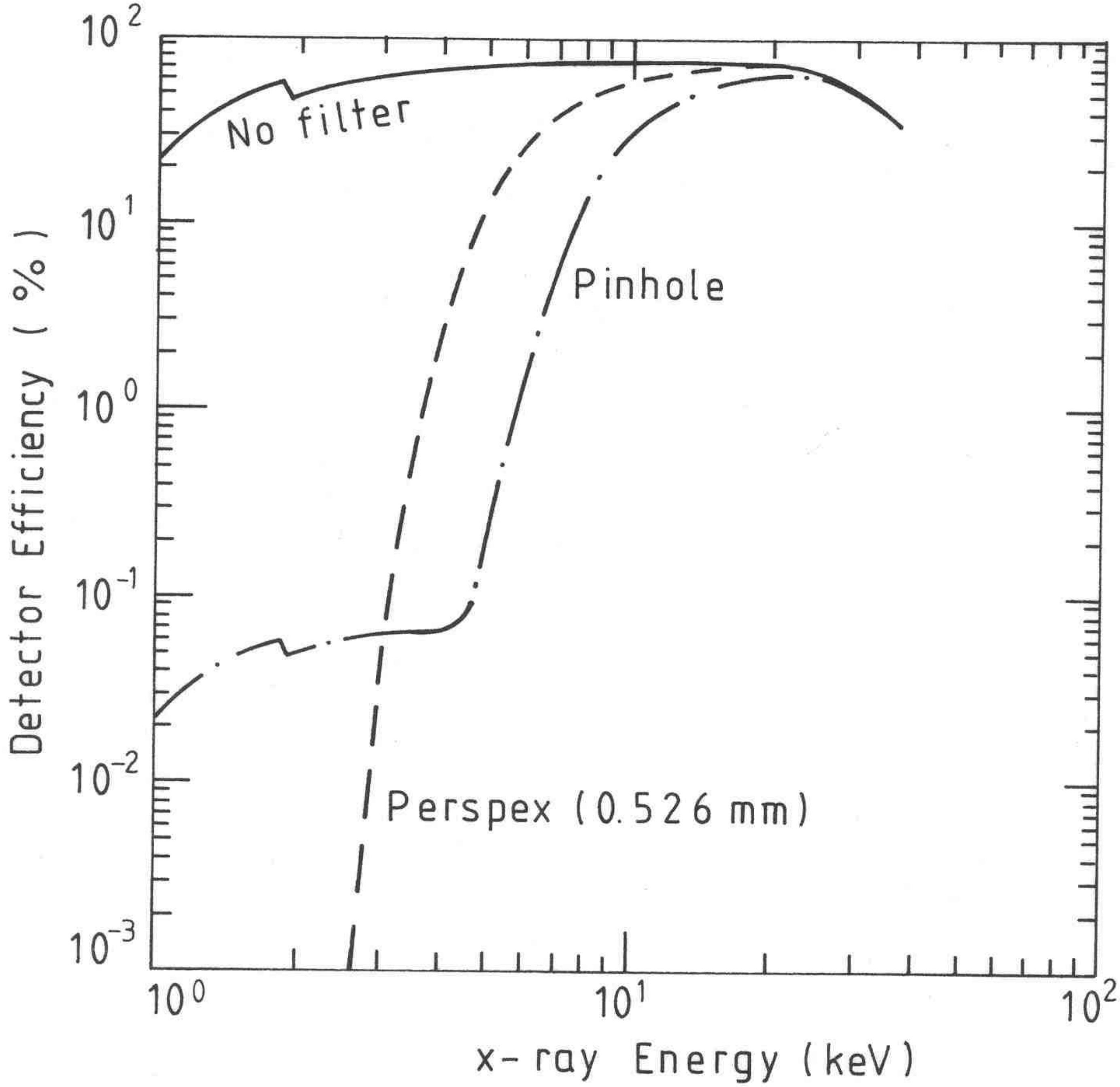
Filters

$$T = T_o \exp\{-(\mu/\rho)\, \rho x\}$$

where $(\mu/\rho) = aE^{-b} Z^c$ ($a \sim 1, b \sim 3, c \sim 3$) is mass attenuation coefficient in (m^2/g), and ρx is the target thickness in (g/cm^2).

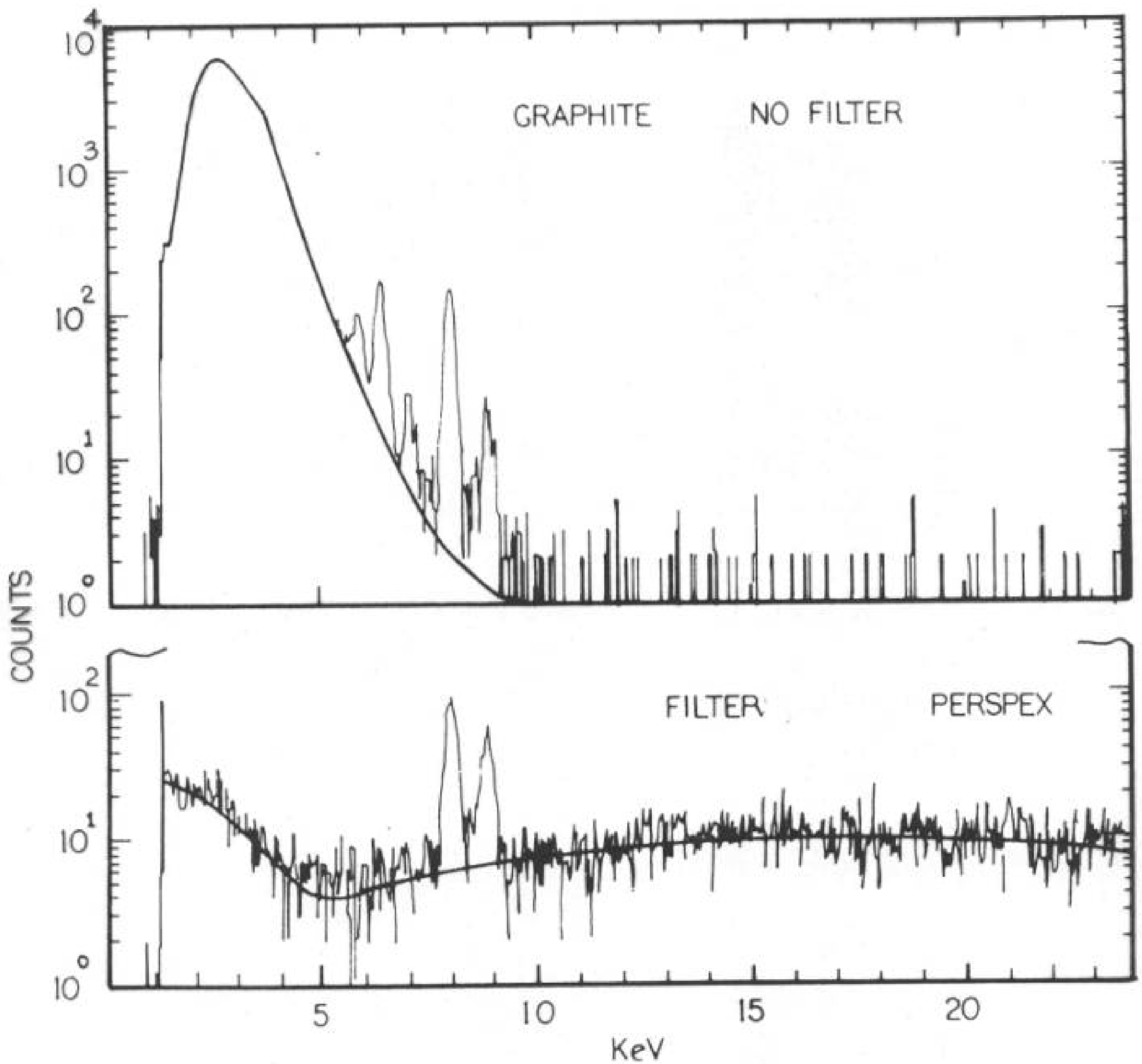






No filter
Pinhole
Perspex (0.526 mm)
Detector Efficiency (%)
x-ray Energy (keV)
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^0
10^1
10^2

Filter Effects on Spectra



6 mm of Perspex filter

PIXE Analysis - DOPIXE

Spectrum analysis - peak areas

Elemental concentrations from peak areas.

- Thin targets.

- Thick targets.

System Calibration against standards

Typical Errors

Minimum Detectable Limits (MDL's).

X-ray Detection Efficiency

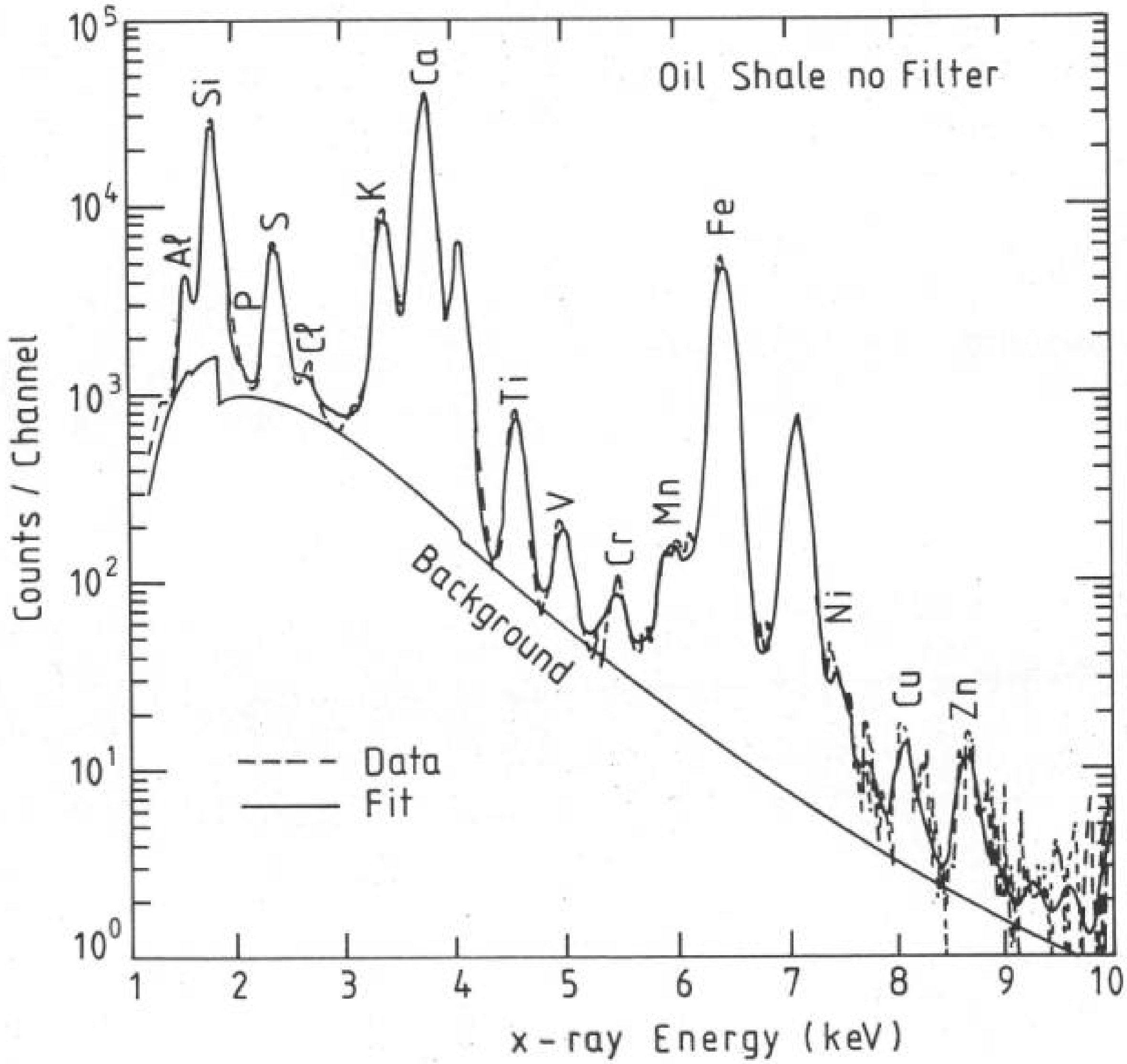
To obtain peak areas you need:

- **a background shape (fixed or free) which is highly variable over many orders of magnitude and may be discontinuous.**

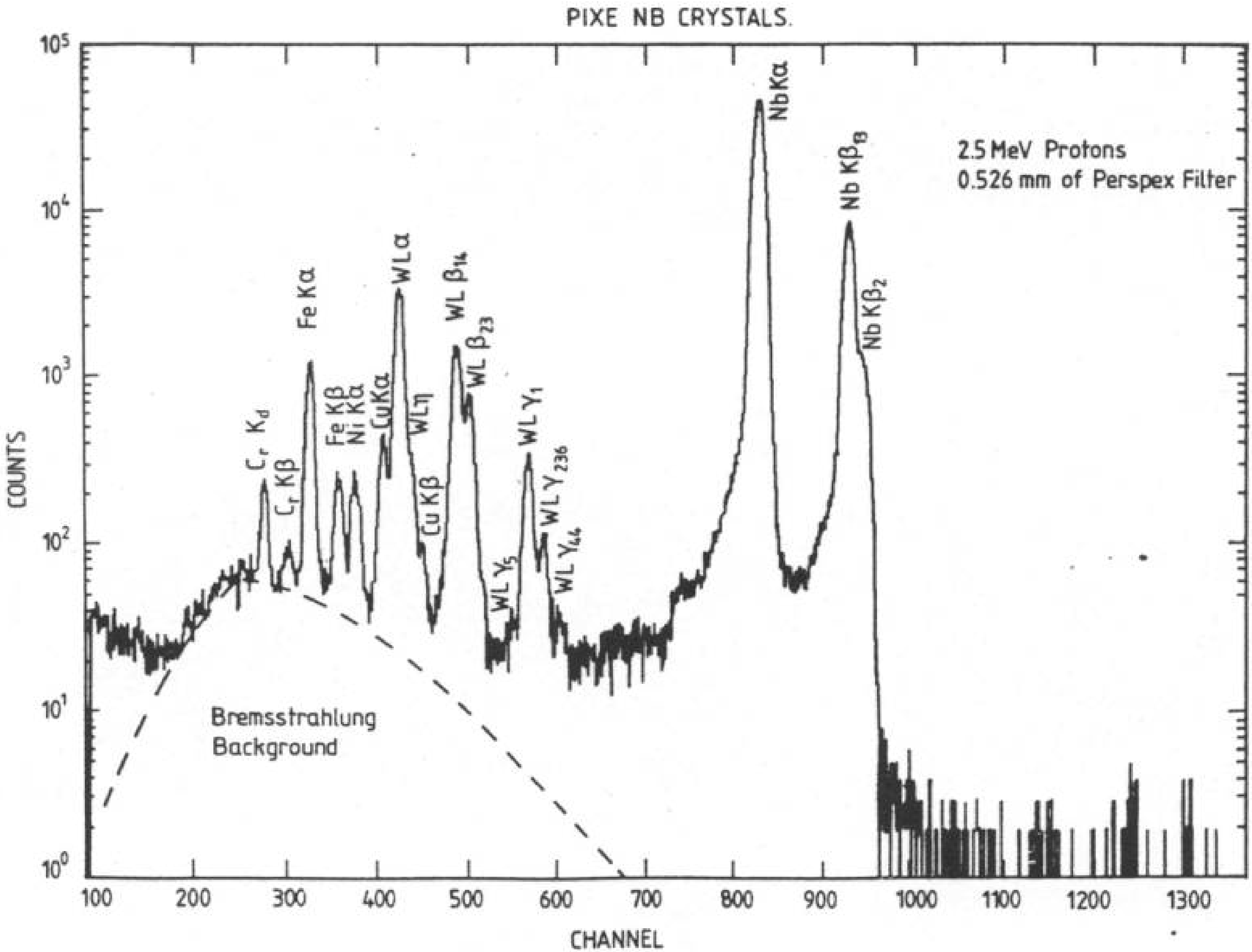
- **a peak shape, Gaussian, tails, steps which sits on this background.**

- **to understand possible interferences, overlaps and relative K, L, and M shell line intensity ratios.**

