Improved EPMA Trace Element Accuracy Using A Matrix Iterated Quantitative Blank Correction

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Problems with measuring background...

- Extended peak tails
  - e.g., crystal resolution, polygonization

- Detector artifacts
  - e.g., Ar or Xe absorption edges

- Sample artifacts
  - e.g., sample matrix absorption edges

- Analyzing crystal artifacts
  - "negative peaks" or "holes"
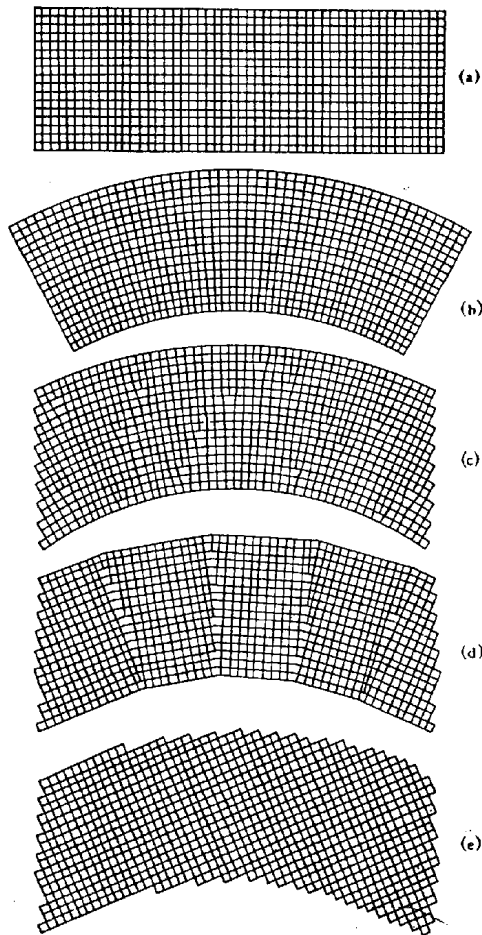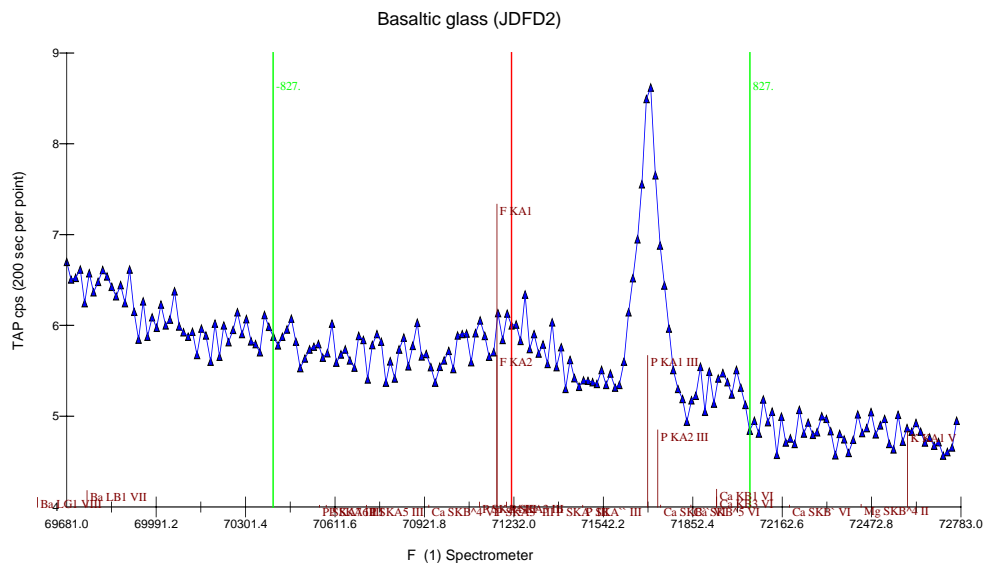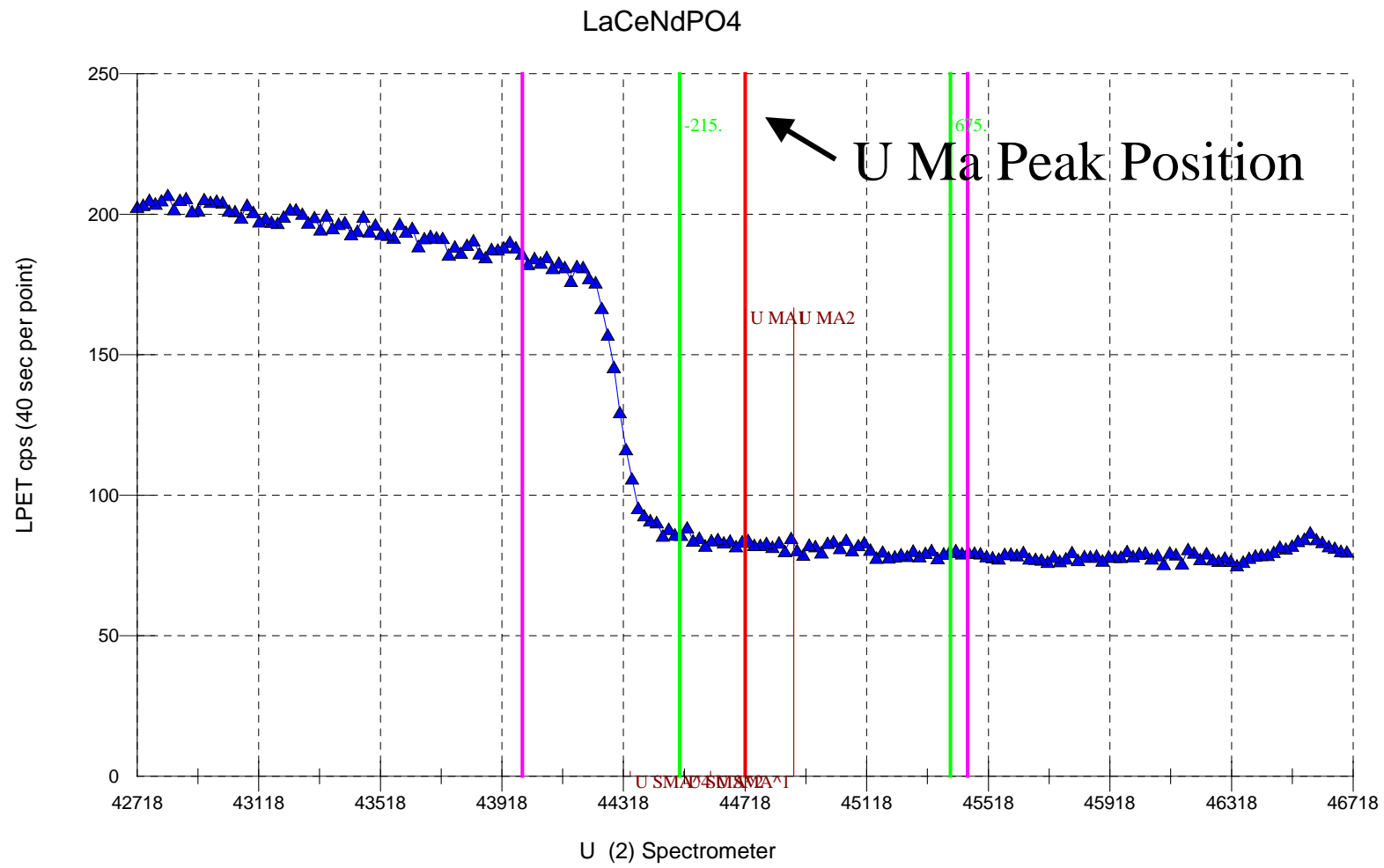
Extended Tails

