Quantitative Analysis

Quantitative analysis using the electron microprobe involves measuring the intensities of X-ray lines generated from your unknown sample, and comparing these to the same lines in suitable standards, using identical instrumental conditions, such as:

*Accelerating voltage
*beam current
*specimen geometry
*beam size
*coating thickness

A number of factors are important components of quantitative analysis:

-Selection of suitable standards

-Selection of suitable crystals and order of analysis

-Choice of appropriate analytical conditions

-Background selection/correction

-Matrix corrections (ZAF, Phi-Rho-Z)

Quantitative WDS analysis

A simplified approximation of the principle of WDS analysis is as follows:

$C_A(sp) \;=\; [I_A(sp)/I_A(st)]C_A(st)$

Where
$C_A(sp)$ = concentration in specimen
$C_A(st)$ = concentration in standard
$I_A(sp)$ = X-ray intensity in specimen
$I_A(st)$ = X-ray intensity in standard
$I_A(sp)/ I_A(st)$ is known as the K ratio

Approach to WDS Analysis

1. Choose appropriate standards for analysis.

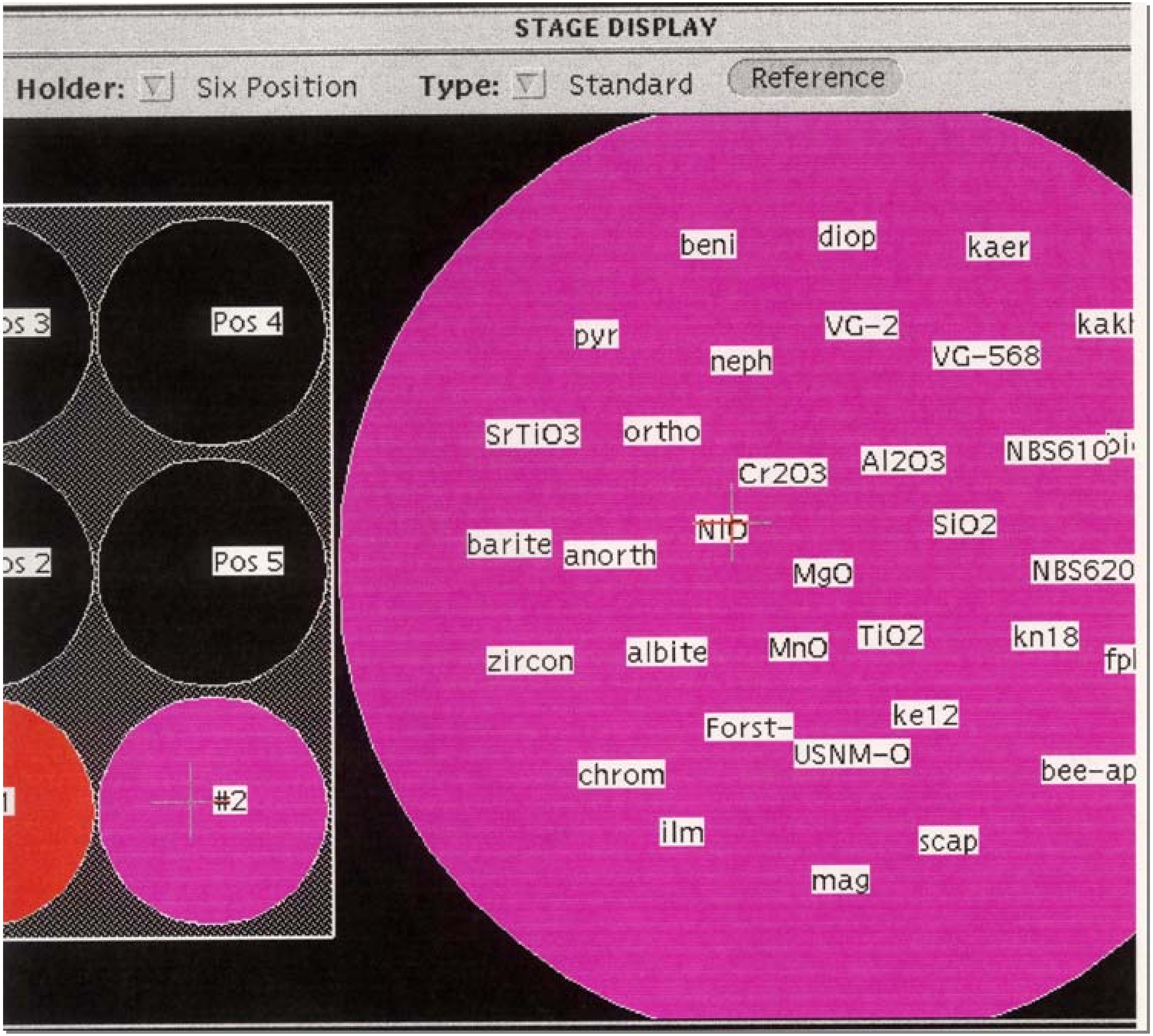
-Good characteristics for standards??

-Pure elements can be unsuitable. High matrix corrections, chemical bonding effects, difficult to polish, oxidation, may not exist in natural form.

-Synthetic compounds can be used. Has the advantage of assured purity. Homogeneity on a very fine scale is desirable.

-Some natural minerals can be well characterized, or compositions can be determined from theoretical formulas and can be used as standards. Must be homogeneous.

-Well-characterized complex phases can be used as reference materials to verify calibration. Kakanui phases.