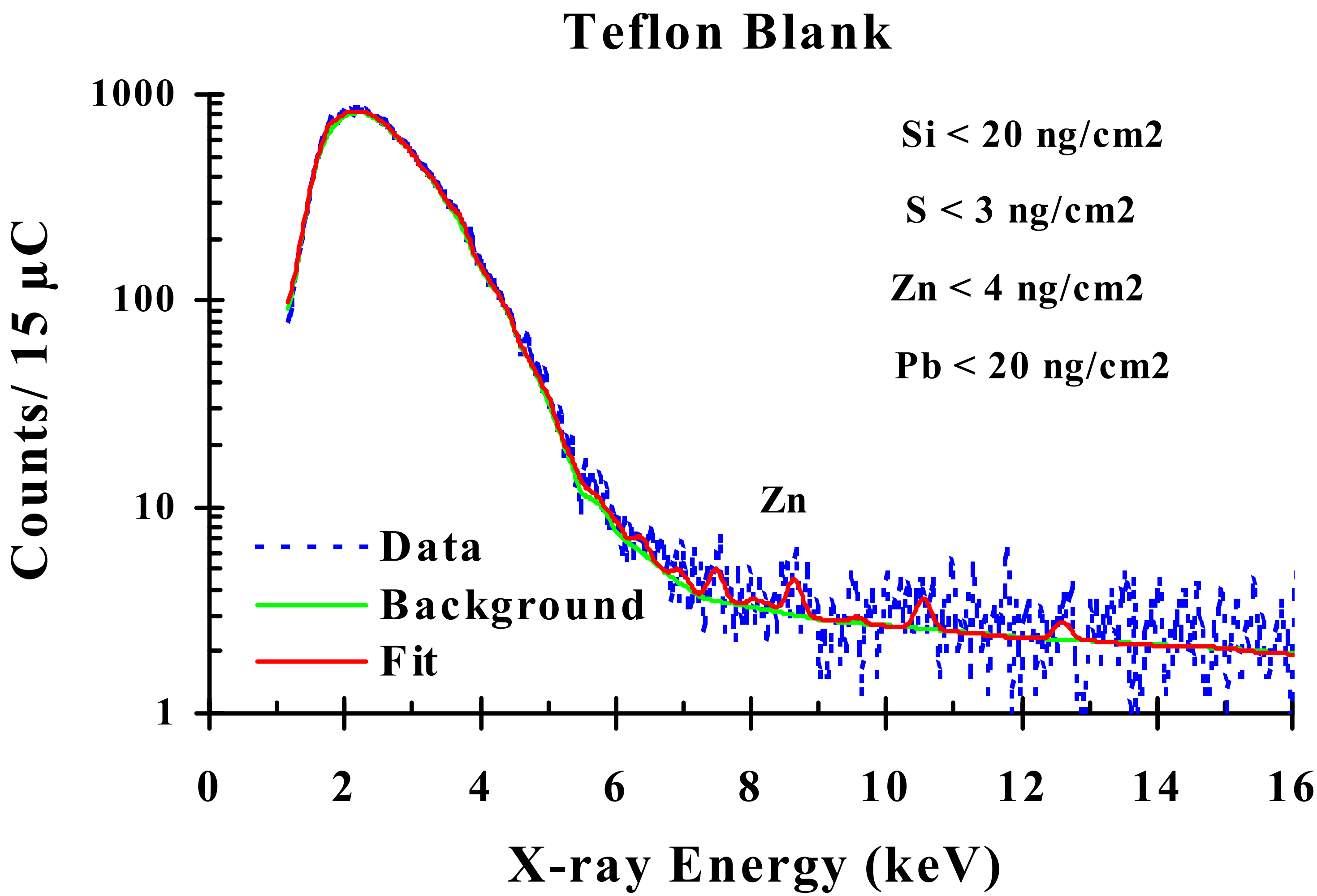
Spectrum Backgrounds



Spectrum Backgrounds



Blank Spectrum



2.6 MeV protons on Teflon

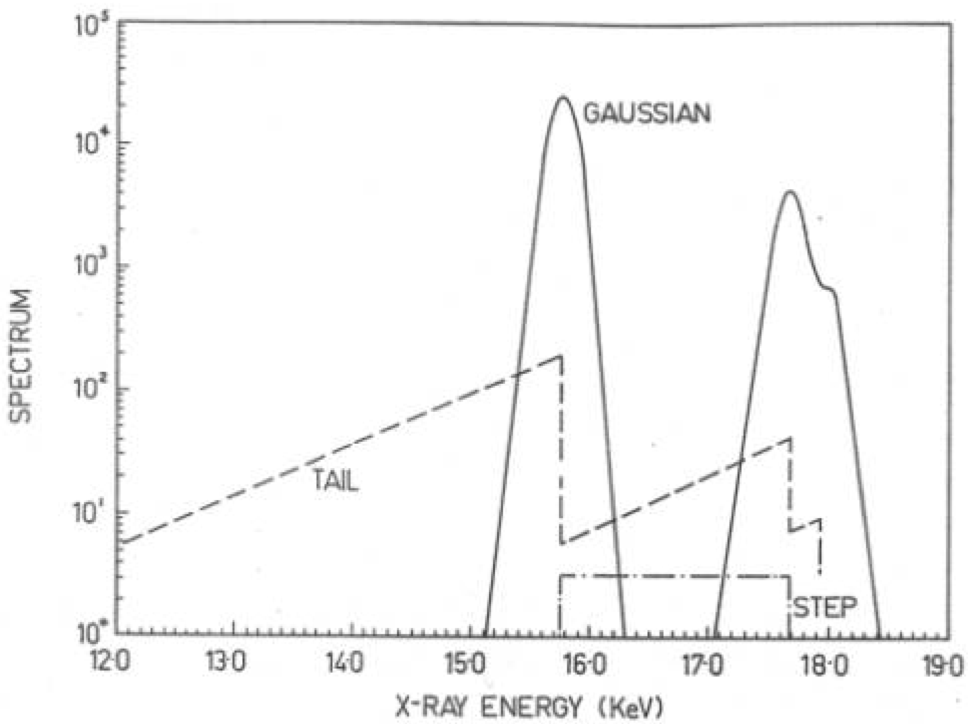
Characteristic Line Shapes

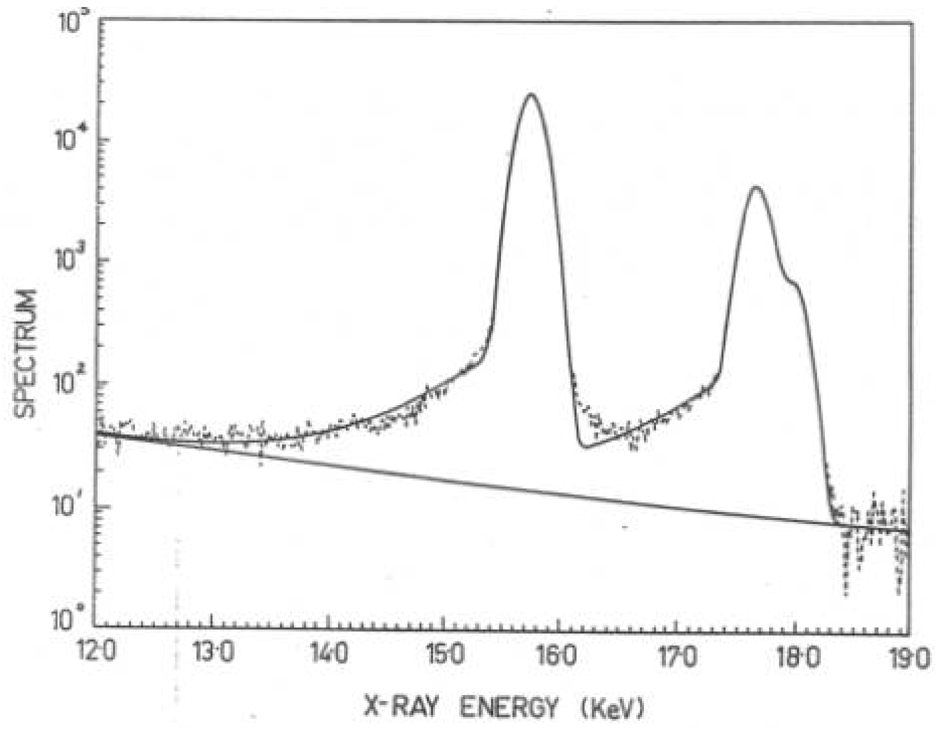
Line shapes are close to Lorentzian convoluted with a Gaussian detector function.

There are detector characteristics that produce long low energy tails due to incomplete charge collection.

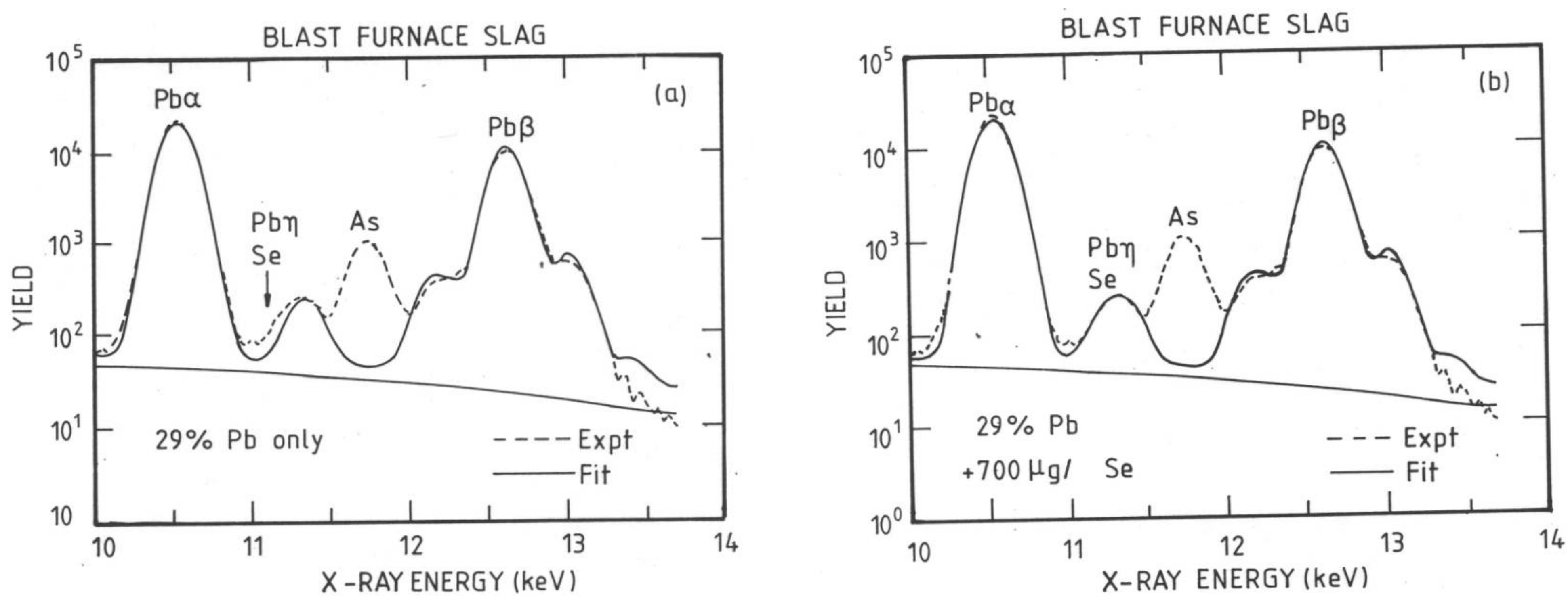
Most analysis routines should include, Gaussians, tails and steps at least to fit experimentally obtained line shapes.

PIXE Line Shapes

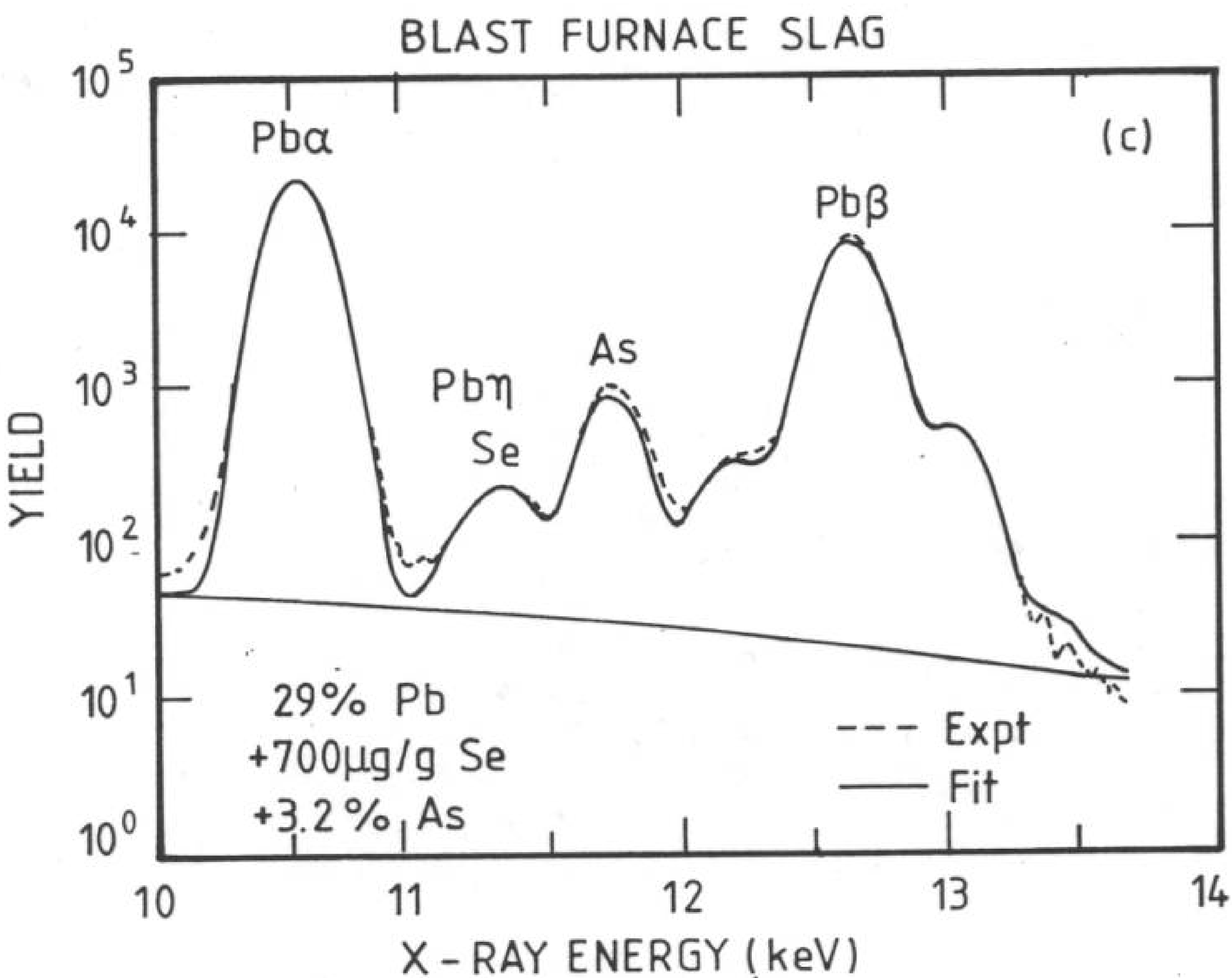




Overlapping Spectral Lines



Overlapping Spectral Lines



PIXE Spectrum

The yield in channel I = E_i is,

$$Y(E_i) = Bkg(E_i) + \Sigma A_j R_{jk} G_{jk}(E_i)$$

where,

A_j = peak height for element j

R_{jk} = relative intensity of element j

G_{jk} = peak shape

The summation is over all elements j and all peaks k for element j

DOPIXE peak area analysis then minimises,

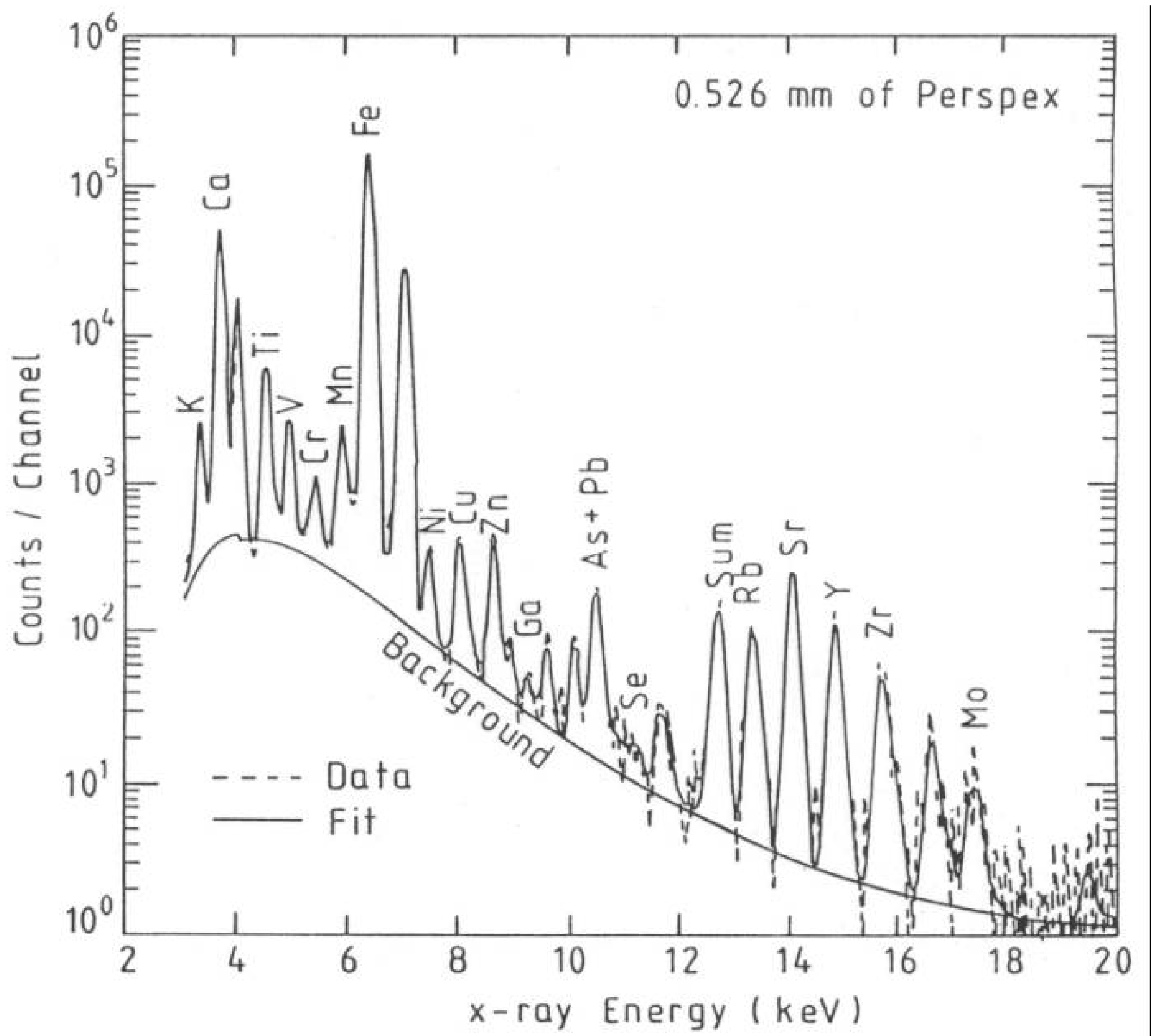
$$\chi = [1/(N-f)] \;\; \Sigma \;\; (y_{exp} - y_i)^2/y^2_{exp}$$

where,

N= number of channels

f = number of free parameters

Typical DOPIXE Fit



2.6 MeV protons, Perspex filter

Concentrations from Peak Areas

To obtain target elemental concentrations from known X-ray peak areas, you need to know:-

- **if the target is thick or thin.**
- **X-ray production cross section for each element peak detected in the sample, including the fluorescence yield, branching ratios.**
- **a range of experimental parameters, including, solid angle, current, detector efficiency, input ion energy, ion energy loss in the target, exit photon absorption in the target.**

Yield Equations for PIXE

Thin targets:-

$$Y = \frac{tN_o \Omega Q \epsilon}{\cos\theta W 4\pi e} \sigma_p(E)$$

t in $\mu g/cm^2$

A target is thin if:

- **the energy loss of the incoming ion is small, $(\Delta E/E_{in}) << 1$.**
- **the intensity loss of the lowest energy photon of interest emerging from the target is small.**

$$\{T/T_o\} = \exp\{-(\mu/\rho)\,\rho x\} << 1,$$

where (μ/ρ) is the mass attenuation coefficient for the emergent photon in the target of thickness ρx.