Polygonization

FIG. 1.27. Five states of a single crystal. (a) Unstrained. (b) Elastically bent. (c) Plastically bent. (d) Polygonized. (e) Recrystallized.
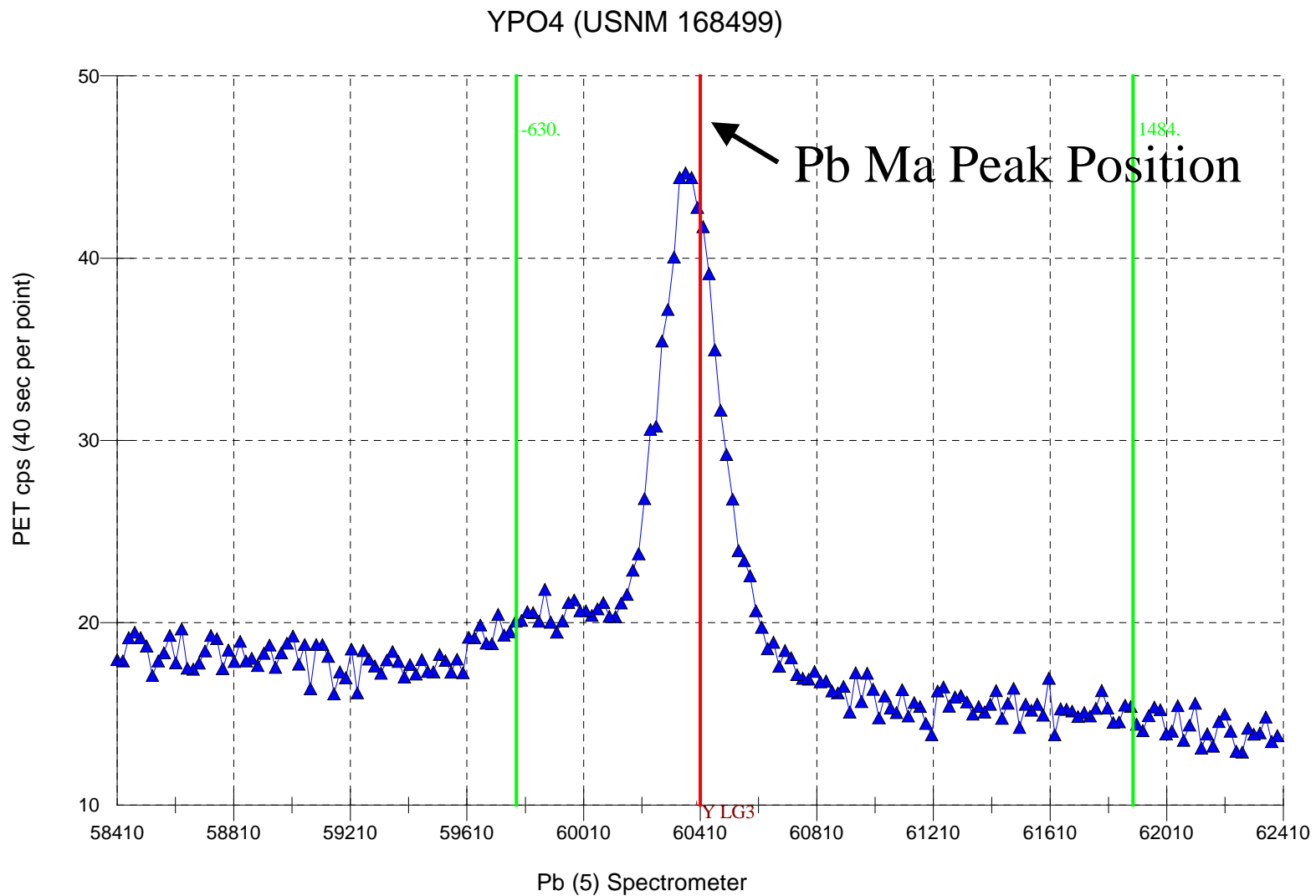
Nabarrro, F.R.N. (1967) <u>Theory of Crystal Dislocations</u>, Oxford, 821 pp.

E.g., Ir-Si system

Basaltic glass (JDFD2)

Detector Absorption Edges...

LaCeNdPO4

And Interferences...