Holder: Six Position

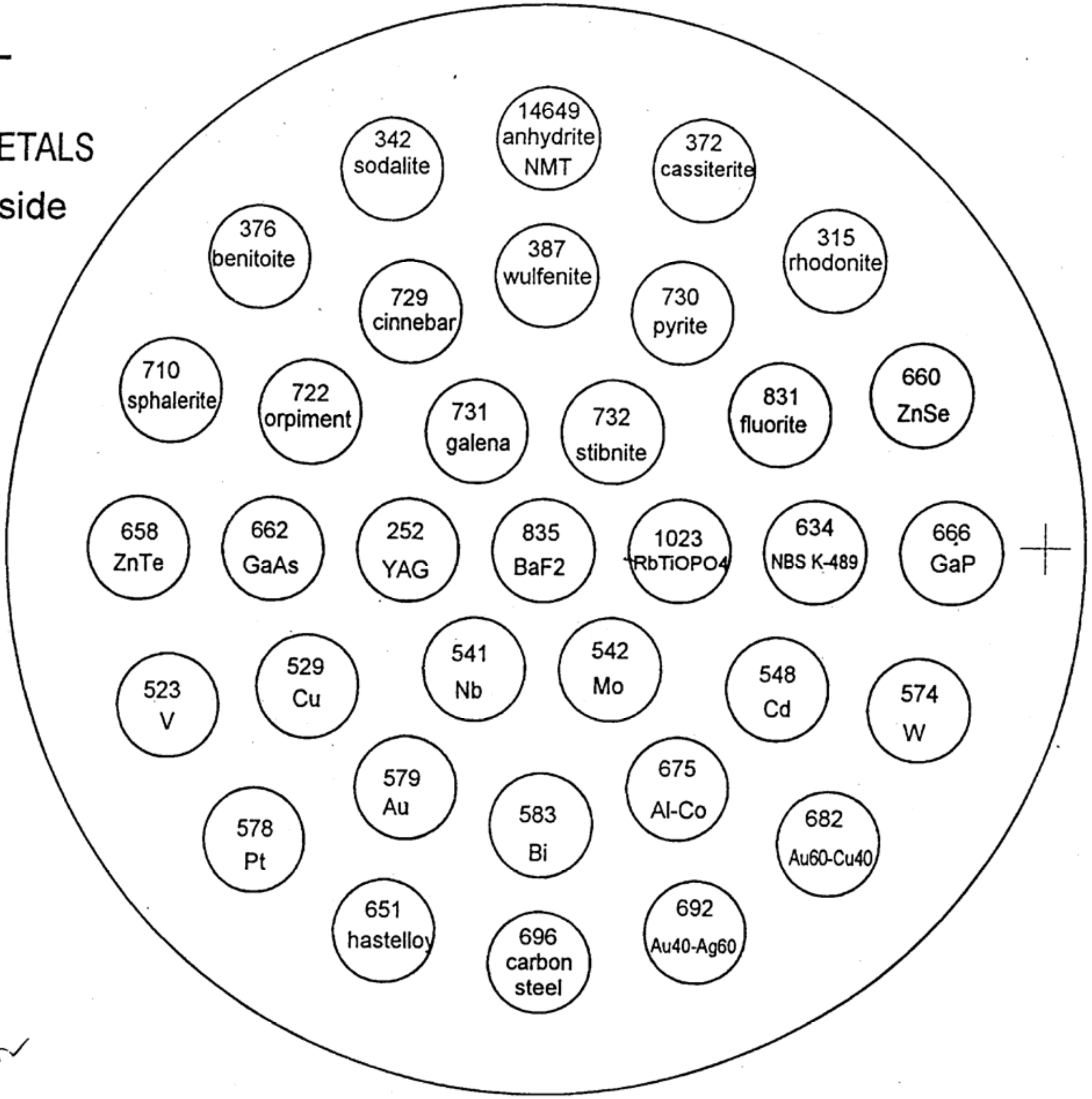
Type: Standard

STAGE DISPLAY
Reference
os 3
Pos 4
os 2
Pos 5
#2
beni
diop
kaer
pyr
VG-2
kak
neph
VG-568
SrTiO3
ortho
NBS610
Cr2O3
Al2O3
NiO
SiO2
barite
anorth
MgO
NBS620
zircon
albite
MnO
TiO2
kn18
fp
ke12
Forst-
USNM-O
chrom
bee-ap
ilm
scap
mag

NMT

ORES & METALS

polished side

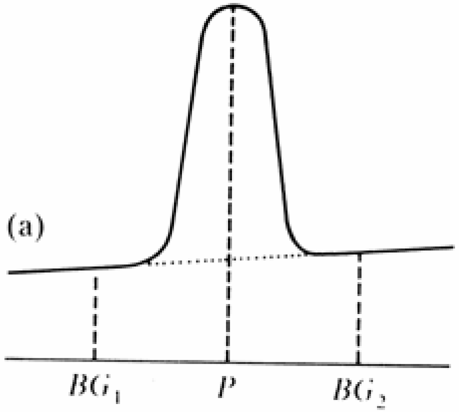

342 sodalite
14649 anhydrite NMT
372 cassiterite
376 benitoite
387 wulfenite
315 rhodonite
729 cinnebar
730 pyrite
710 sphalerite
722 orpiment
731 galena
732 stibnite
831 fluorite
660 ZnSe
658 ZnTe
662 GaAs
252 YAG
835 BaF2
1023 RbTiOPO4
634 NBS K-489
666 GaP
523 V
529 Cu
541 Nb
542 Mo
548 Cd
574 W
579 Au
675 Al-Co
578 Pt
583 Bi
682 Au60-Cu40
651 hastelloy
696 carbon steel
692 Au40-Ag60

See back for compositions

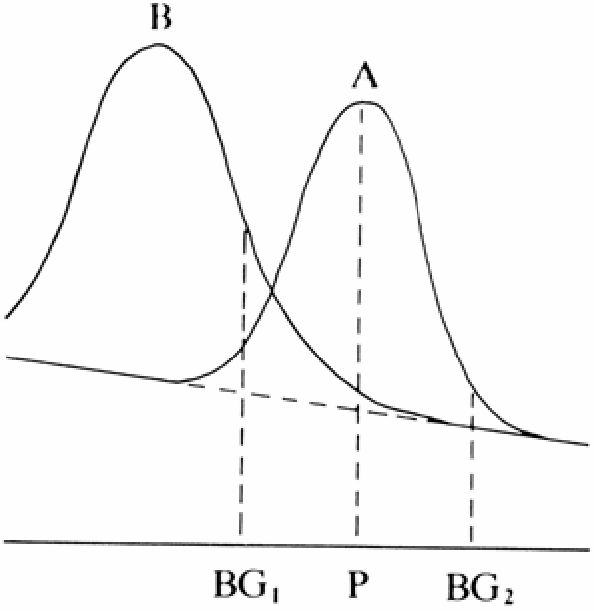
2. Peak search and choose appropriate background values.

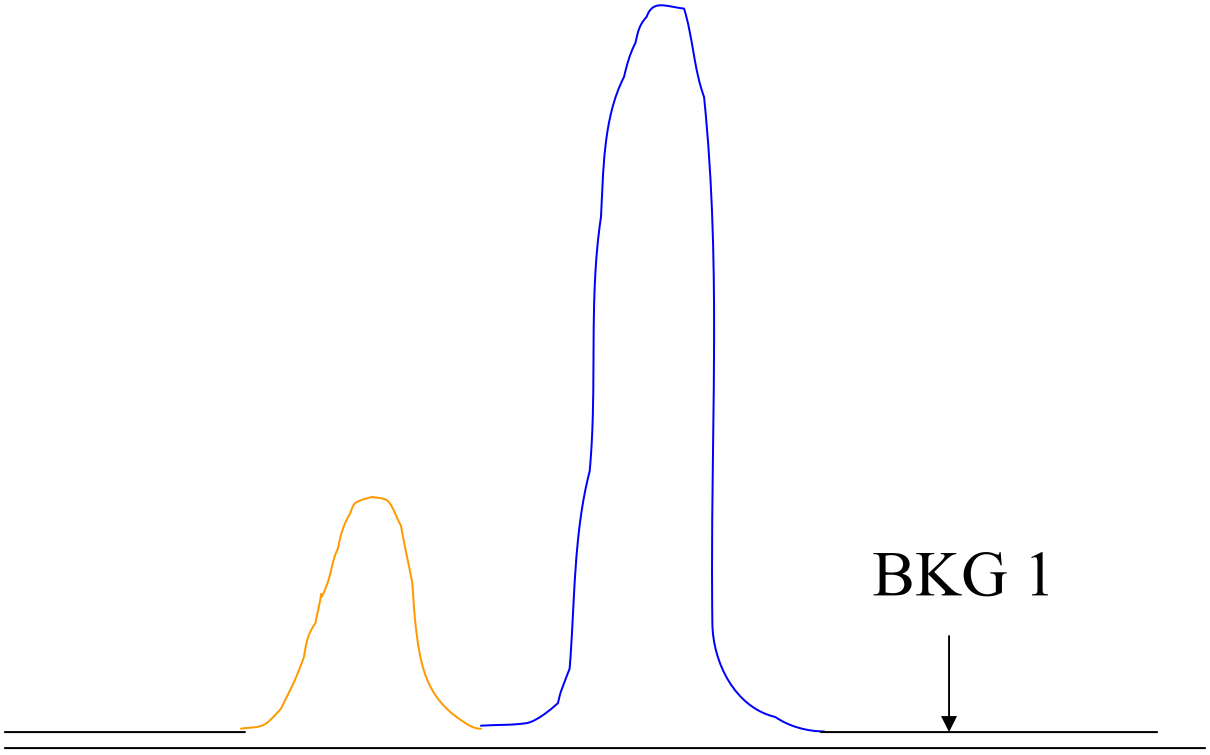
-Measured peak intensities include a contribution from the background. This must be evaluated. Preferable to measure backgrounds on both sides of the peak, but can use one side only to save spectrometer wear.