Typically target thickness less than a few hundred $\mu g/cm^2$ thick.

For ions in carbon, 10% energy loss occurs at a depth of a few μm.

Energy MeV	Proton 10% Loss	Alpha 10% Loss
1 3	0.45 mg/cm^2 2.9 mg/cm^2	54 $\mu g/cm^2$ 280 $\mu g/cm^2$
1 3	1.9 μm 12.4 μm	0.23 μm 1.2 μm

For 2 keV photons in Mylar 10% intensity loss occurs for targets of 300 $\mu g/cm^2$ (2.2 μm) thick. This increases to 32 mg/cm^2 (230 μm) for 10 keV photons.

Hence for most applications thin targets are usually less than a mg/cm^2 thick and may need to be less than a few hundred $\mu g/cm^2$ thick if heavy low energy ions or low energy photons are used.

Thick Targets

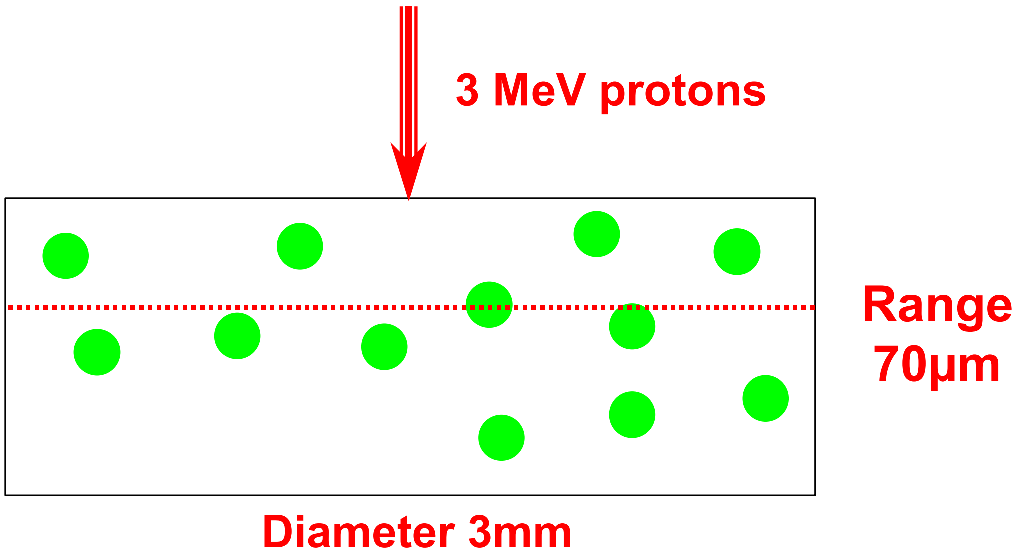
Thick targets have,

- large proton energy loss
- large photon attenuation

For thick target PIXE typically >80% of yield comes from <30% of the ion range

(ie in first 15-20 μm).

This small sample volume must be representative of sample bulk.



Particle Size Effects

For 3mm beam of 3 MeV protons in carbon interacting with FeO particles,

If n=10,

then 5 μm diam FeO particles corresponds to

8 μg/g of Fe.

If particle diam =10 μm,

then need n>100 if your reference Fe standard has concs < 635 μg/g!

	Conc of Fe (μg/g) in Carbon		
Diam μm	n=1	n=10	n=100
1	0	0.1	0.6
5	0.8	8	80
10	6.3	63	635
50	793	7,930	79,300
100	6,350	63,500	63.5%

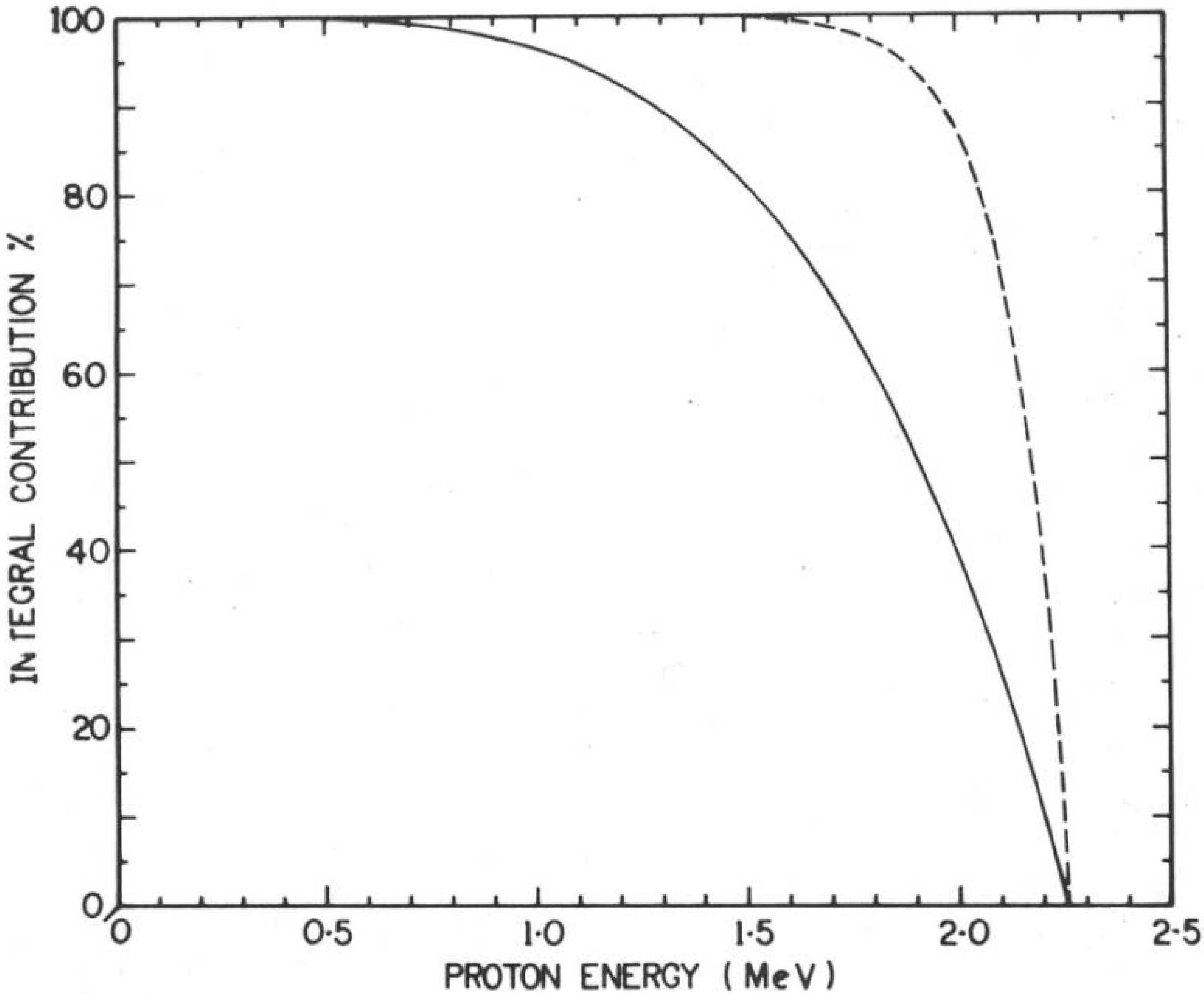
Yield Equations for PIXE

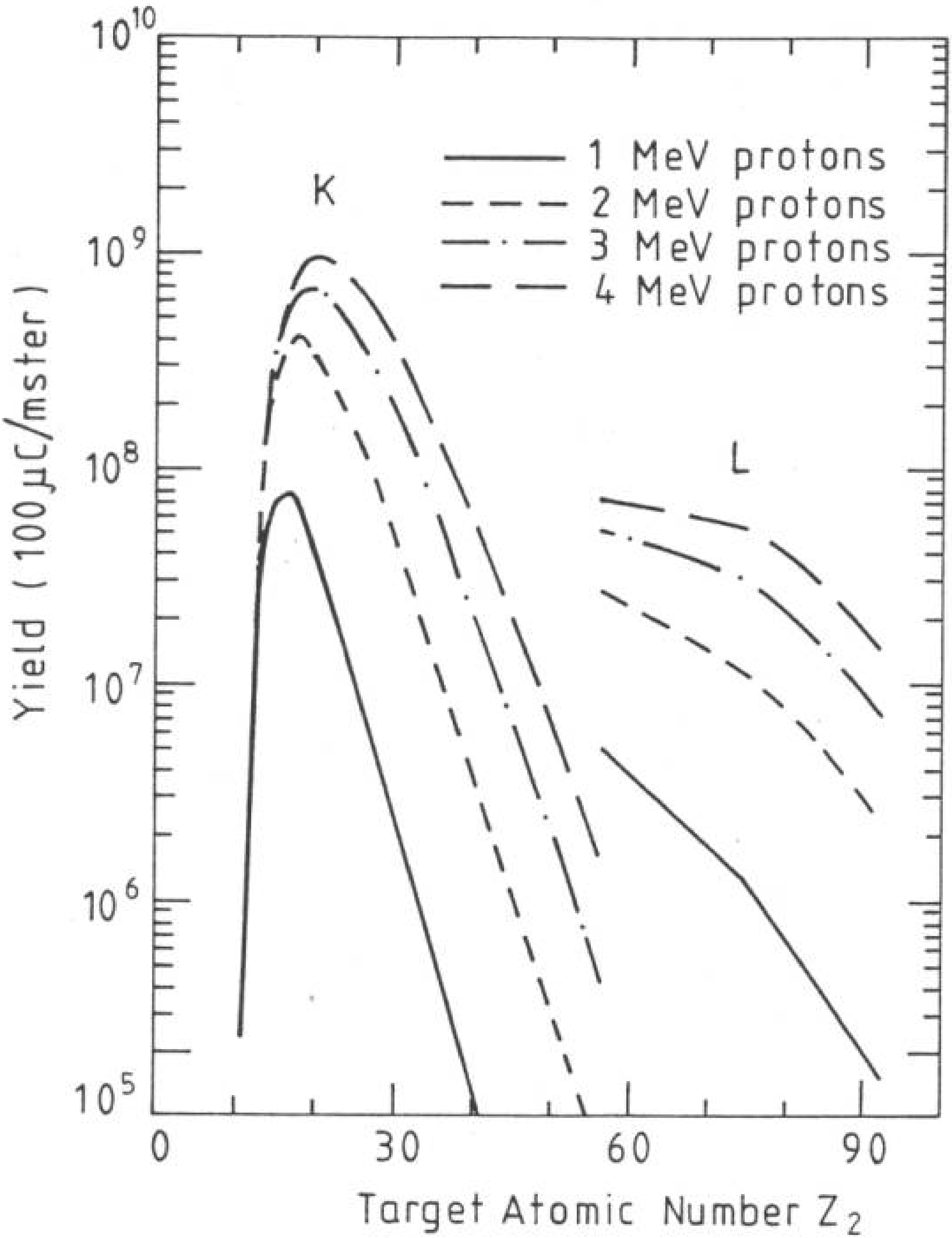
Thick targets:-

$$Y = \frac{CN_o \Omega Q \epsilon}{4\pi We} \int_{E_{Hi}}^{E_{Lo}} \sigma_p(E) \frac{dE}{S(E)} T(E)$$

$$T(E) = \exp\left[-\mu \frac{\cos\theta_i}{\cos\theta_o} \left[\int_{E_{Hi}}^{E} \frac{dE^1}{(S(E^1)} \right] \right]$$