YPO4 (USNM 168499)
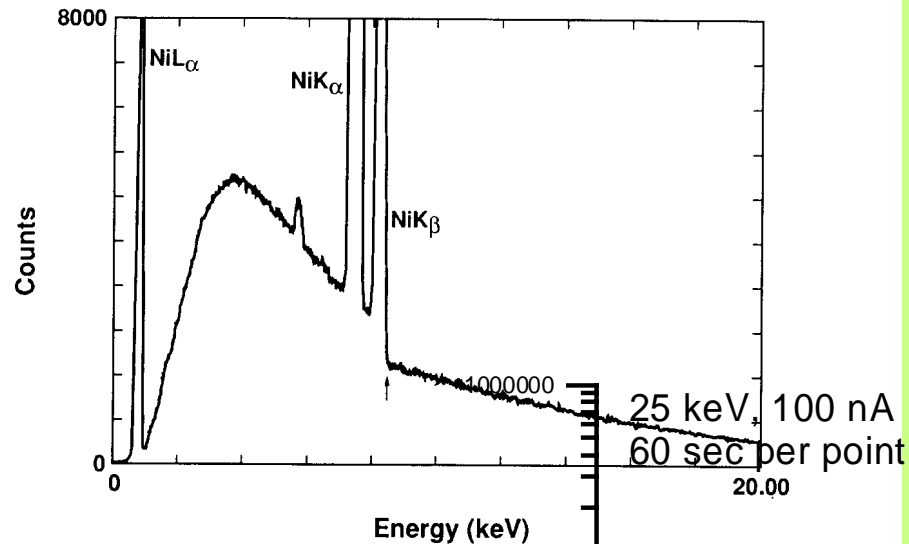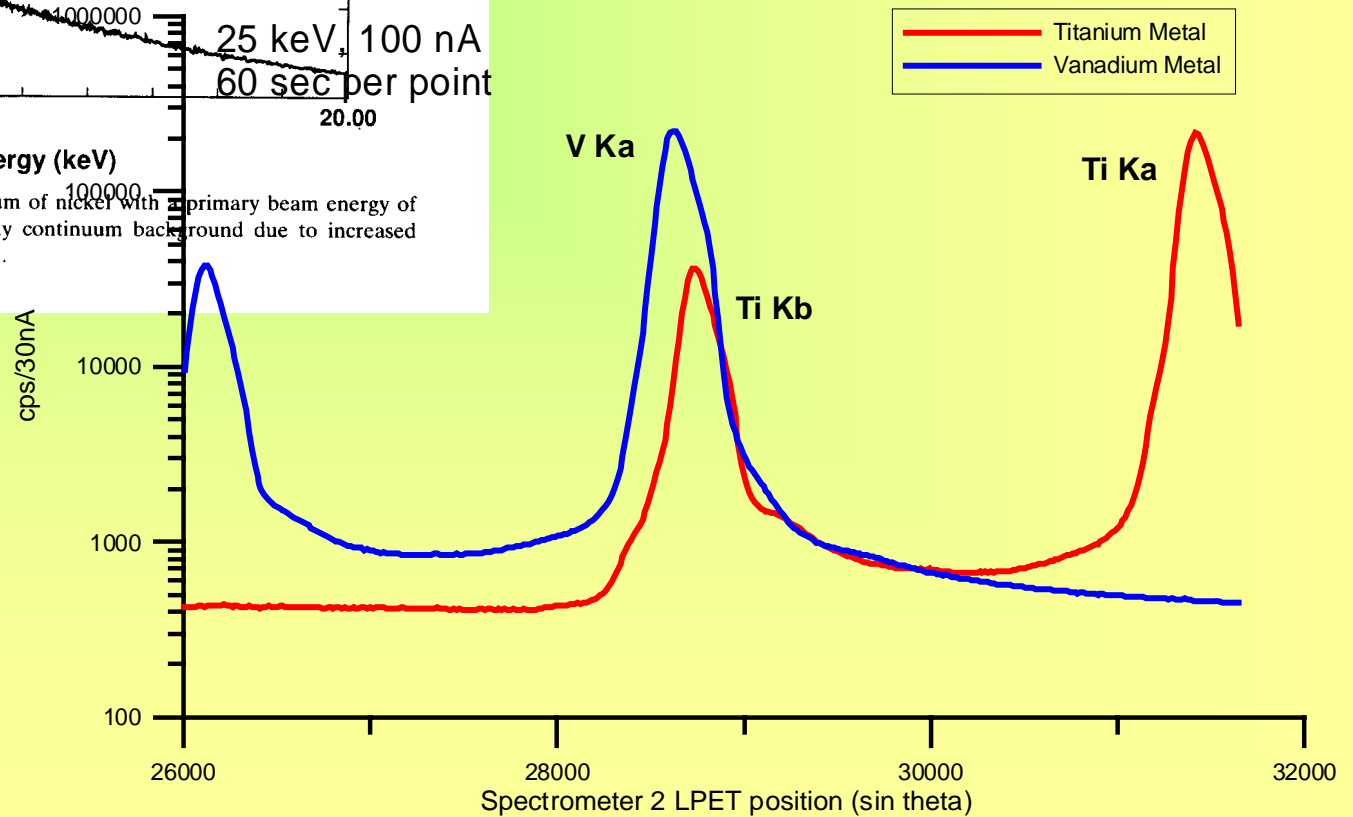
Sample Absorption Edges