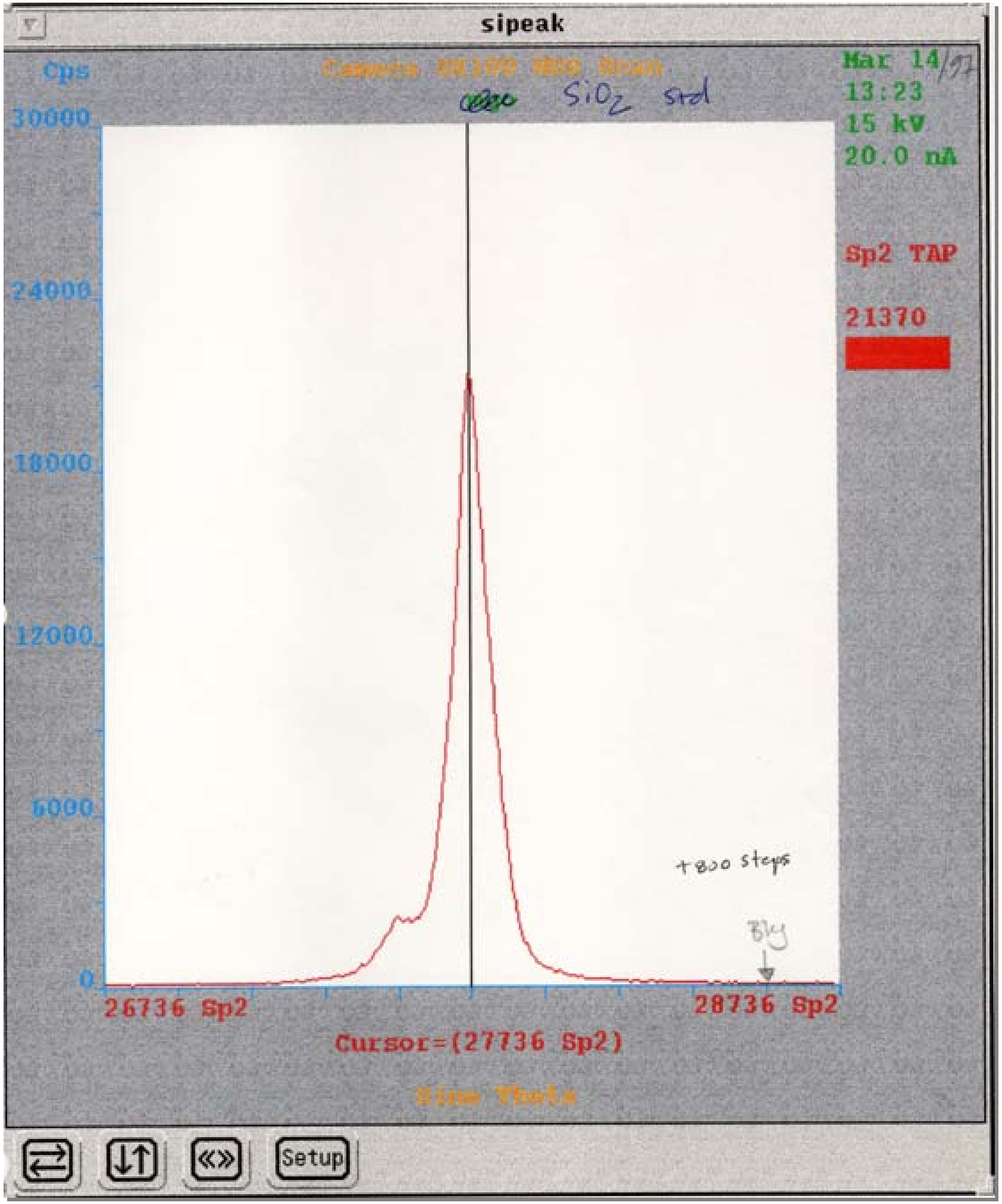
-Problems can arise if standards have different backgrounds than unknowns (ie. Fe interference on F).



Quantitative WD analysis




BKG 1


sipeak
Cps
30000
24000
18000
12000
6000
0
26736 Sp2
28736 Sp2
Setup

Cameca SX100 WDS Scan

SiO_2 std

Mar 14/97
13:23
15 kV
20.0 nA

Sp2 TAP

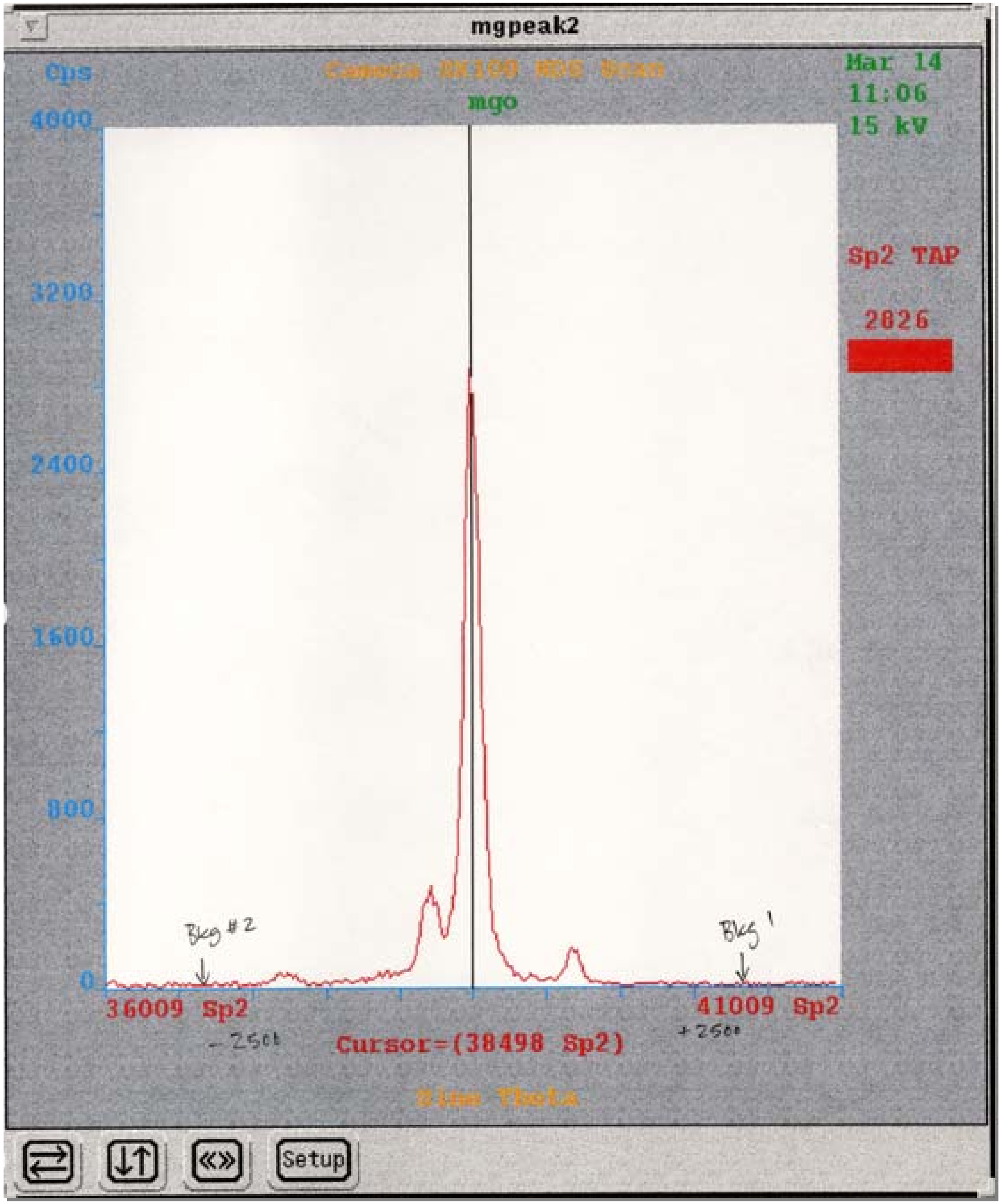
21370

Cursor=(27736 Sp2)