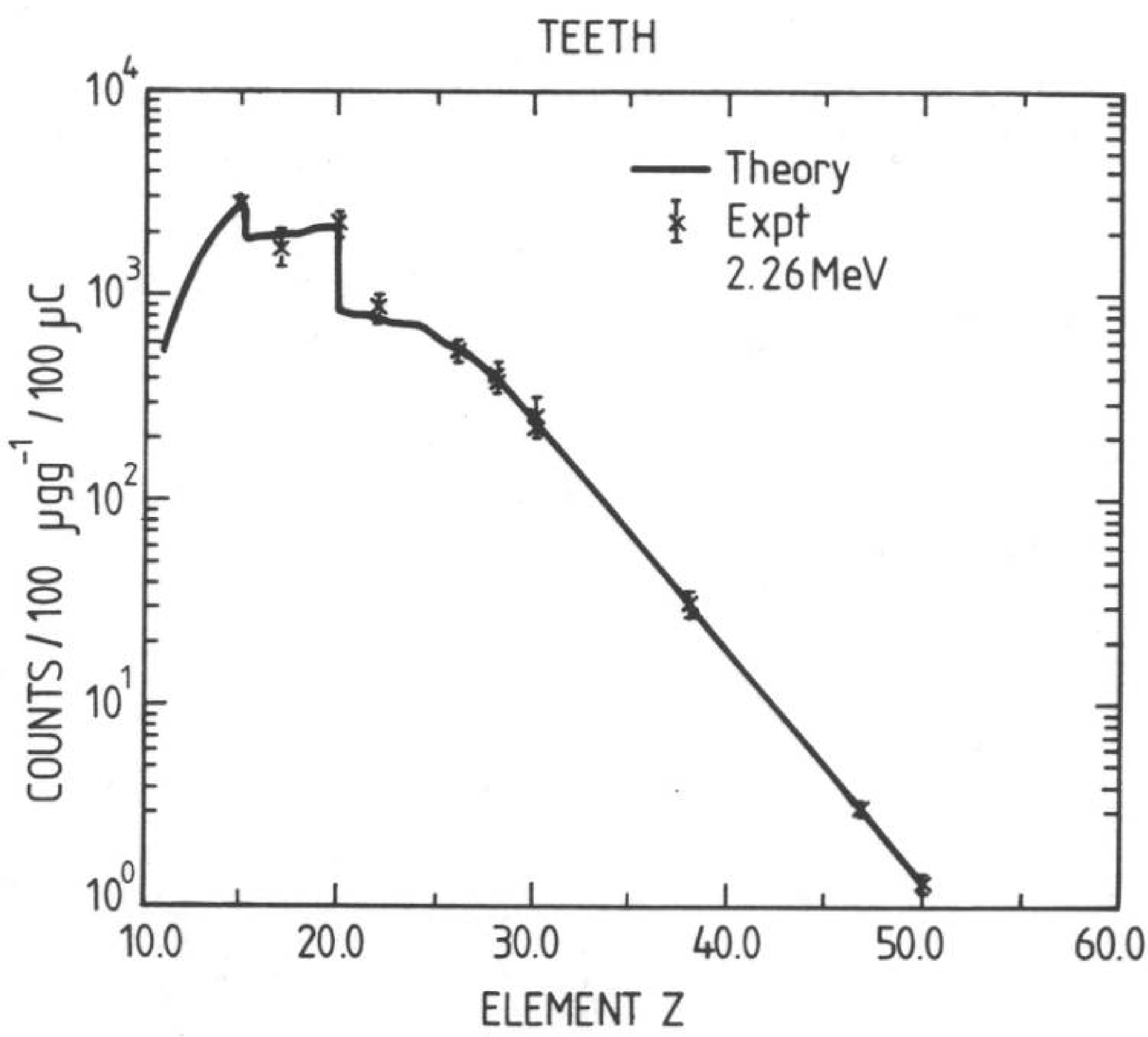
Thick Target Integrand

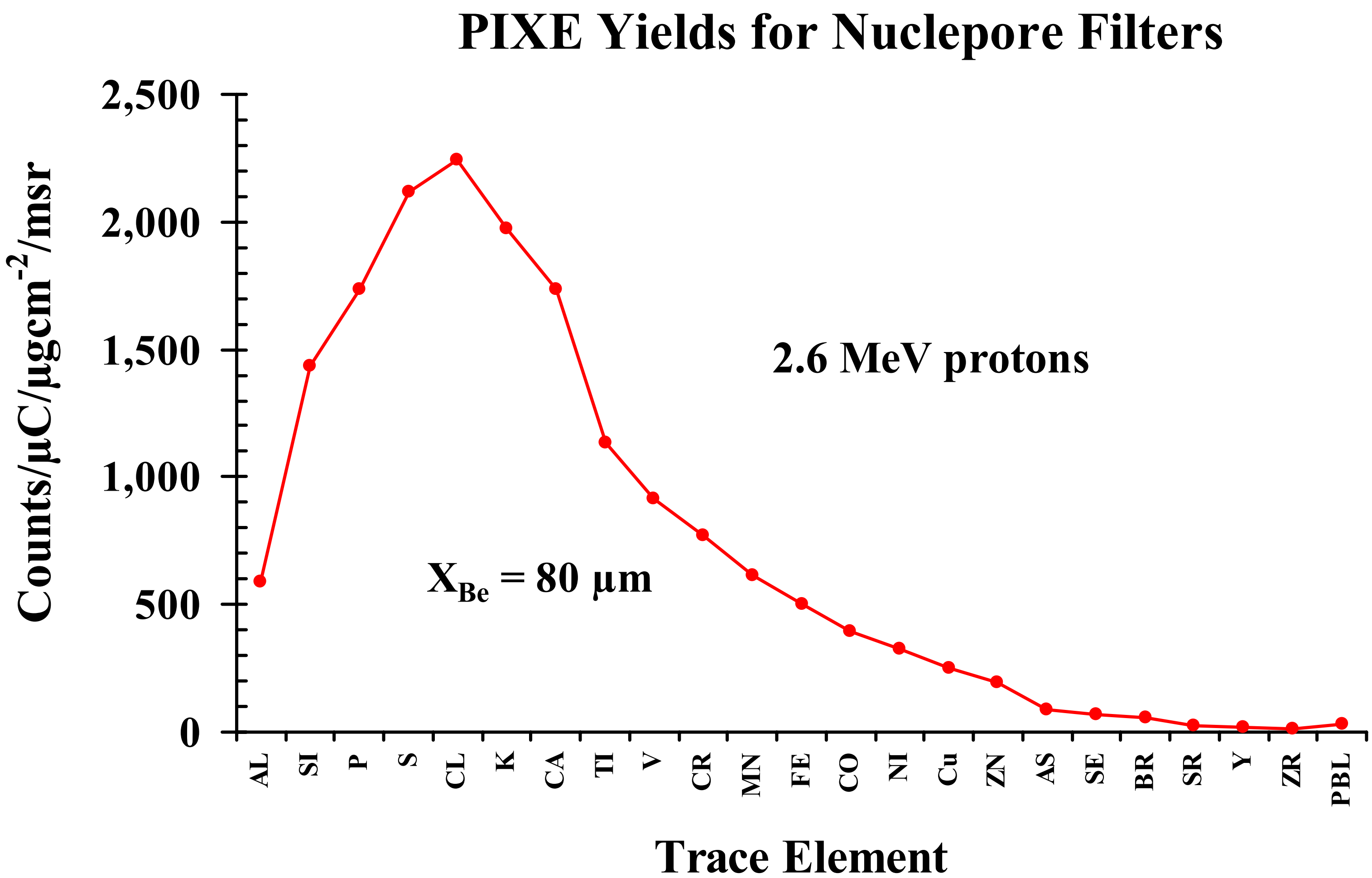




Thick Target Yields

Thick Target Yields





Calculated thin target yields

Calibration of PIXE Systems

Most analysis systems are generally calibrated against known reference standards (NBS, IAEA, Micro-matter). These can be thin or thick targets.

Standards can be internal or external.

For light ion PIXE using protons the theoretical cross sections and ion stopping powers are generally accepted to around ±5%.

Hence if the system is calibrated against thin targets of known composition thick target yields can be calculated generally with a precision approaching ±5 to ±15%.

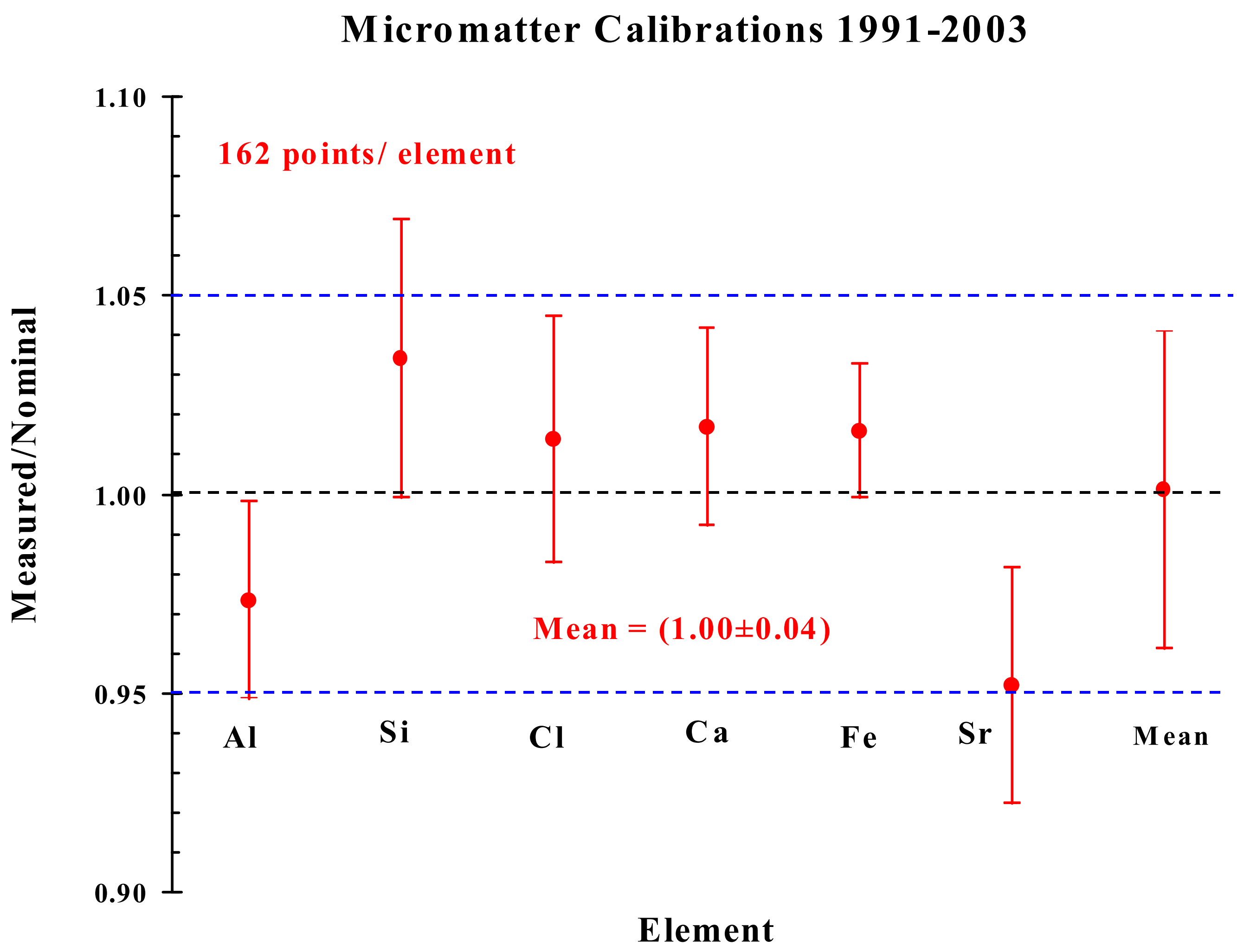
For an internal standard:

$$C_{elt} = [(C_{stand}\ Y_{elt}\ M_{stand}) / (Y_{stand}\ M_{elt})]$$

where M is the yield / unit concentration at the same input ion energy as defined by the yield equations.

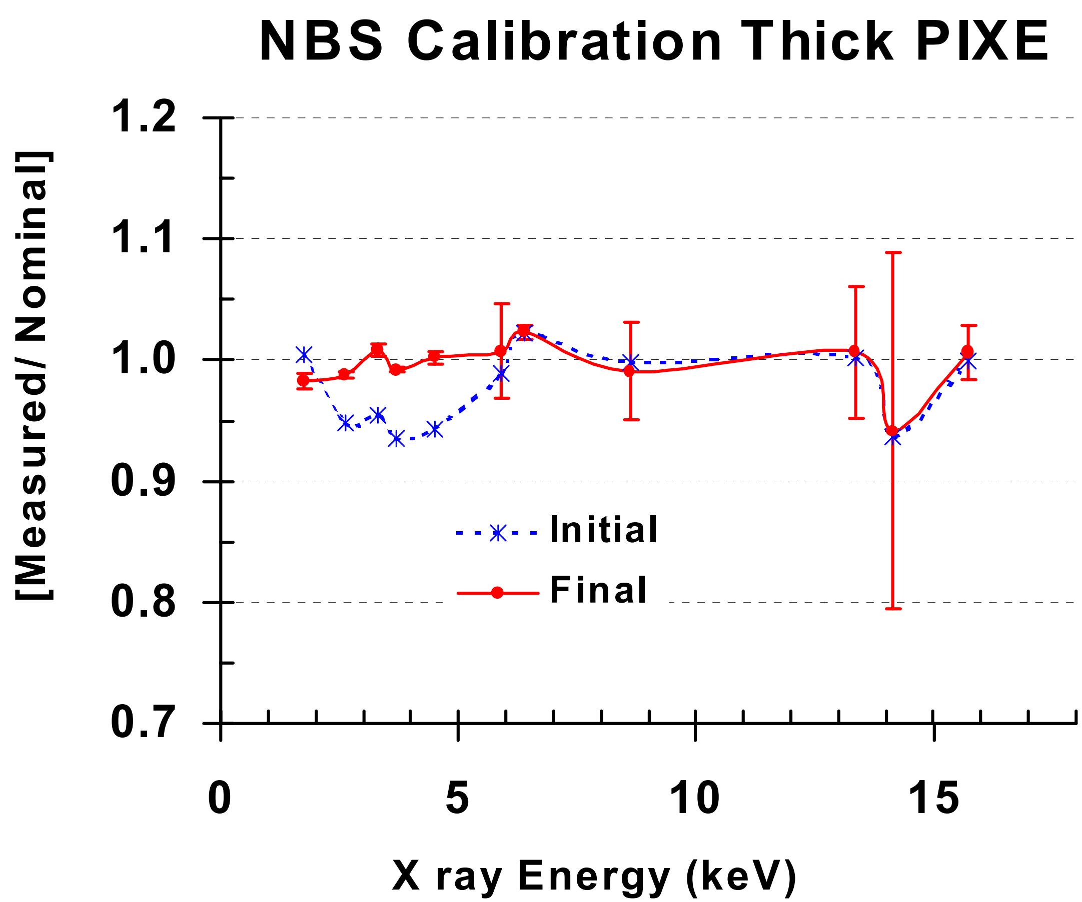
For an external standard the experimental and theoretical yields are compared directly and any or all of the detector efficiency, solid angle, target current, filter thicknesses adjusted to make experiment and theory agree.

Thin Micro-matter Standards



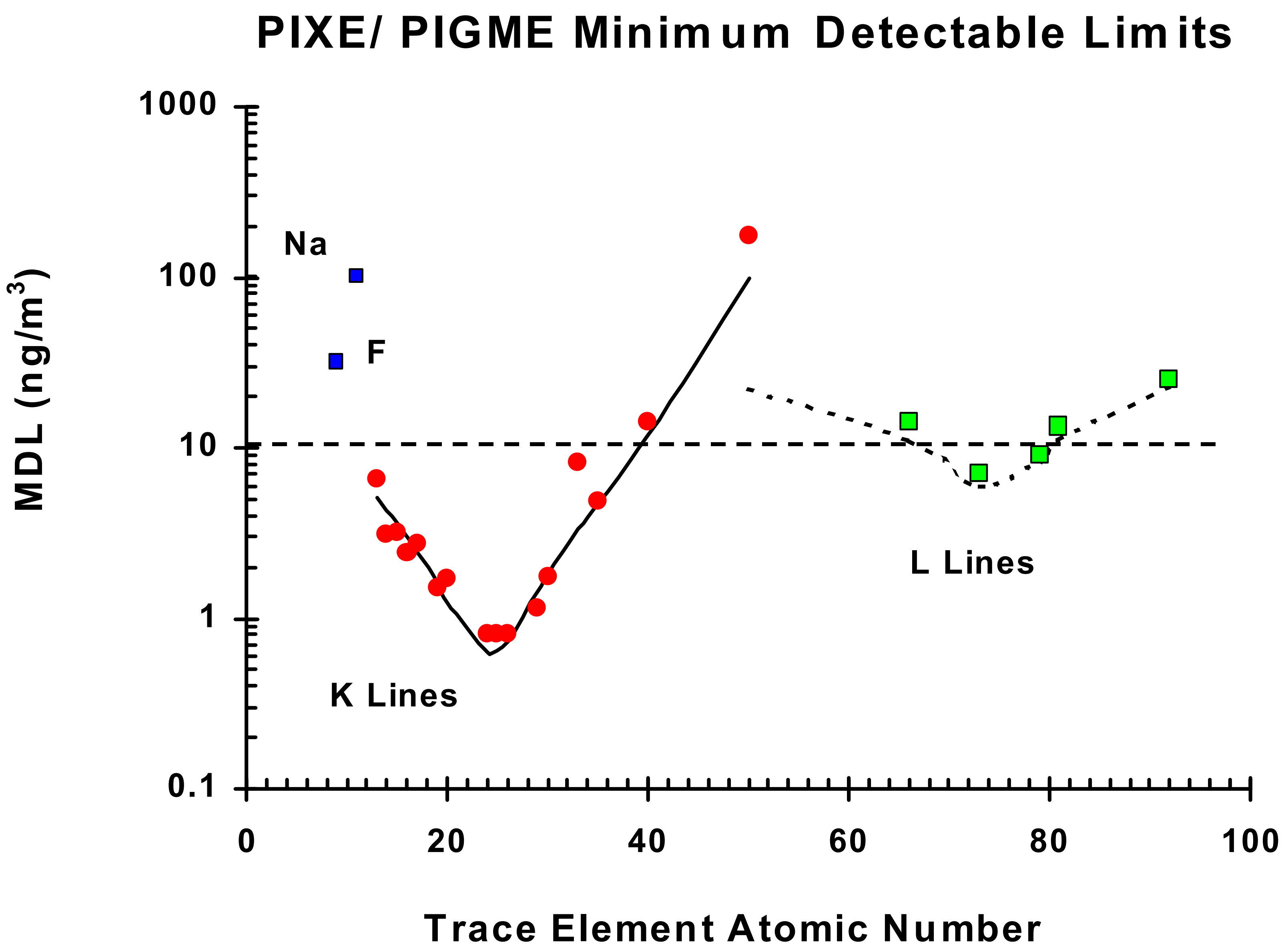
2.5 MeV protons

Thick Standards



Typical pinhole efficiency calibration using NBS278 Certified Reference Standard thick target for selected elements from Si to Zr. 1.68 mm thick Perspex, 9% hole, 47 μm Mylar.

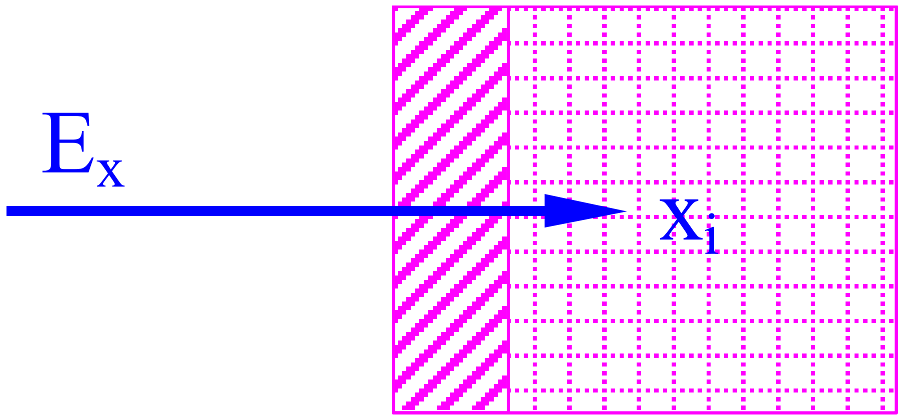
Minimum Detectable Limits



X-ray Detection

Electron/ hole pairs at LN_2 temperatures in Si – 3.6 eV.

E_x(keV)	x_i (mm)
5	0.018
10	0.13
20	0.87
40	2.2
60	2.4



E_x small – does not enter the detector E_{min}
E_x Large – goes right through the detector E_{max}
Between $E_{min} < E_x < E_{max}$ can be close to 100% efficient, depending on the interaction depth x_i and the electron/ hole pair collection efficiency.

X-ray Detection Efficiency

Form of the efficiency is the product of all transmissions,

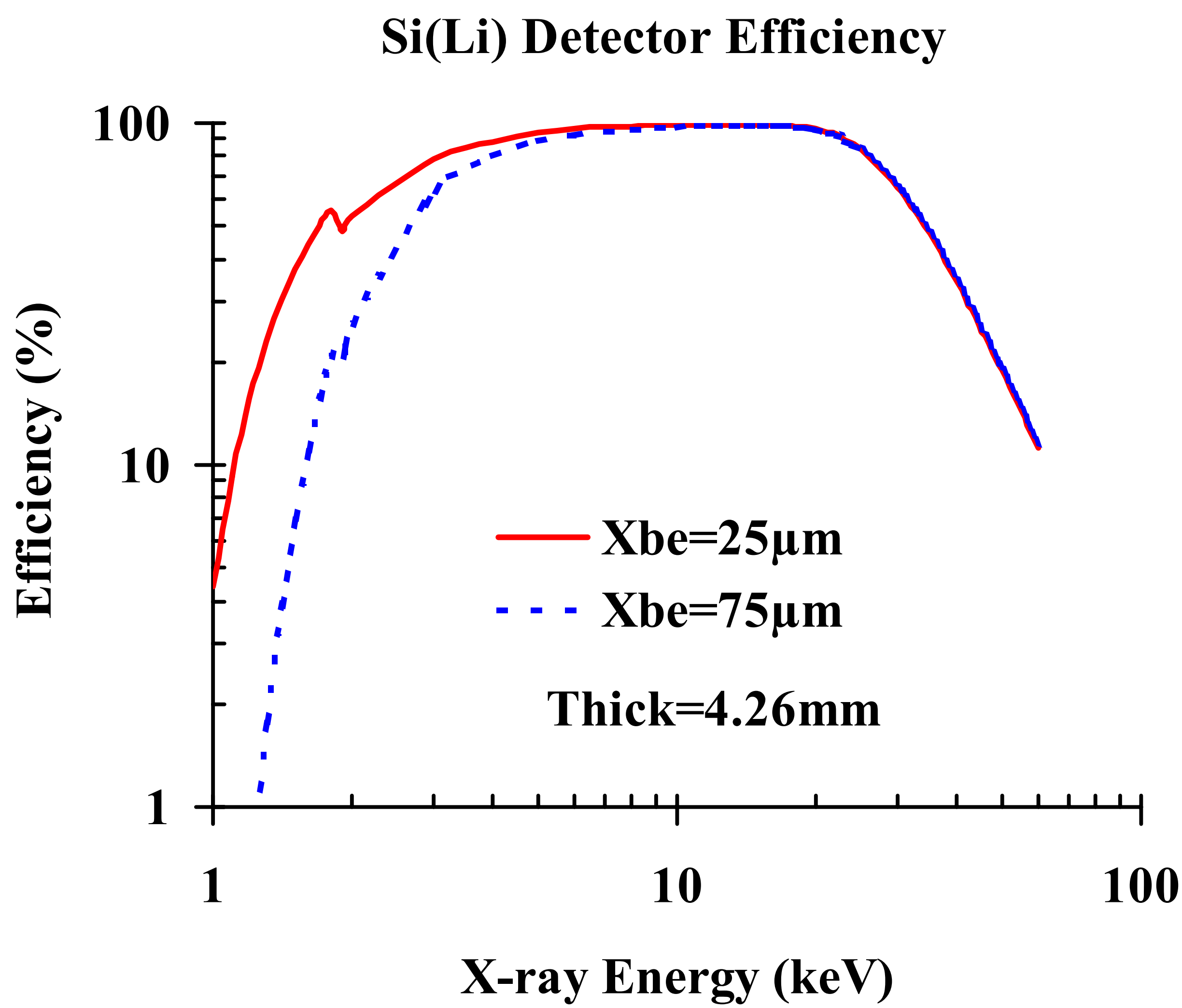
$$\varepsilon = f_{Be}*f_{Au}*f_{d}*f_{g}*f_{R}*f_{ice}*\varepsilon_{I}*f_{f}$$

$$f \sim \exp[-(\mu/\rho)\rho x]$$

$$\varepsilon_{I} \sim 1- \exp[-(\mu/\rho)D]$$

So what is the efficiency shape?

X-ray Detection Efficiency

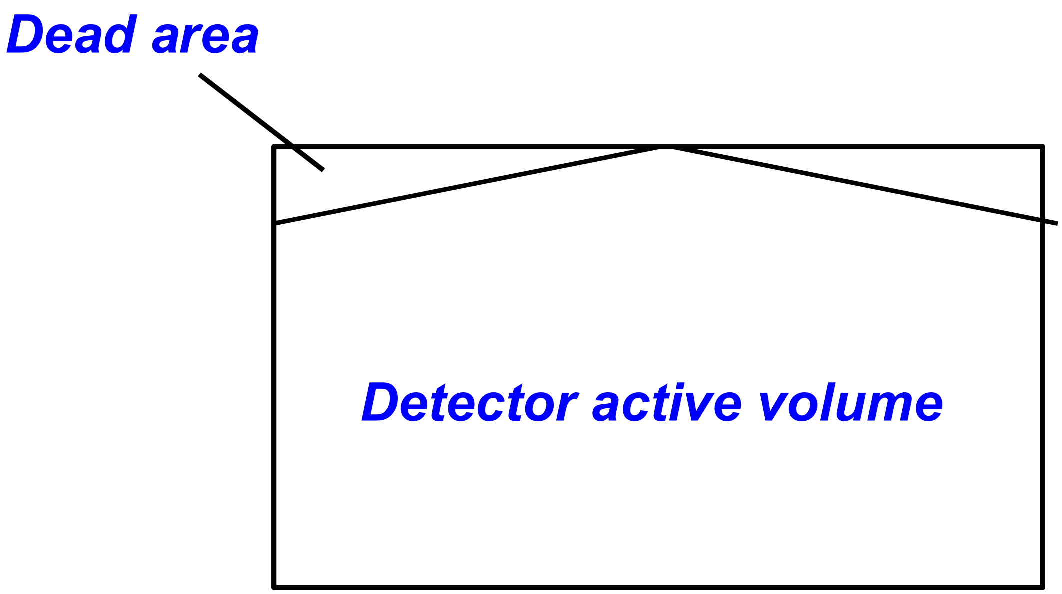


Radial Dependence

$$\epsilon(r) = \epsilon_o \exp[-\alpha r^2]$$

α maybe 0 no dependence

0.3 30% edge effect



Geometric Factor

Different solid angles for different energies.

$$fg = \frac{2}{x}\left[1 - \frac{1}{(1+x)^{1/2}}\right]\left[1 + \frac{Z}{d}\right]^{-2}$$

$$x = r_s^2 / (d + z)^2 \qquad r_s = source\ radius$$

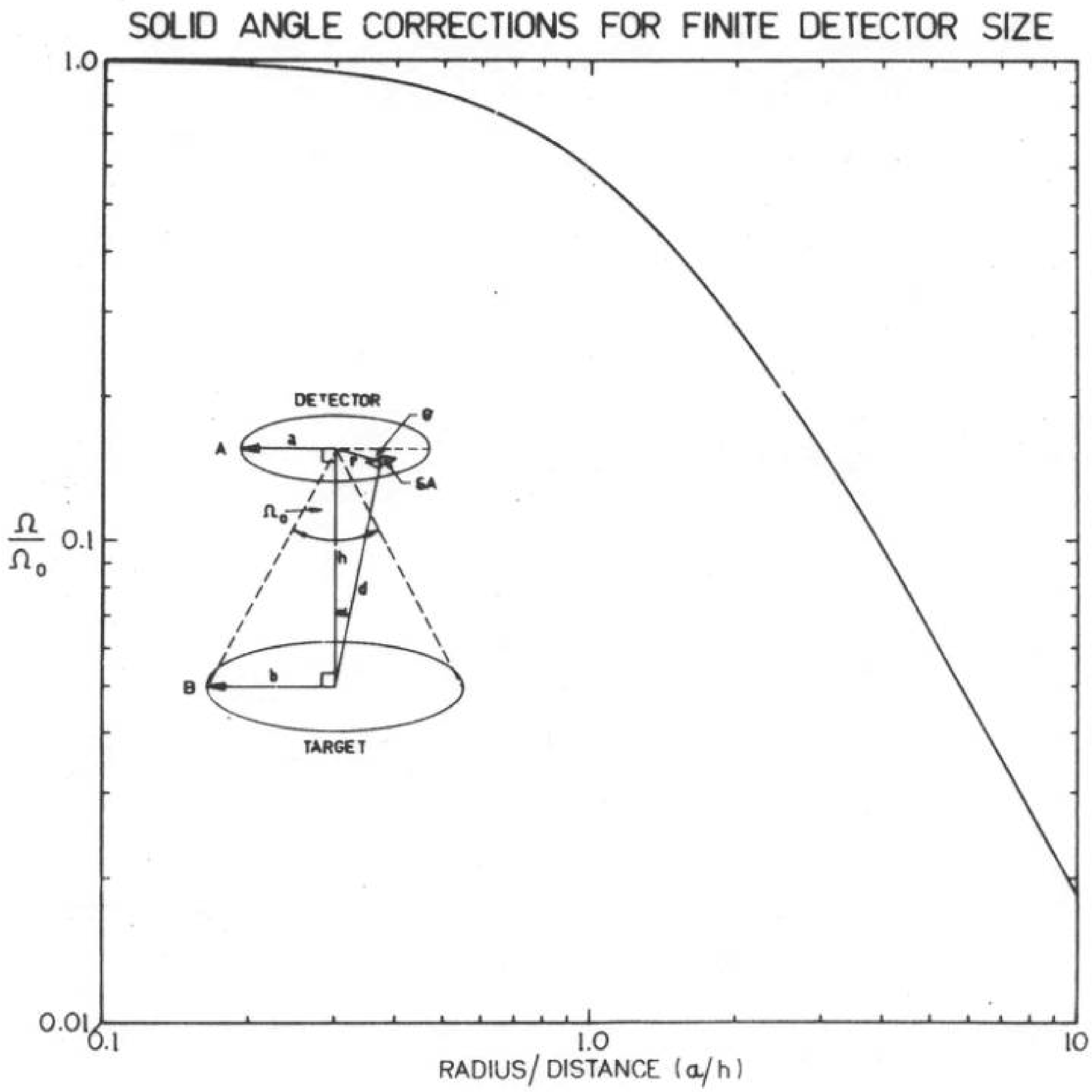
d = detector front face - source distance

Z= Z(E_x) is the photon interaction depth in the detector.

Correction largest for small *d* high E_x (large Z)

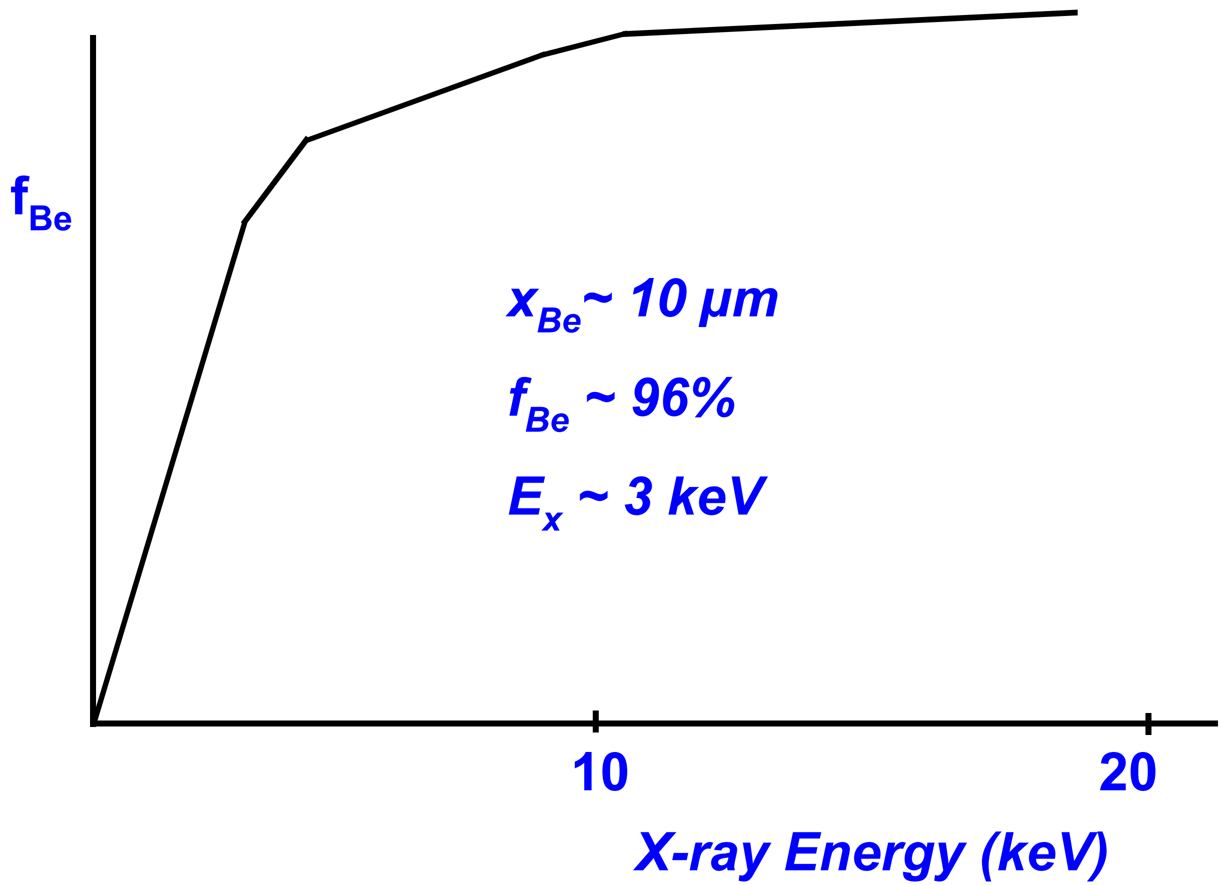
For most situations f_g is less than 8% correction.

Geometric Factor



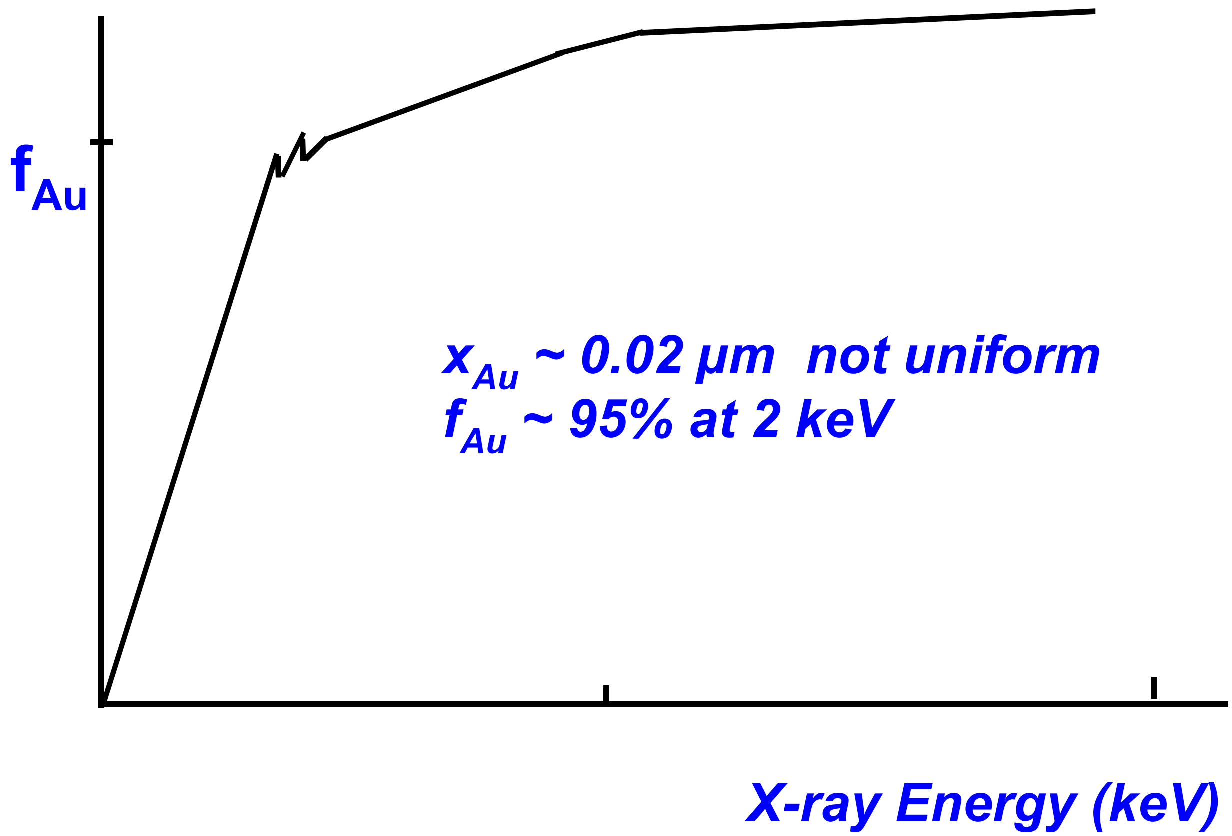
Be Window

$$f_{Be} = \exp\left[-0.1098\, x_{Be}\, E^{-2.92}\right]$$



Au Contact Layer

$$f_{Au} = \exp\left[-80.85\, x_{Au}\, E^{-2.55}\right]\; 3.4 < E < 11.9 < 3$$
$$= \exp\left[-2.8\, x_{Au}\ \right] 2.2 < E < 3.4\, M1 - M5$$
$$= \exp\left[-11.20\, x_{Au}\, E^{-2.16}\right]\; 0.76 < E < 2.2$$