Sine Theta

+800 steps

Bkg

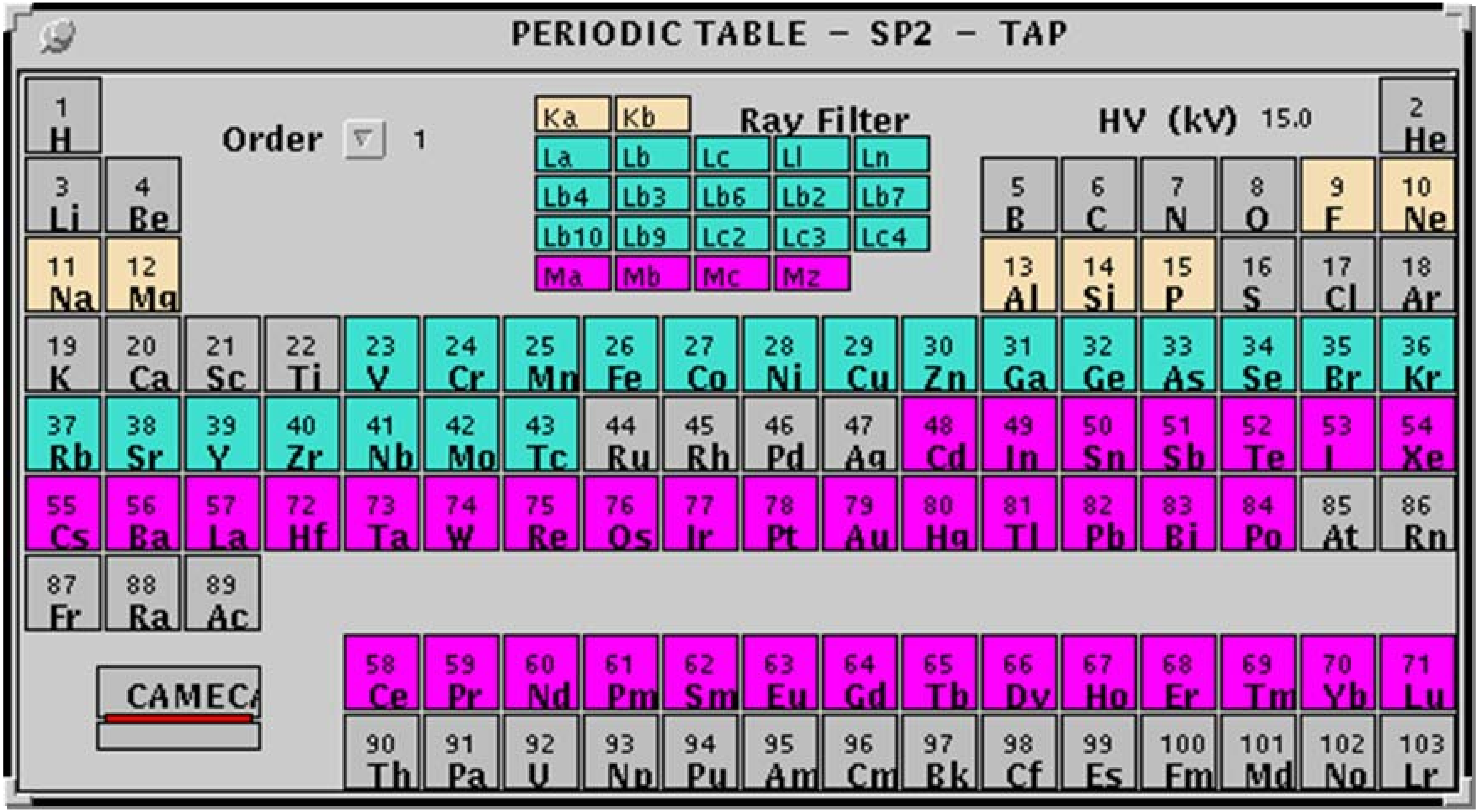

mgpeak2
Cps
Cameca SX100 WDS Scan
mgo
Mar 14
11:06
15 kV
4000
3200
2400
1600
800
0
Sp2 TAP
2826
Bkg #2
Bkg 1
36009 Sp2
41009 Sp2
-2500
+2500
Cursor=(38498 Sp2)
Sine Theta
Setup

3. Choose suitable crystals and order of analysis.

A. Choose suitable crystals for each element

B. Minimize analysis time

C. Organize order of analysis in order to minimize spectrometer wear.



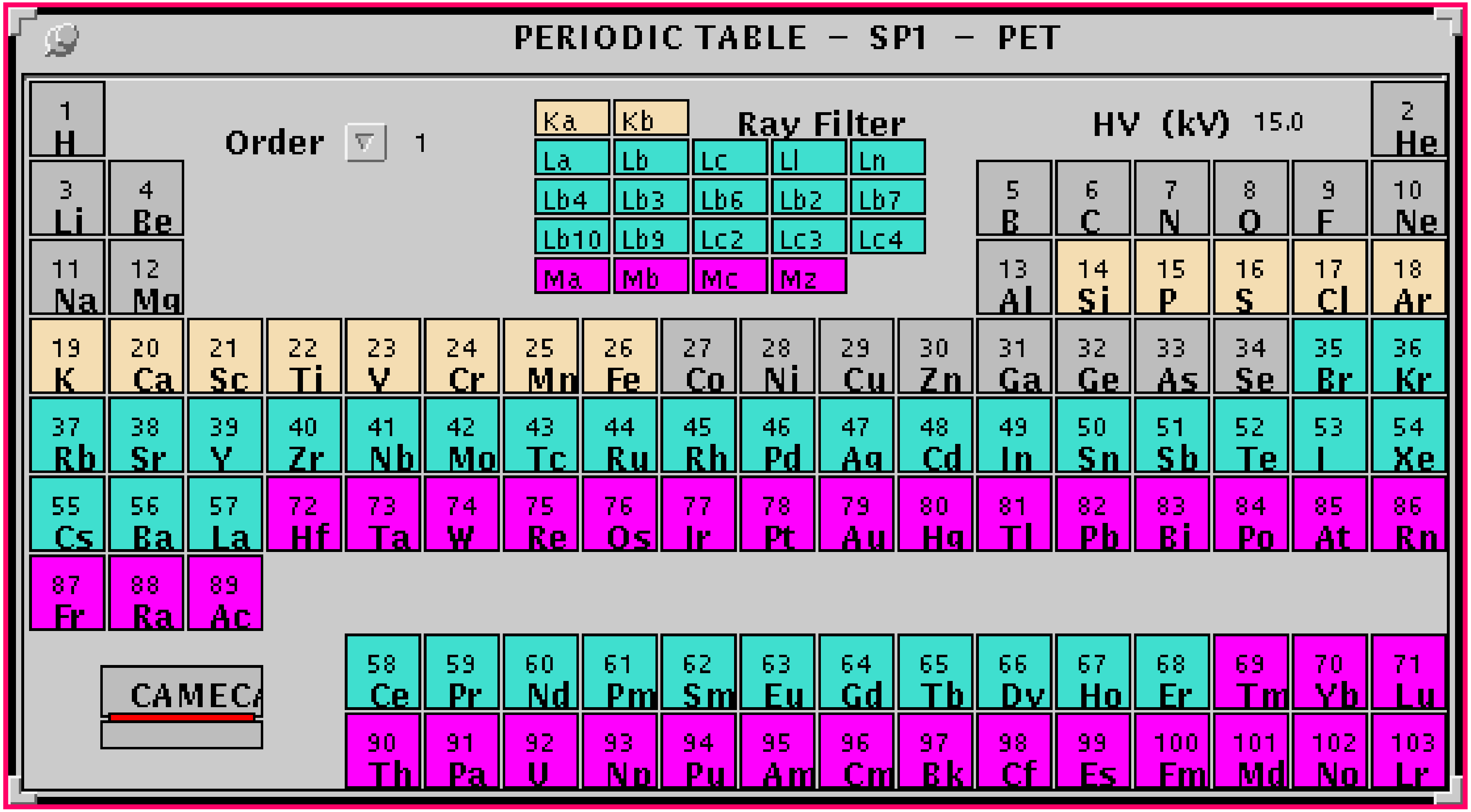
Ray Filter
Ka
Kb
La
Lb
Lc
Ll
Ln
Lb4
Lb3
Lb6
Lb2
Lb7
Lb10
Lb9
Lc2
Lc3
Lc4
Ma
Mb
Mc
Mz
CAMEC