Dead Layer

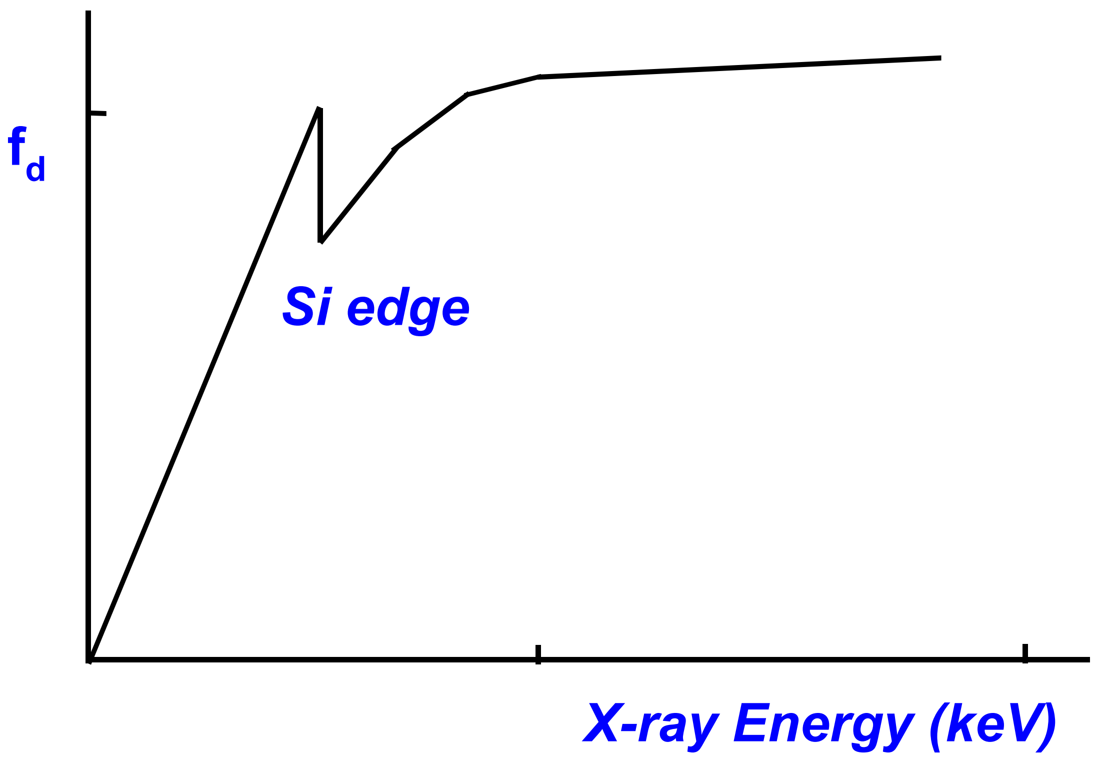
$$f_d = \exp\left[-4.830\, x_{si}\, E^{-2.79}\right] \quad E > 1.838$$

$$= \exp\left[-0.3631\, x_{si}\, E^{-3.03}\right] \quad 0.2 < E < 1.838$$

$$x_{si} \sim 0.3 \mu m$$

$$f_d \sim 77\% \text{ above K edge at 1 kev}$$

$$\sim 98\% \text{ below K edge at 1 kev}$$



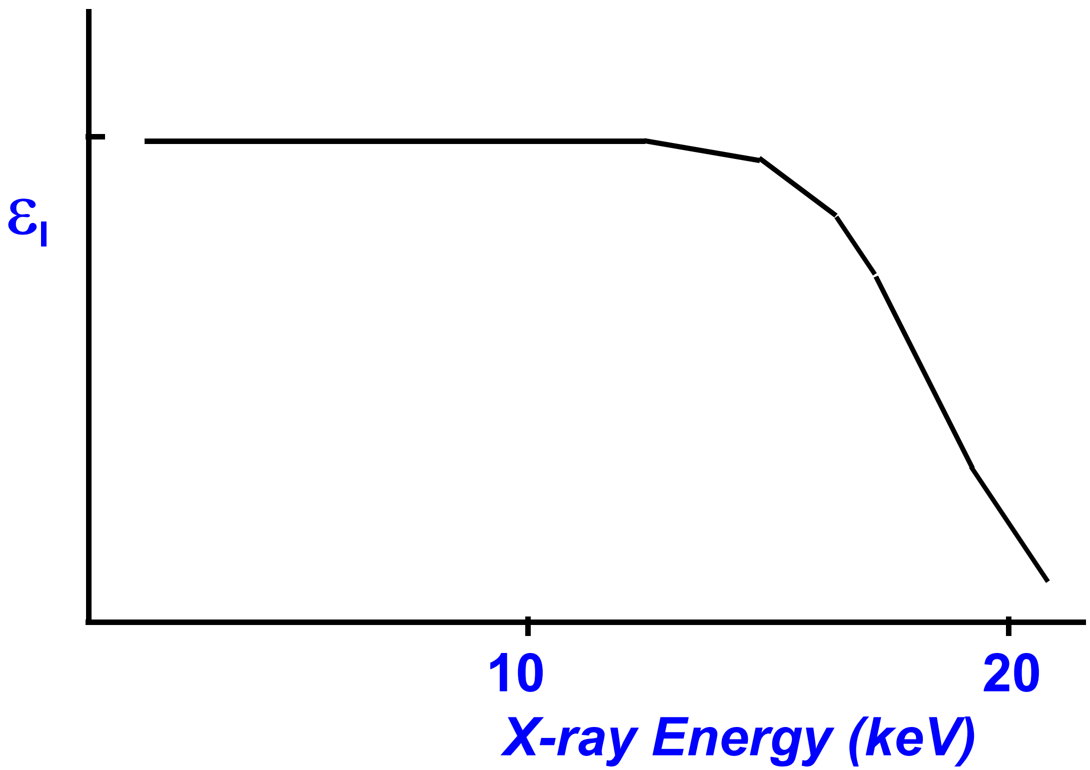
Sensitive Volume

$$\in_I = 1 - \exp\left[-15.ODE^{-3.22}\right] E > 20$$

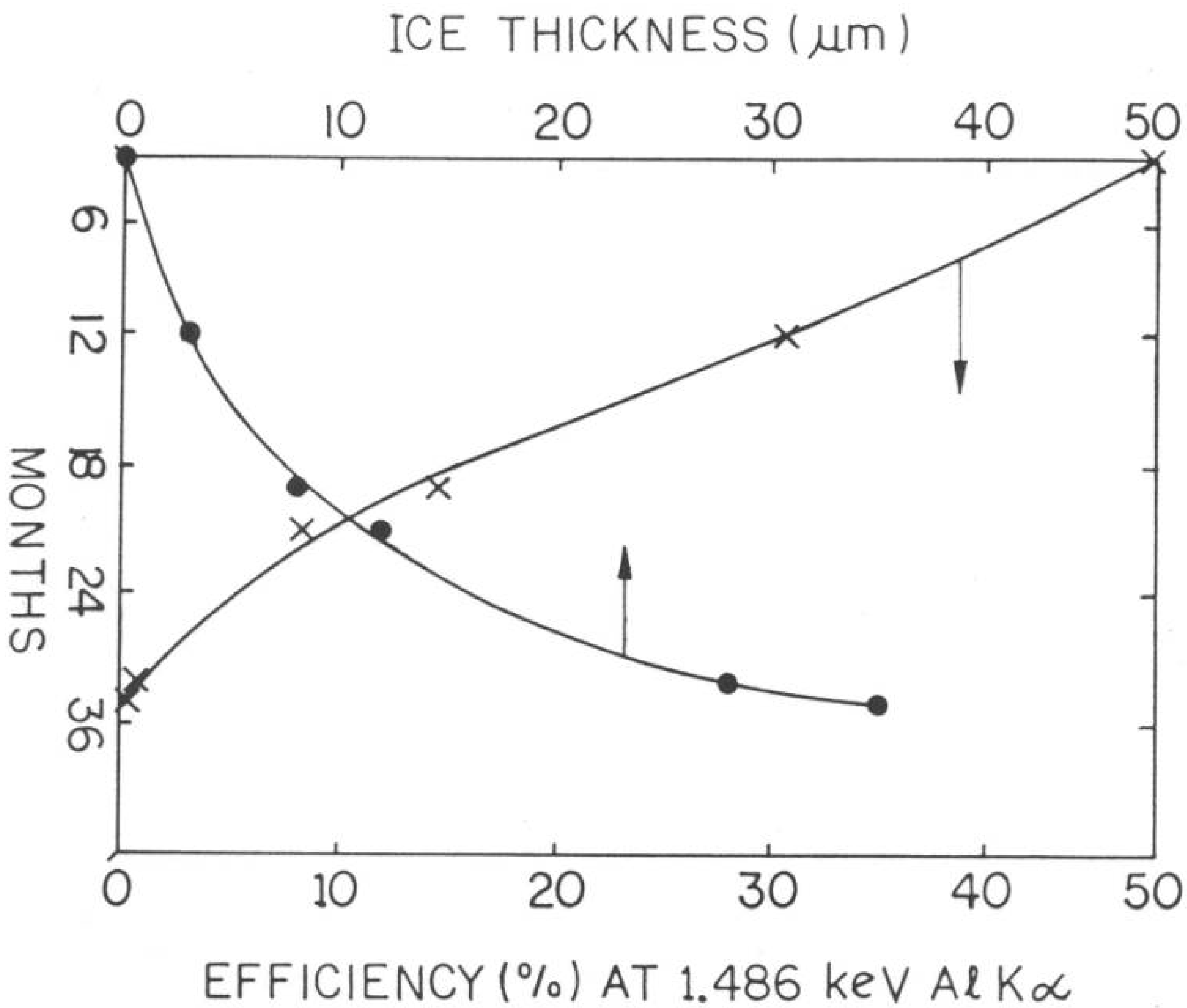
$\varepsilon_I \sim 67\%, 11\%$

E ~ 30 keV, 60 keV

for 4.26 mm detector



Ice Build Up with Time



Summary

We have discussed:-

PIXE Systems

- PIXE end station designs
- Current measurement
- X-ray detection
- PIXE spectra, escape peaks
- PIXE electronics, pileup, sum peaks
- Filters and spectrum shaping
- Spectrum analysis, line shapes, backgrounds
- Peak areas to concentrations
- PIXE system calibrations
- X-ray detectors, efficiency

Next is –

PIXE Analysis Methods

DOPIXE – areas, concentrations, calibrations, thin, thick samples.

1) Run batch file DoibaWIN98.bat in Dopixepc directory.

2) IBA analysis menu appears.

3) Do not click on anything !

4) Many buttons do not work in this cut down PC version!

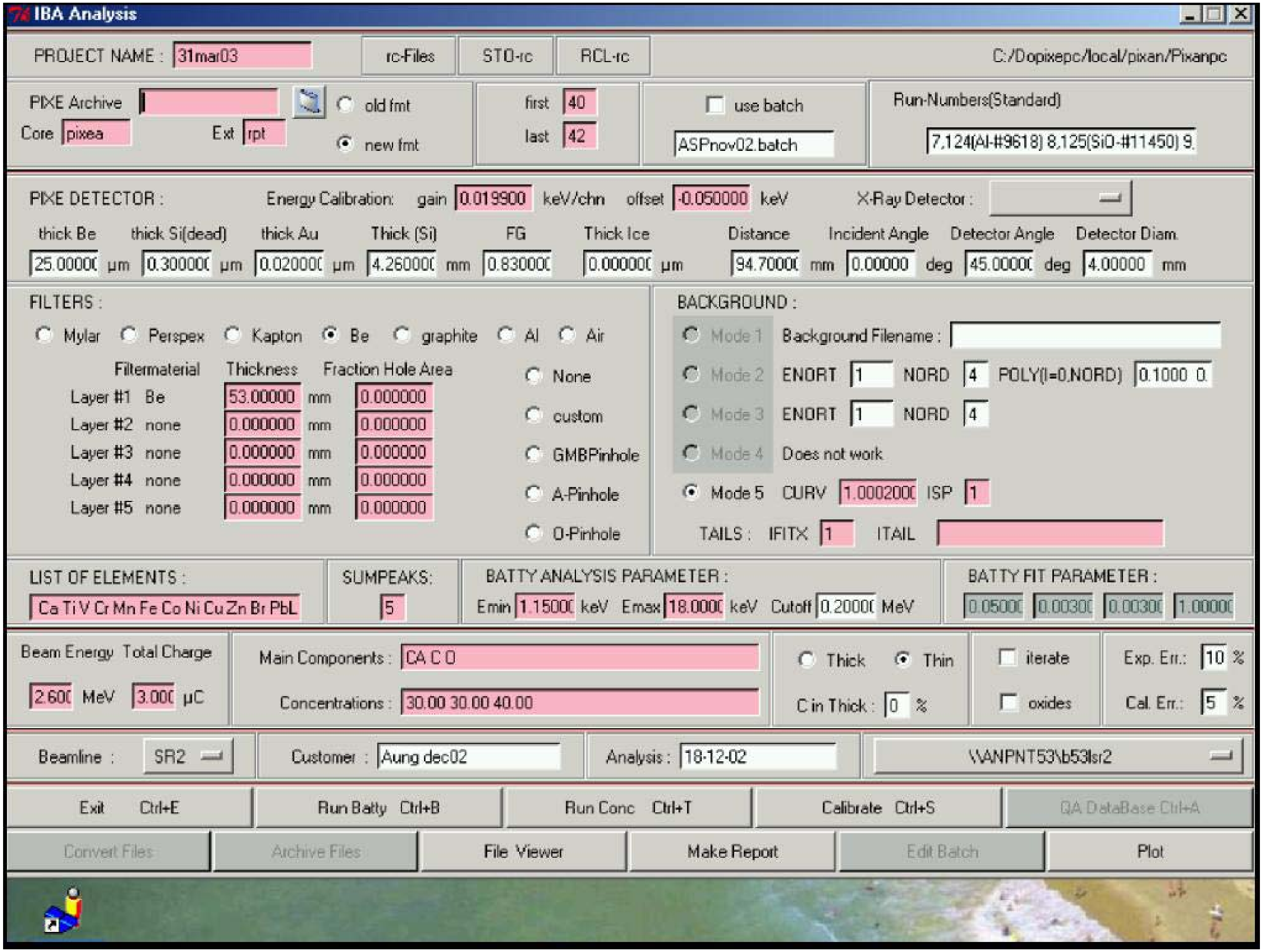
5) Select rc-Files

6) Click on Get Defaults

7) Double click on IAEAXApr.Xrc in ../doiba/data

8) Click on Read to load

DOPIXE MAIN MENU



1) Double click in batch window (ASPnov02.batch)

2) Type *.batch in window then return

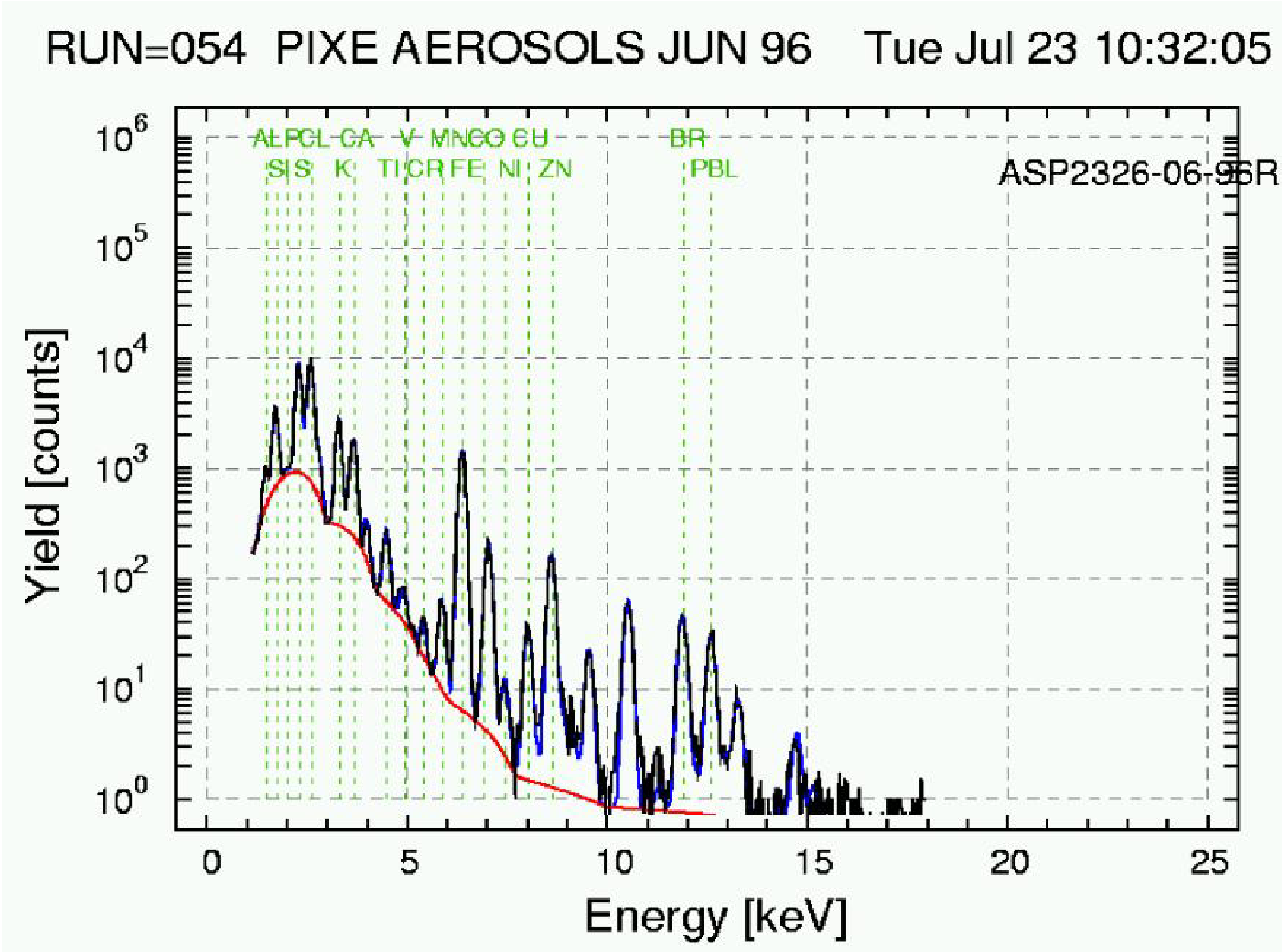
3) Double click on ASPnov02.batch in ../PIXAN/Pixanpc

4) Select Run Batty to find peak areas

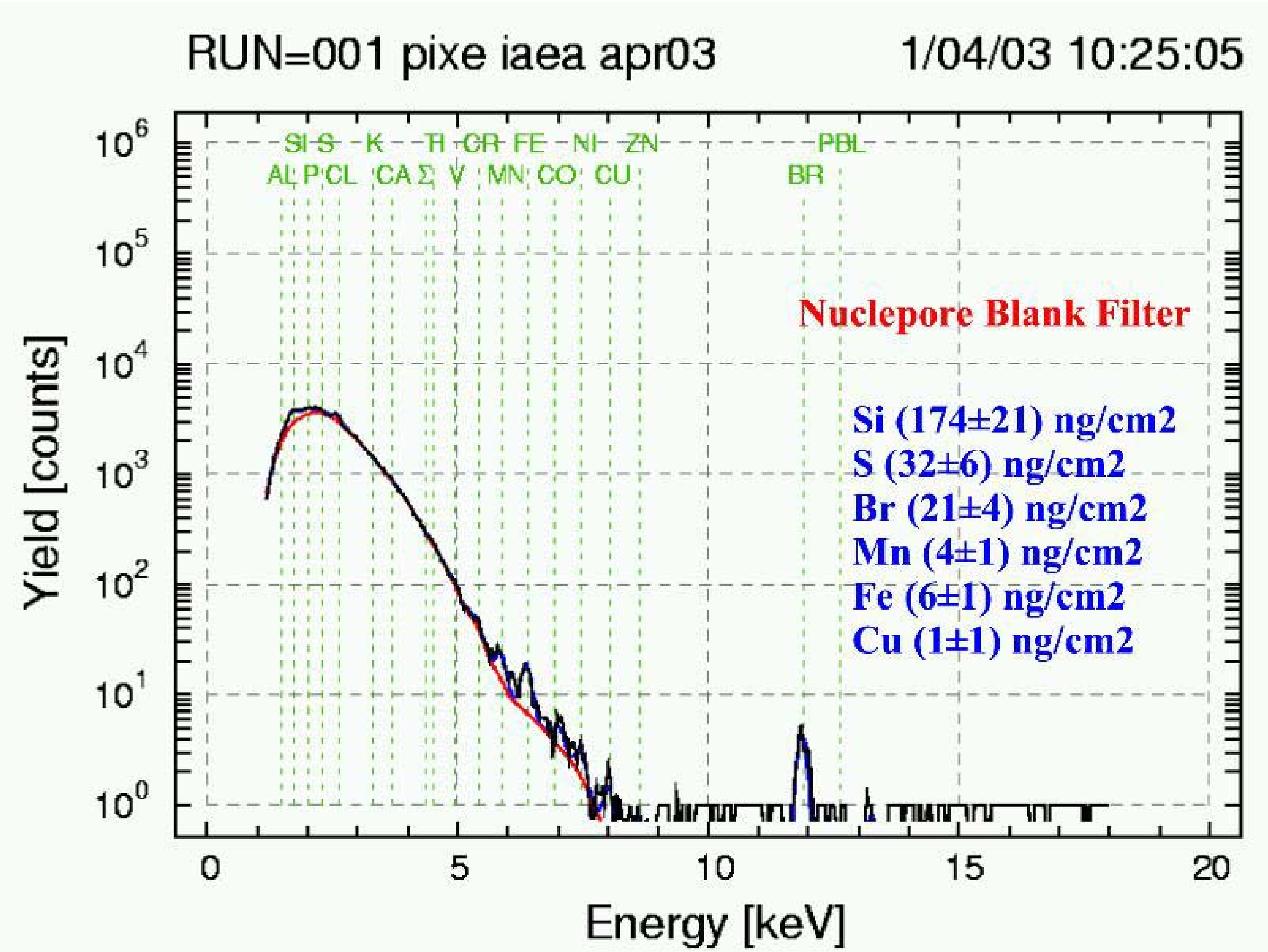
5) Select Continue and wait

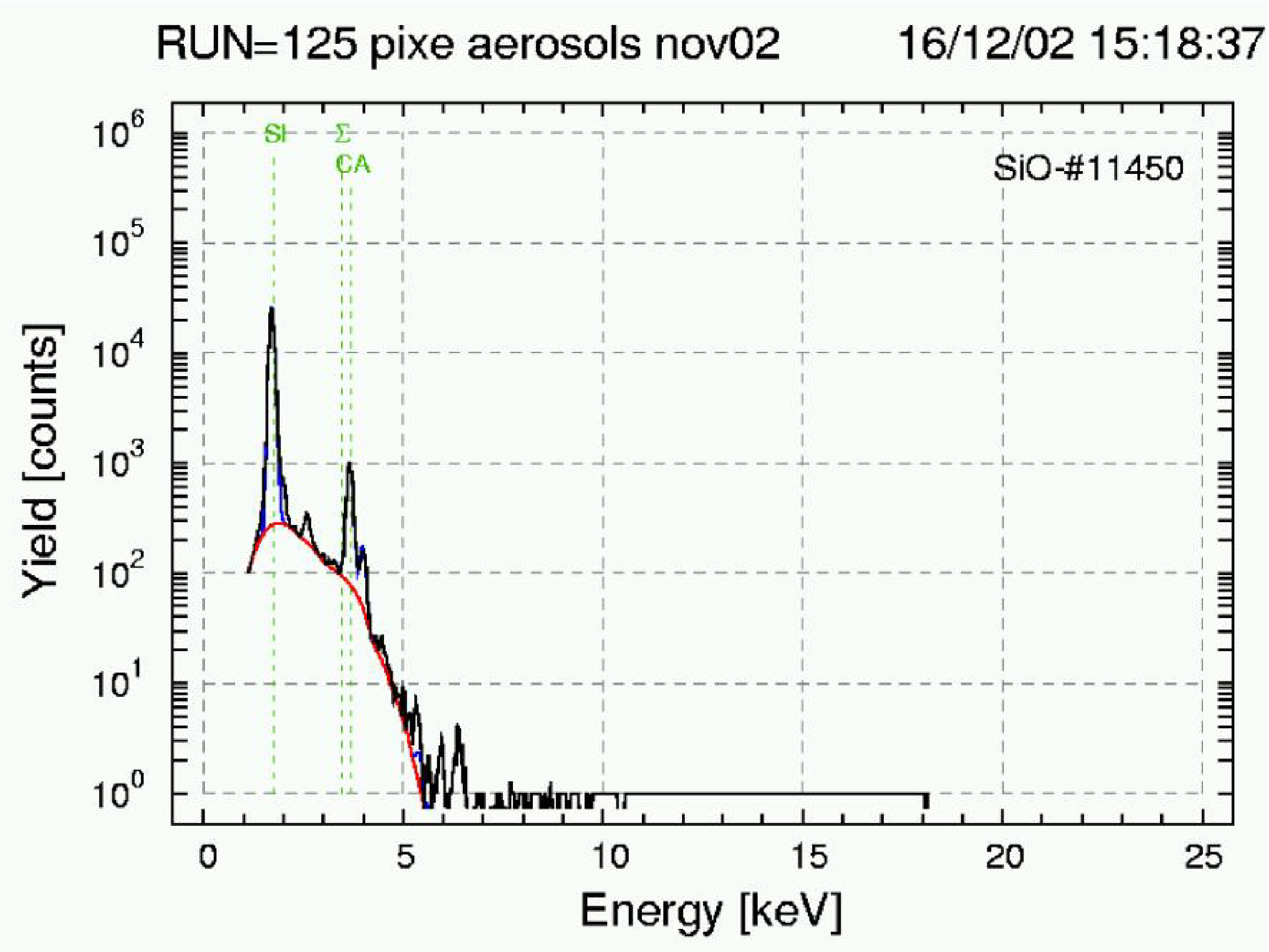
6) This will generate peak areas and plots

7) Select Run Conc to calculate absolute concentrations

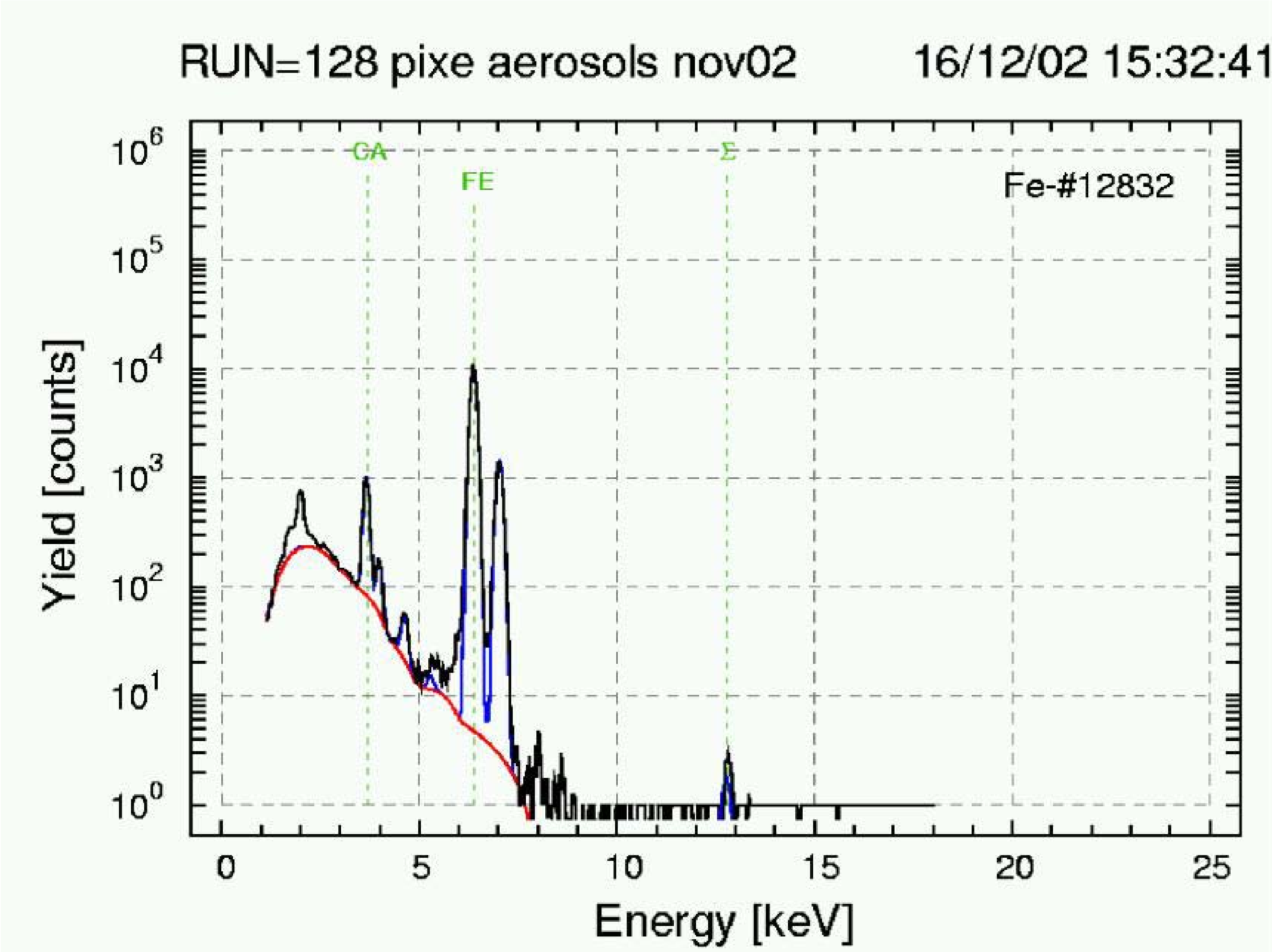


Typical PIXE spectrum and fit for Mascot Jun 1996

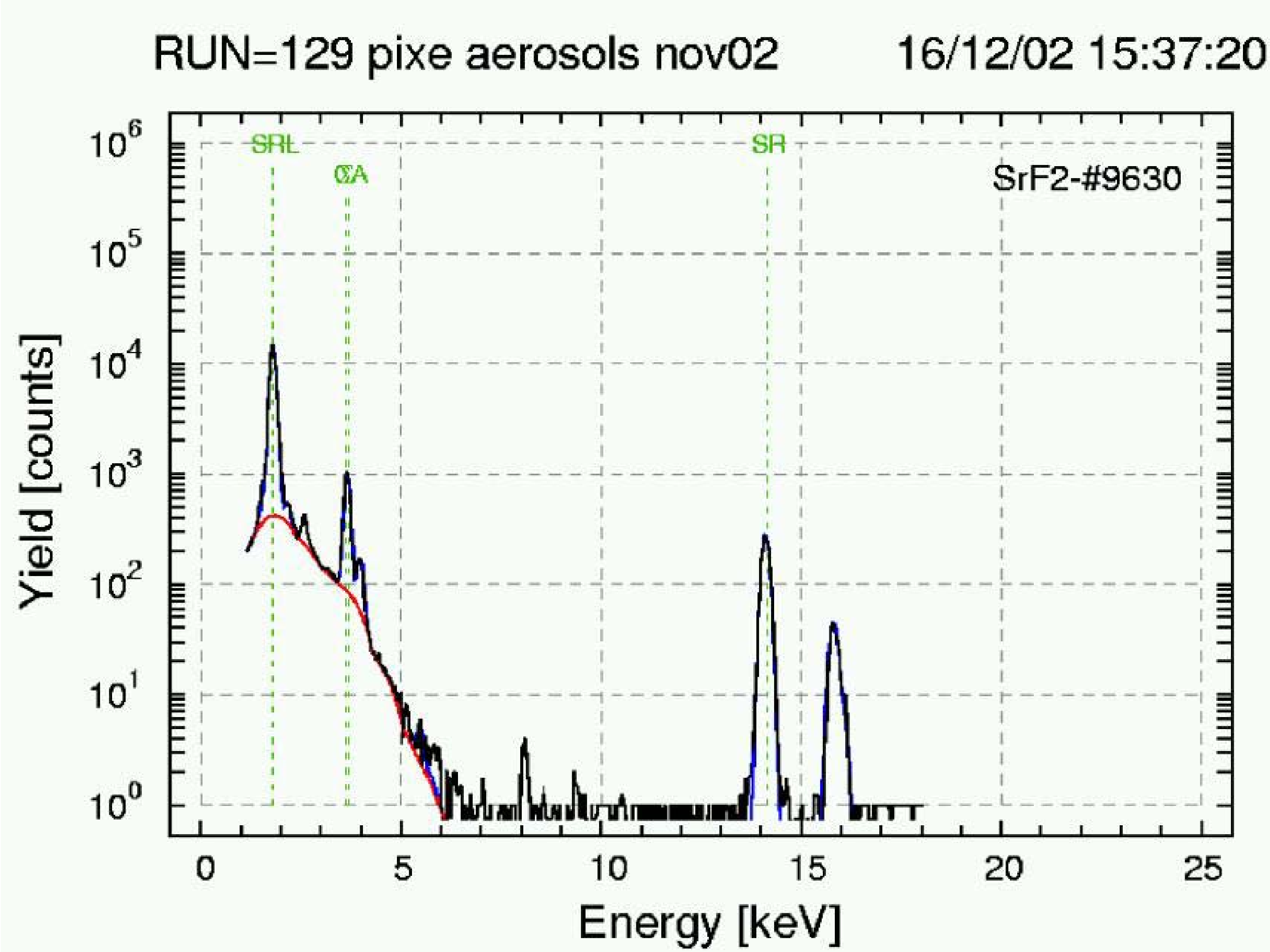

RUN=001 pixe iaea apr03
1/04/03 10:25:05
SI S K TI CR FE NI ZN PBL
AL P CL CA Σ V MN CO CU BR
Nuclepore Blank Filter
Si (174±21) ng/cm2
S (32±6) ng/cm2
Br (21±4) ng/cm2
Mn (4±1) ng/cm2
Fe (6±1) ng/cm2
Cu (1±1) ng/cm2
Yield [counts]
Energy [keV]
0
5
10
15
20