PERIODIC TABLE – SP2 – TAP

Order 1

HV (kV) 15.0

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



PERIODIC TABLE – SP1 – PET

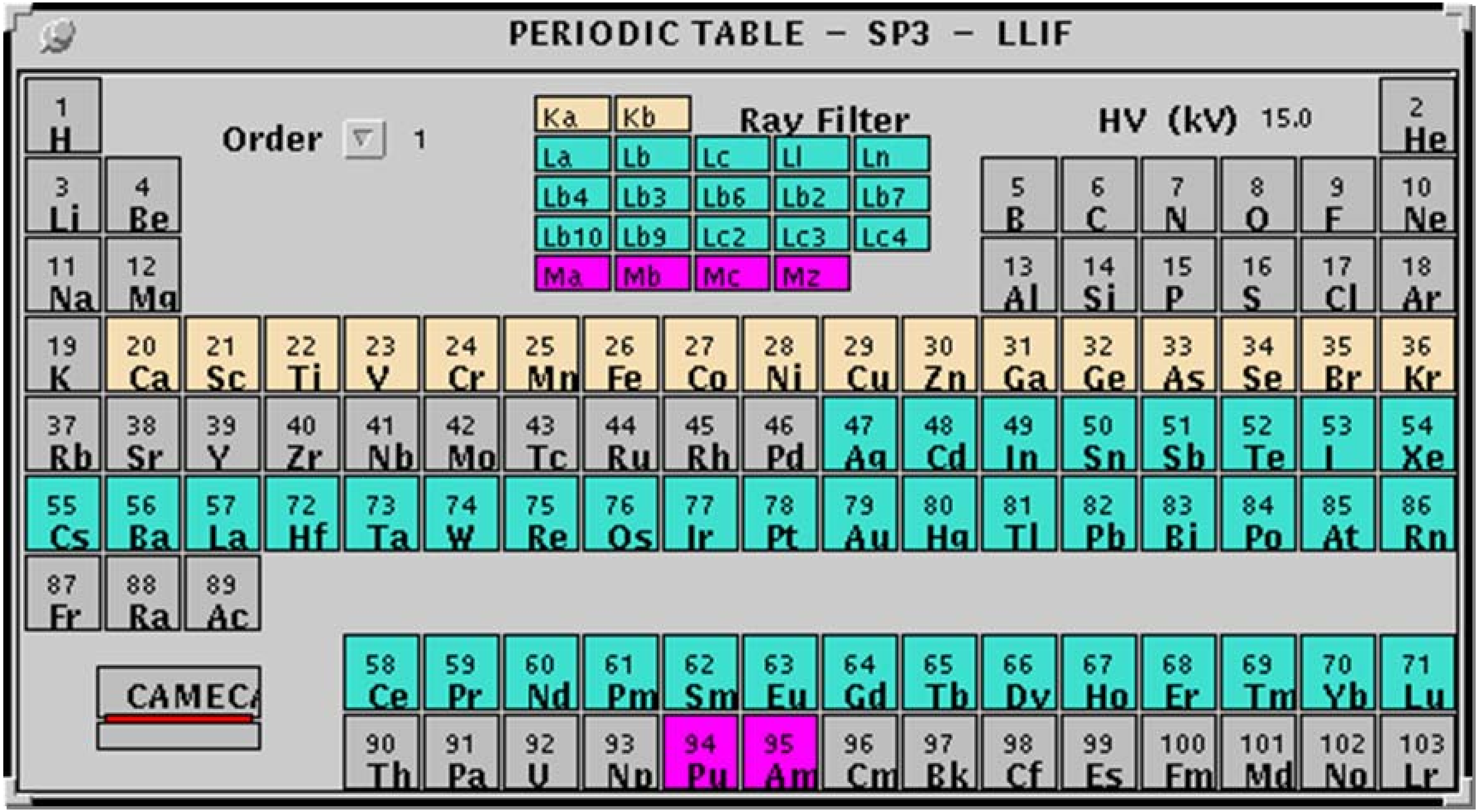
Order ▽ 1

Ray Filter

HV (kV) 15.0

Ka
Kb
La
Lb
Lc
Ll
Ln
Lb4
Lb3
Lb6
Lb2
Lb7
Lb10
Lb9
Lc2
Lc3
Lc4
Ma
Mb
Mc
Mz
CAMECA

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



PERIODIC TABLE – SP3 – LLIF

Order 1

HV (kV) 15.0

Ray Filter
Ka Kb
La Lb Lc Ll Ln
Lb4 Lb3 Lb6 Lb2 Lb7
Lb10 Lb9 Lc2 Lc3 Lc4
Ma Mb Mc Mz
1 H
2 He
3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne
11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
55 Cs 56 Ba 57 La 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
87 Fr 88 Ra 89 Ac
58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr
CAMECA

Matrix corrections:
Bence-Albee Alpha Coefficients

Used to be widely used for electron microprobe quantitative analysis. Has been replaced by other methods.

Empirical correction factors. Are only valid for a given accelerating voltage and X-ray take-off angle.

Matrix Corrections

The matrix of the sample (ie. the chemical makeup of the sample) has a strong effect on the X-rays generated by any element. Must apply matrix corrections to uncorrected concentrations (K ratios) to obtain "true" compositions.

Three main controlling parameters:

Z - atomic number

A - absorption

F - fluorescence

Z corrections

Related to the dependence of the efficiency with which X-rays are excited on the mean atomic number of the sample.

Two distinct phenomona:

1. Electron penetration
2. Backscattering

1. Electron penetration.

Proportionately more electrons produce X-rays when interacting with a sample of higher atomic number. So, if Z of a sample is higher than Z of a standard, the uncorrected concentration of the unknown must be corrected downwards.

2. Backscattering.

High-Z material produced more BSE than low Z material. So, a higher Z material will have less X-rays produced than a low Z material. This offsets, and normally outweighs, the electron penetration effect.

Incident electrons lose energy by interacting with bound electrons within the sample

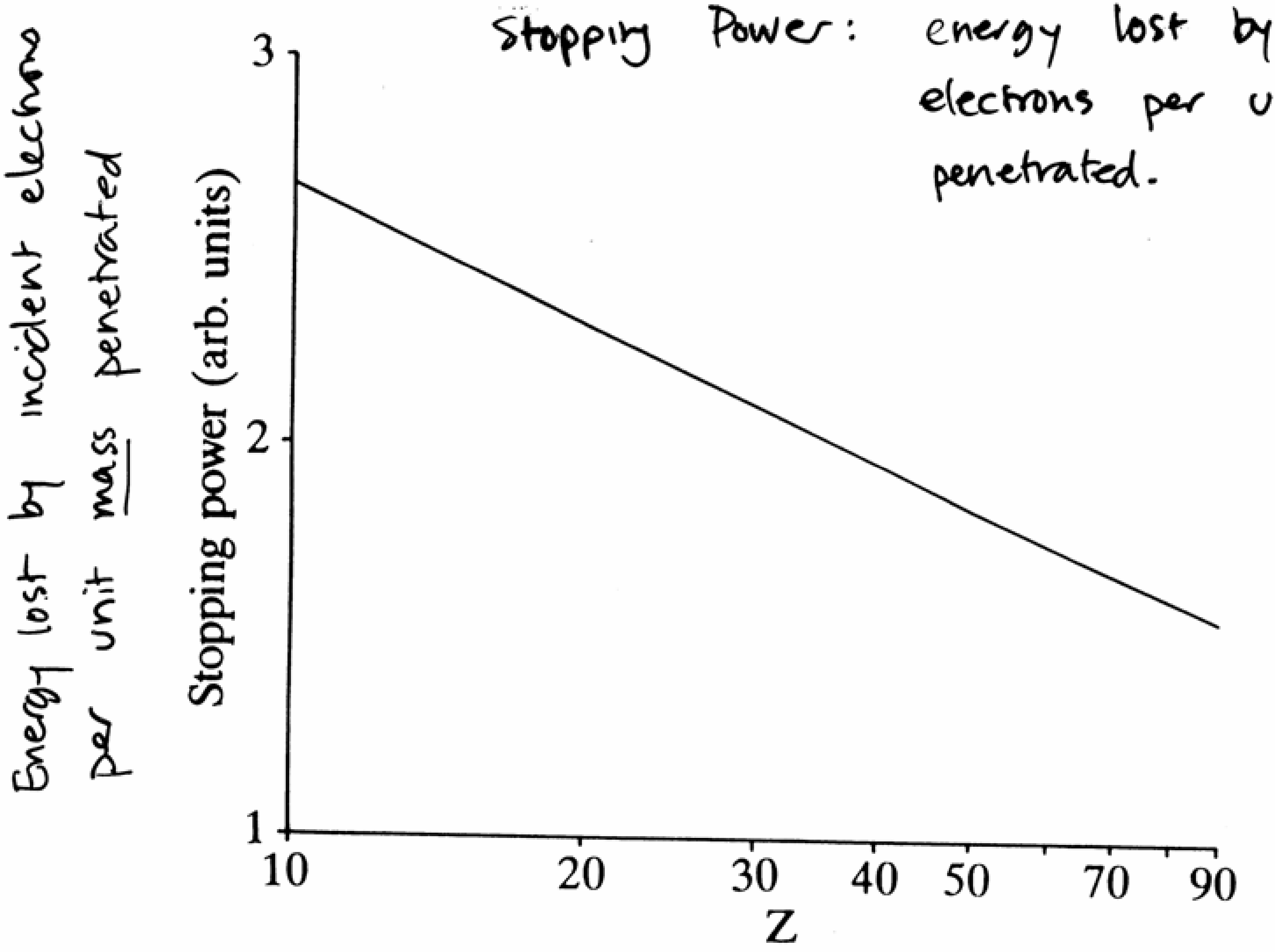
# of electrons per atom = Z
Atomic mass per electron = A/Z

A/Z increases with increasing Z

So:
Mass penetrated by incident electrons increases with increasing Z

------>>> X-rays intensities increase with increasing Z

Stopping Power: energy lost by incident electrons per unit mass penetrated.