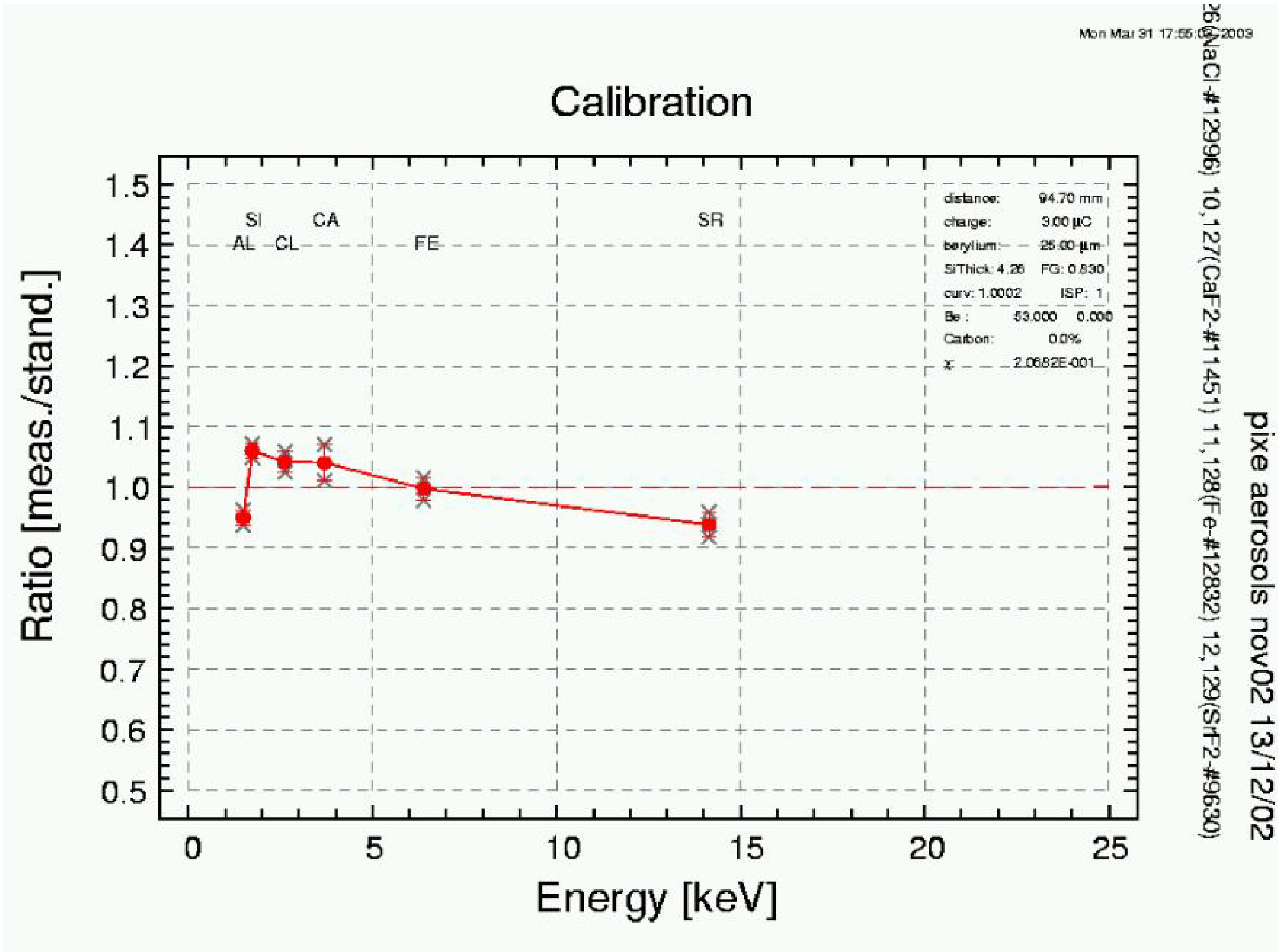
Si MM Calibration spectrum



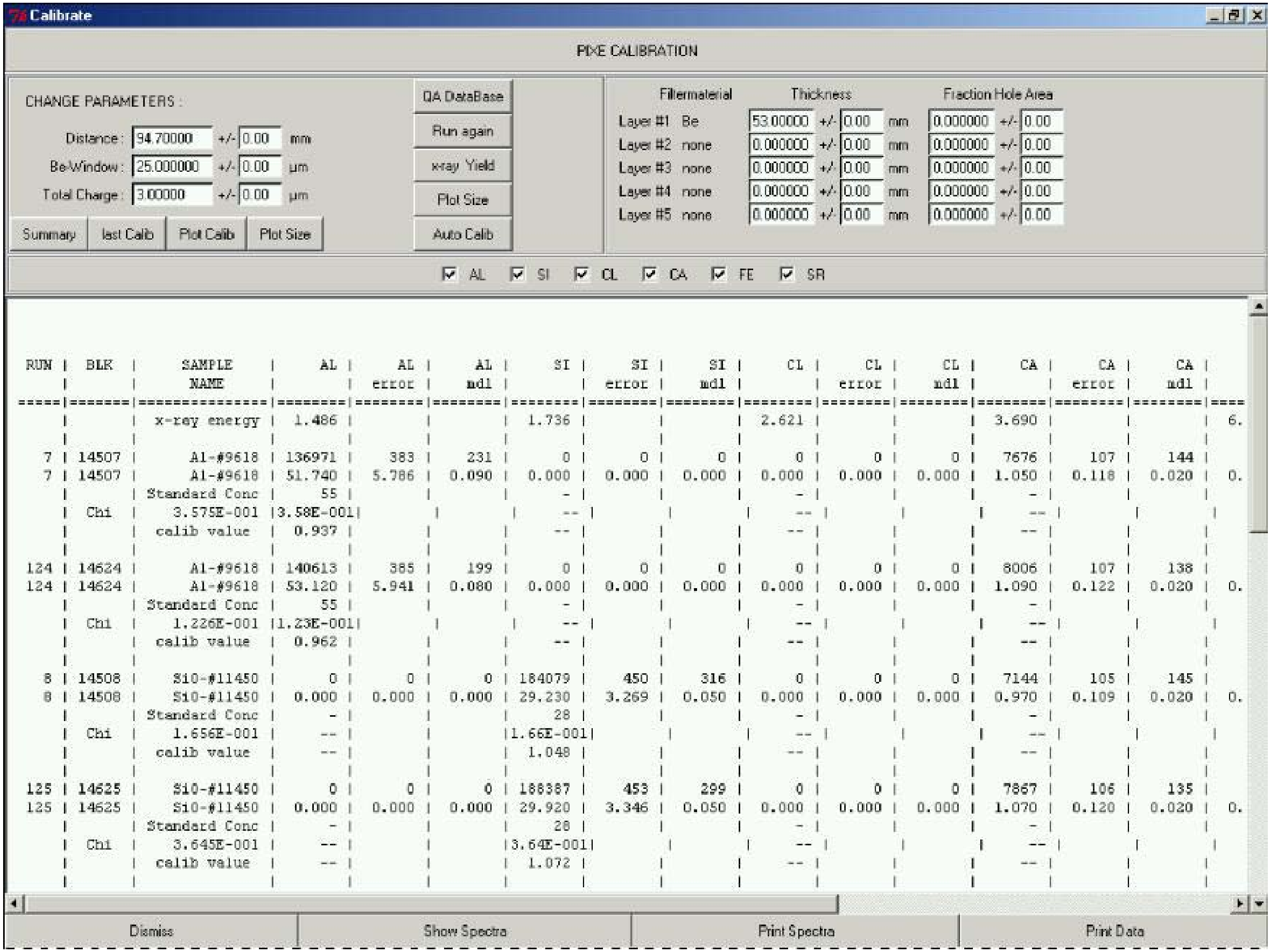
Fe MM Calibration spectrum



Sr MM Calibration spectrum

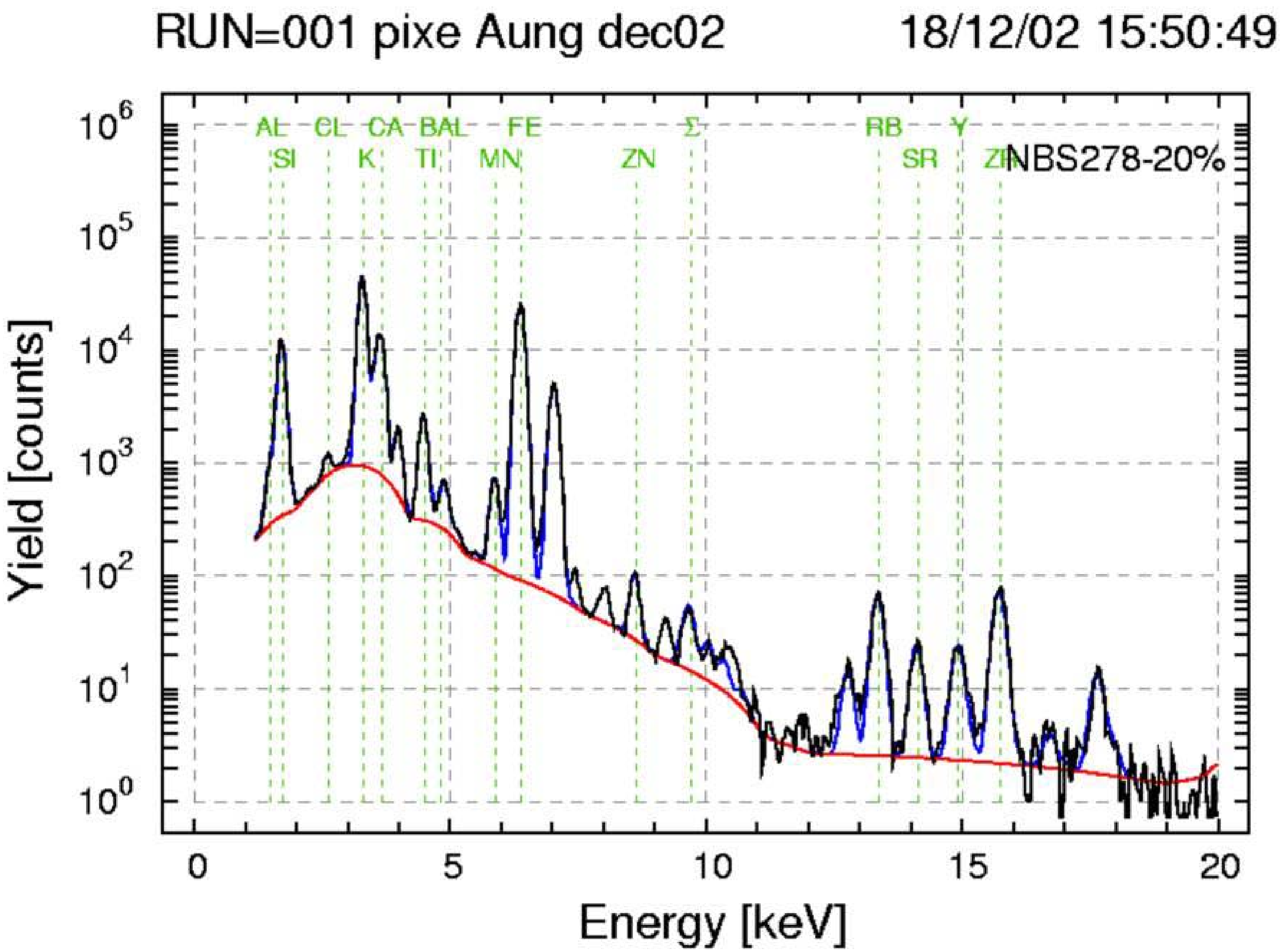


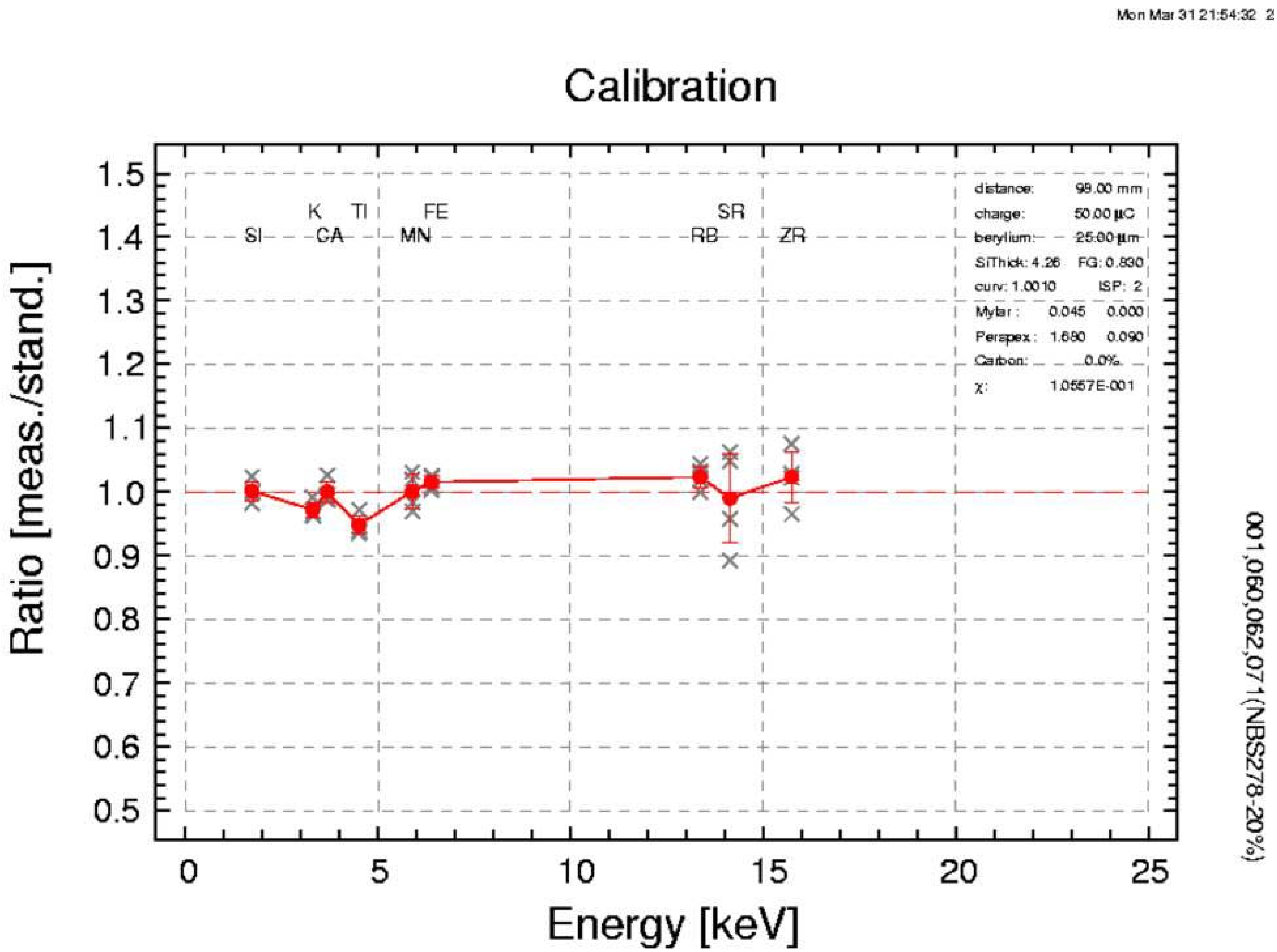
MM Calibration Plot



MM Calibration Menu

NBS270 Rock Standard





NBS270 Calibration Plot

PIXAN Analysis Package - ANSTO

The PIXANPC directory should contain several *.ZIP files. The PIXANPC.ZIP file should already be unzipped. DO NOT unzip is again. The file PKUNZIP.EXE has been provided to run under DOS to unpack *.ZIP files. It works by typing:-

PKUNZIP *filename.zip*

EXERCISES

1) First, let's analysis some Micromatter Standard thin foils using the PIXANPC analysis code developed at ANSTO.

Unzip the MMSTD.ZIP file (Type *PKUNZIP MMSTD.ZIP*). This contains all you need to analysis the Micromatter Foils. PIXE spectra are contained in MMSTD.SPC.

Open the MMCALIB.DAT file (using the DOS editor, EDIT) and note the calibrated foils nominal thickness. Print if you have a printer as you will need these later.

The analysis program BATTYPC.EXE requires an input run file this is called MM.RUN. Open it with the DOS editor and find out what each parameter does from the notes provided. Note the input and output file names so you can find them later (MM.OUT).

DO NOT change anything in this file as it may not run later if you do.

You can use BATMAKER.EXE to generate your own MMY.RUN file by typing BATMAKER and answering the questions. Do this and compare MM.RUN with MMY.RUN it will also help you to understand the input file for BATTYPC.

To run the spectrum analysis type BATTYPC

It will ask you for the input file name type MM.RUN

Wait till it runs and then look in the MM.OUT file it contains all the peak areas you need to convert these to concentrations later.

Note this file contains ERRORS and MDL's for each element found. What is the significance of these ?Try doing this analysis with your own MMY.RUN file. Change the fitting options (extra elements, curvature, etc) note the difference in peak areas.

Try the PLOTSPEC.EXE option on *.PLT files to replot data just analysed using BATTYPC.

2) To convert the peak areas from MM.OUT to concentrations you will need to run the THIKPC.EXE file. This will ask you for the corresponding input run file MMYLD.RUN.

PIXAN Analysis Package - ANSTO (cont)

Open MMYLD.RUN and understand all the input lines before running it using THIKPC. Use the notes provided.

DO NOT change this file, keep it as a master.

In a similar fashion to BATMAKER you can use THKMAKER.EXE to generate your own YLD.RUN files. Try it by typing THKMAKER and answering the questions. Compare the YLD.RUN generated with the original MMYLD.RUN file and note the differences.

Copy MMYLD.RUN into MMYLDME.RUN and make changes to this file as required. Note the output from THIKPC is in THIKPC.OUT.

It may help to load MM.OUT and THIKPC.OUT into a spreadsheet to assist in the calculation of Micromatter foil concentrations from their PIXE peak areas.

Compare these concentrations with the calibrated values in MMCALIB.DAT using the errors and the MDL's provided. Plot this comparison.

3) Repeat 1) and 2) above for other blocks of data contained in *.ZIP files.

TEFJAK.ZIP	Teflon filters from Jakarta PM2.5
TEFMAS.ZIP	Teflon filters from Mascot in Sydney PM2.5
TEFGRIM.ZIP	Teflon filters from Cape Grim in Tasmania PM2.5
GASJAK.ZIP	Course Nuclepore filters fro Jakarta 2.5-10 µm
BLKS.ZIP	Blank filters from various places.

Note TEFJAK.RUN, GASJAK.RUN and BLKS.RUN files are used to run BATTYPC and TEFYLD.RUN, GASYLD.RUN and BLKSYLD.RUN files are used to run THIKPC.

Add extra elements and check the areas of each of these elements against their ERRORS and MDL's when converting to concentrations. Use the spreadsheet where possible to do any calculations required.