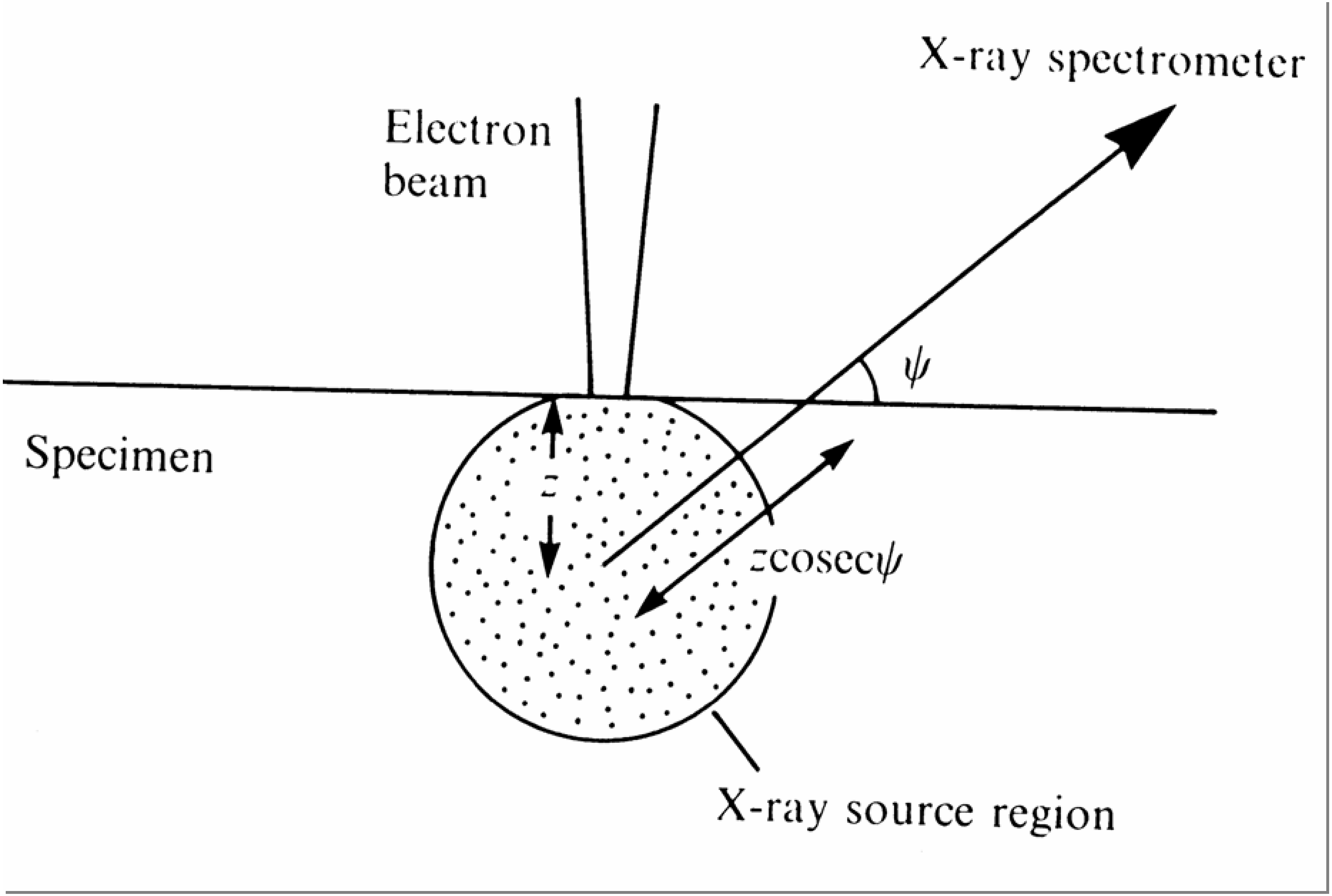


Absorption corrections

X-rays must travel through some amount of sample before exiting the sample surface. X-rays can be absorbed by the sample during this travel.

$$\chi = \mu \operatorname{cosec} \psi$$

χ = absorption parameter (khi)
μ = mass absorption coefficient (mu)
ψ = takeoff angle (psi)


X-ray spectrometer
Electron beam
ψ
Specimen
z
zcosecψ
X-ray source region

X-rays produced at depth Z

Absorption parameter
μ cosec ψ

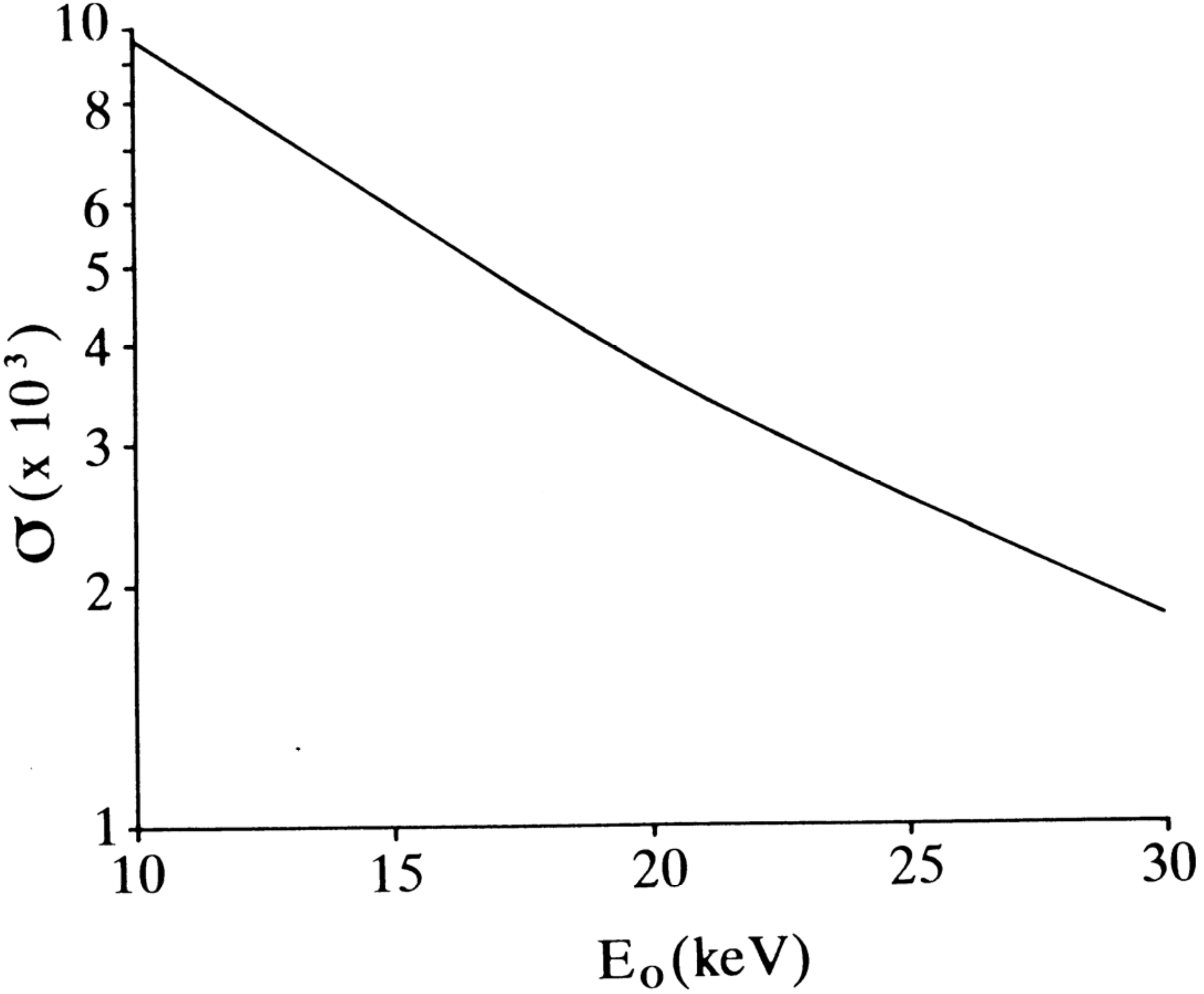
$$\text{Intensity} = I_o^{(-\chi\rho Z)}$$

ρ = density (rho)
Z = depth

Depth-distribution production of X-rays must be knows.
Approximated by:

$$\text{Intensity} = I_o^{(-\sigma\rho Z)}$$

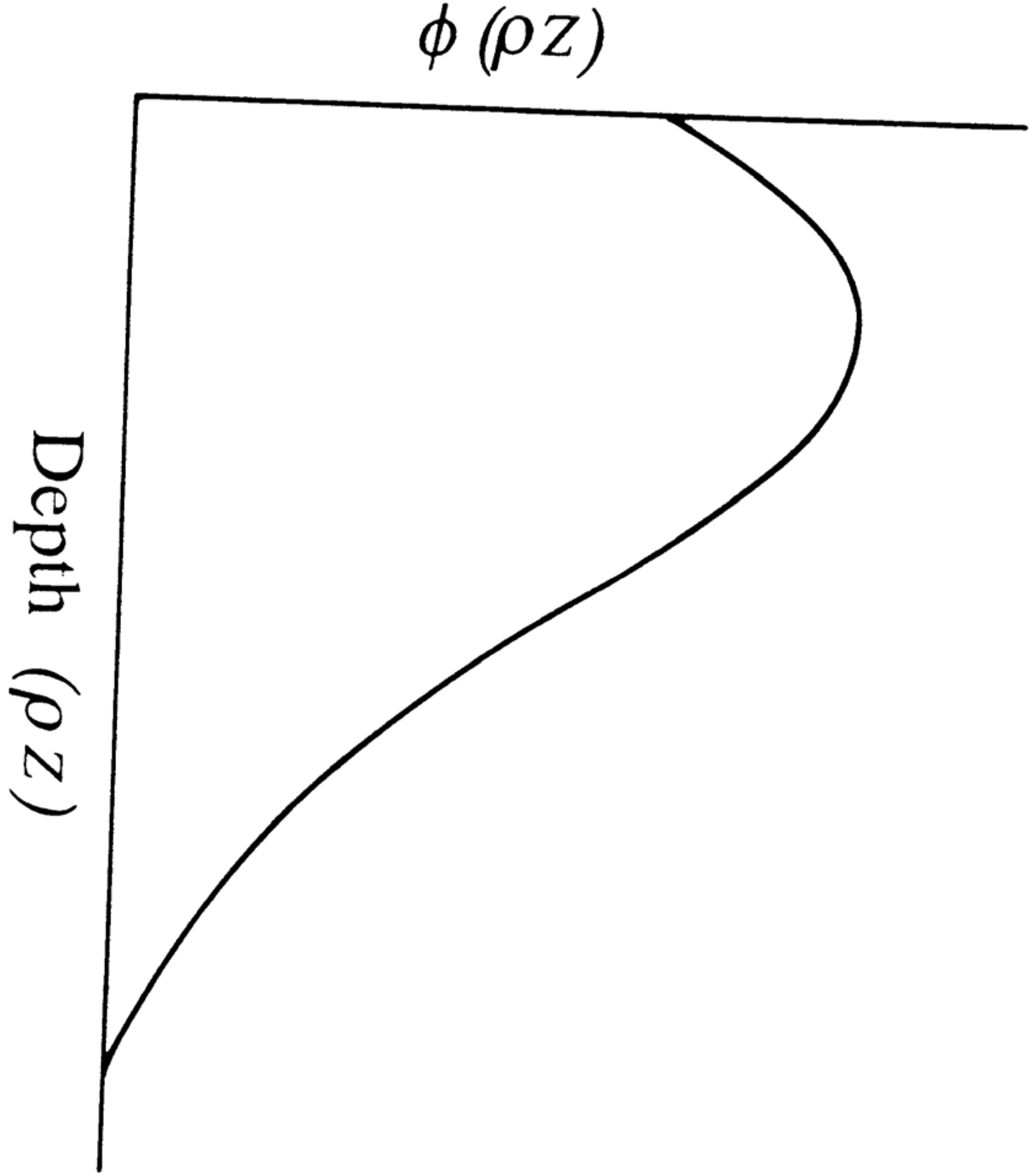
Where σ is the absorption parameter


10
8
6
5
4
3
2
1
σ (x 10³)
10
15
20
25
30
E₀(keV)

More sophisticated methods to calculate absorption are derived from expressions which better represent the depth distribution of X-ray production.

Termed Phi-Rho-Z $\varphi(\rho Z)$

Depth-distribution function that is defined as the X-ray intensity generated by a thin layer at depth z relative to an isolated layer of the same thickness.

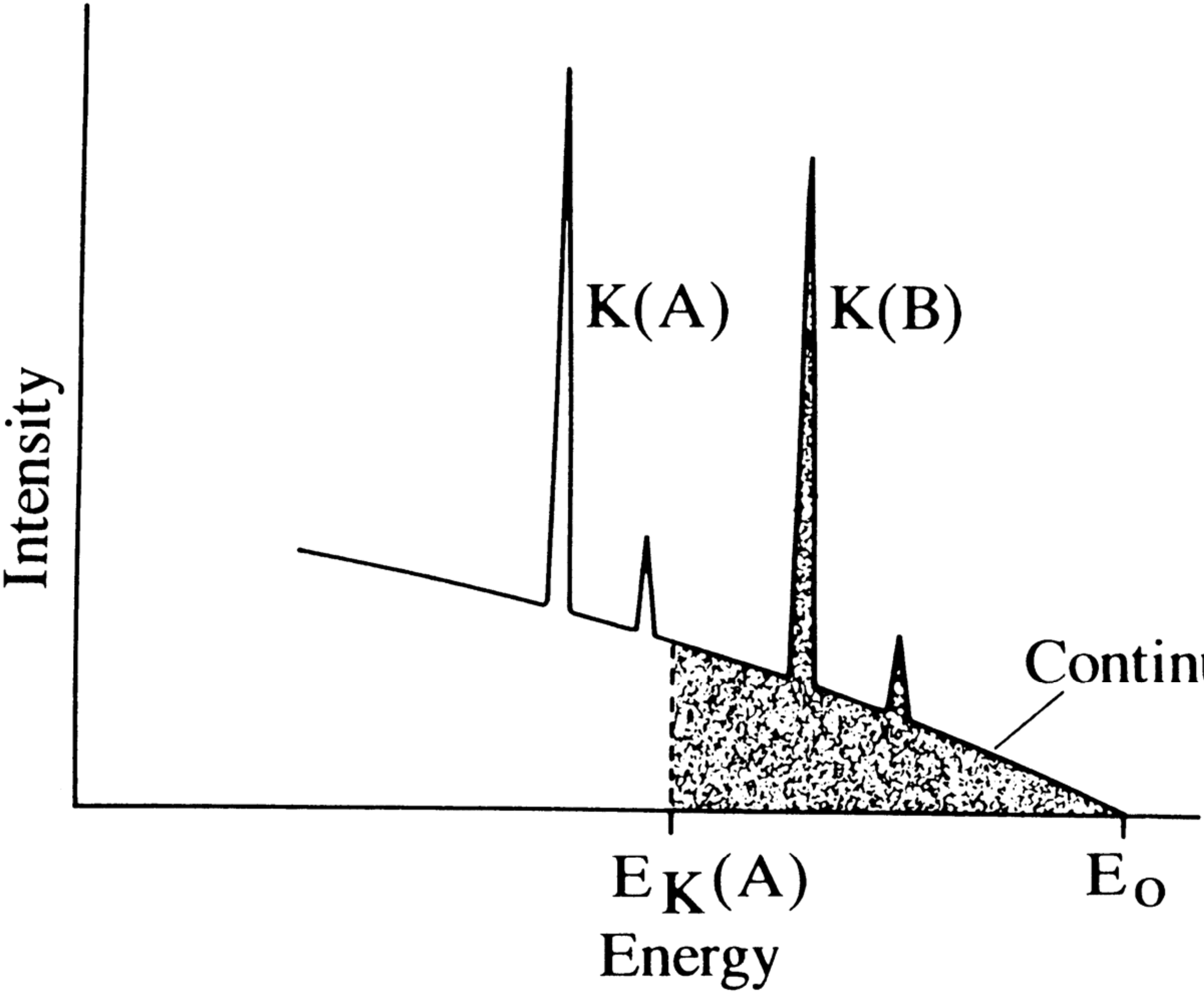

$\phi(\rho z)$
Depth (ρz)

Fluorescence corrections

Characteristic X-rays of a given element can be excited by other X-rays when the energy of the latter exceeds the critical excitation energy of the former. Can be caused either by continuous or by characteristic X-rays.

For example, Ni Kalpha X-rays (7.48 keV) can excite Fe (critical excitation energy 7.11 keV). But, Fe Kalpha X-rays (6.4 keV) cannot excite Ni (critical excitation energy 8.33 keV).

Correction factors can be calculated. In geological samples, this correction is relatively small. The effect decreases with decreasing atomic number. More important in metallurgical samples.


Intensity
K(A)
K(B)
Continuum
$E_K(A)$
E_o
Energy

Correction calculations are iterative. A composition must first be assumed. Then, correction factors are calculated from that assumed composition, and a new composition is determined. Typically, three to six iterations are made. This requires **COMPUTERS!**

Unanalyzed Components

Our electron probe cannot analyze H, He, Li, Be, B, C, N, and O.

This is an issue when the unknown sample contains one or more of these elements. For example, silicate rock samples all contain a large amount of O. Some also contain H_2O. Carbonate rock samples contain C and O.

Unanalyzed components can be treated in 2 ways:

-Difference.
Assuming that the difference between the electron microprobe total and 100% is due to the unanalyzed component (s).

-Stoichiometry.
Appropriate amount of the unanalyzed component is allocated to the analyzed elements in the sample. For instance, O in a silicate rock.
Si -> SiO_2
Ti -> TiO_2
Al -> Al_2O_3
etc...

Some minerals, such as clays, contain H_2O in addition to H, and the recalculation is more difficult.

CAMECA software handles a large number of geological recalculations.

Choice of conditions for Quantitative Analysis

-Electron acceleration

Must be higher than the excitation potential of elements to be analyzed. Preferably twice this value.

Advantages of higher kV
Better analytical statistics and precision
Better peak/background, leading to better detection limits

Disadvantages of higher kV
Decreased spatial resolution
Increased absorbtion corrections

For geological samples, typically use 15 kV. Can use lower kV for light element analysis

-Beam current

High beam current yields higher X-ray intensities. But... can lead to sample damage.

For geological samples, typically use 20 nA. For glasses, use 10 or 15 nA.

Special Cases

A. Tilted samples

If necessary, corrections can be made for analysis to tilted samples. Tilt angle must be precisely known.

B. Broad-beam analysis

Can broaden beam to determine average compositions. However, area must be <100 microns in order to not run into spectrometer defocalization. However, ZAF corrections are not accurate for a combination of phases. However, this technique can be useful for rapid, semiquantitative analysis.

C. Whole rock analysis

Fuse samples into a glass. Should not compete with conventional bulk rock analysis techniques, but can sometimes be useful.

D. Particle analysis

Small particles mounted on carbon backing can be analysed. Net X-ray intensities can be reduced relative to a flat standard, but calibrations may be done using X-ray ratios. Also, modified ZAF corrections can be made to reflect particle geometry.

E. Thin sample analysis

Spatial resolution can be increase by preparation of a very thin (100 nm) sample wafer. If sample is sufficiently thin, ZAF corrections can be neglected.

F. Fluid inclusions

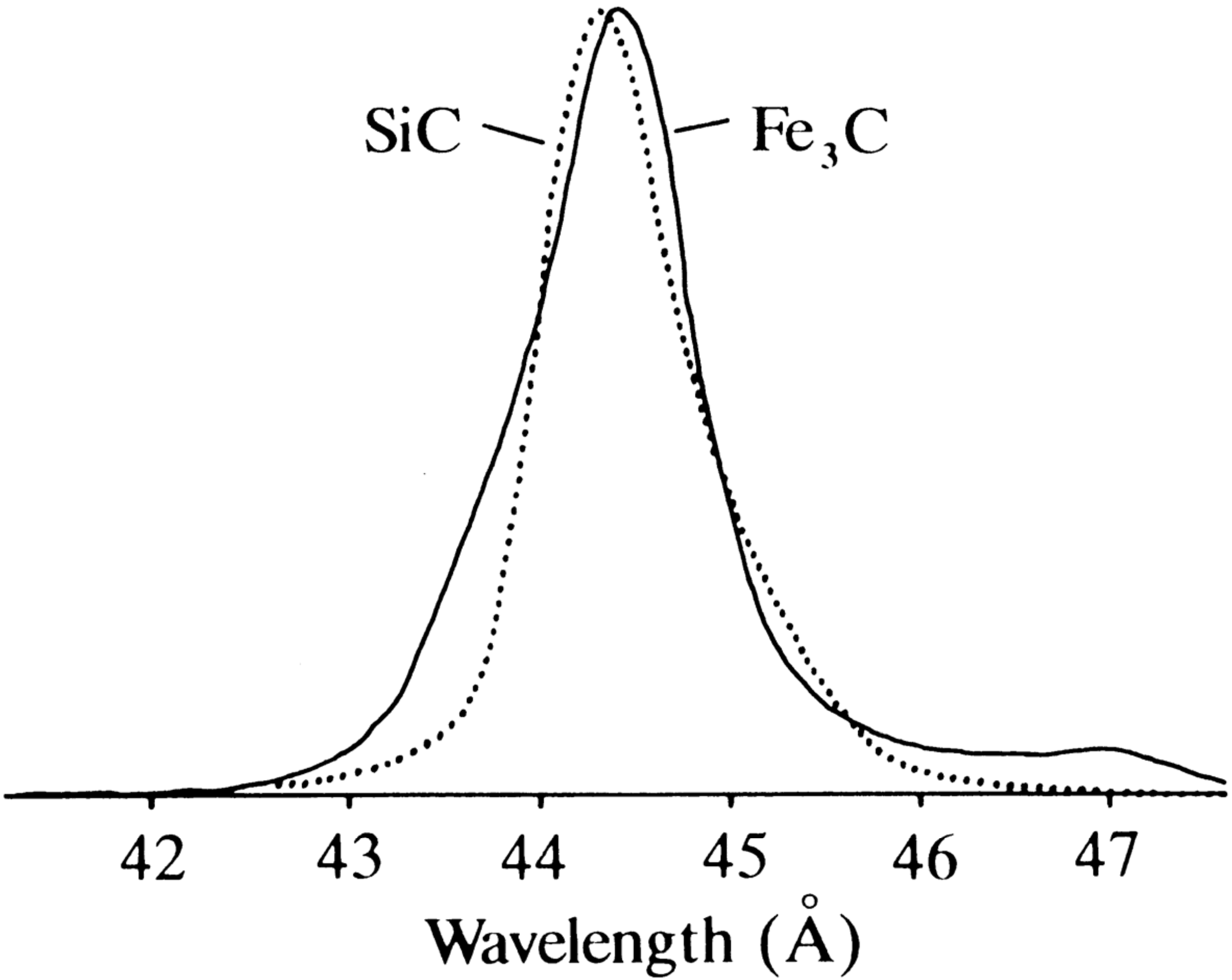
Frozen fluid inclusions can be analyzed using a cryo-stage. Must prepare frozen standards. Must use very low beam currents (1 nA).

G. Valence determinations

Peak shifts can be observed for some elements related to valence of the element.

Fe+2/Fe+3 using L peaks

S-2/S6+ ratio in glasses by 0.003 angstrom shift in S K alpha peak.


SiC
Fe_3C
42
43
44
45
46
47
Wavelength (Å)