Figure 3.47. Energy-dispersive x-ray spectrum of nickel with a primary beam energy of $E_0 = 40$ keV showing a sharp step in the x-ray continuum background due to increased absorption just above the Ni K absorption edge.

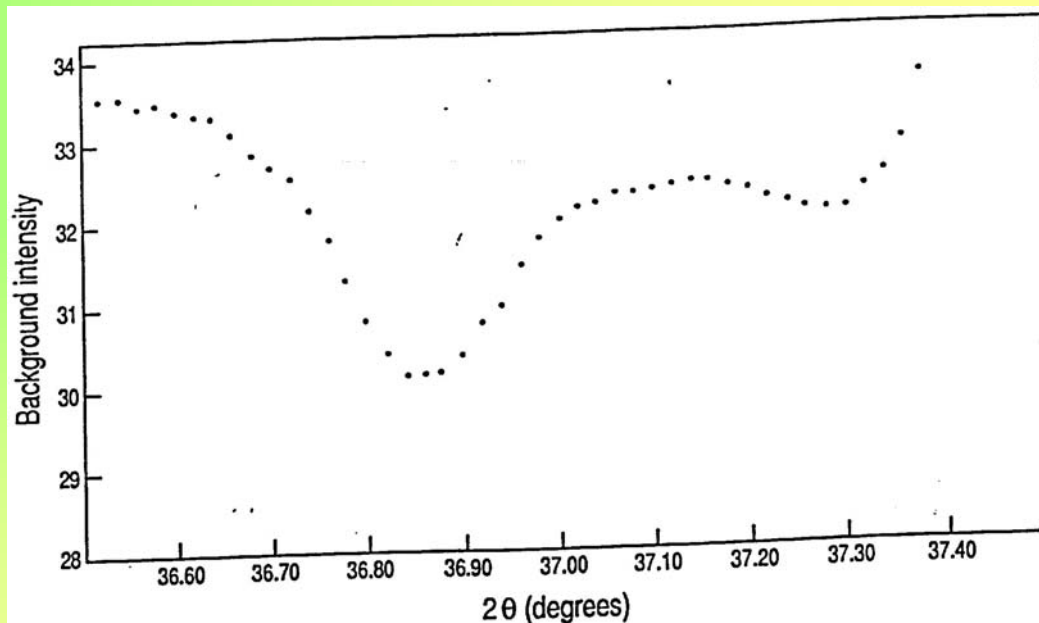25 keV, 100 nA
60 sec per point

"Holes" or "negative peaks"...

Figure 1. Intensity trace showing a distinct negative line at a two-theta value of around 36.8°. This angle is just below that for AuLα radiation.

Secondary diffraction...

If an x-ray beam makes an angle θ_1 with the (200) surface of LiF, then the diffracted wavelength will be

$$\lambda_1 = 2\, d(200)\, \sin\theta_1.$$

However, the x-ray beam will also be at an angle θ_2 with the (hkl) planes as shown in Fig. 2a. The (hkl) planes will therefore be diffracting radiation with a wavelength of

$$\lambda_2 = 2\, d(hkl)\, \sin\theta_2$$

where d(hkl) is the interplanar spacing of the (hkl) atomic planes. The (200) and (hkl) planes will diffract radiation of the same wavelength when $\lambda_1 = \lambda_2$, that is when

$$2\, d(200)\, \sin\theta_1 = 2\, d(hkl)\, \sin\theta_2. \tag{1}$$

In this situation, diffraction by the (hkl) planes will cause a reduction in the intensity of the primary beam which in turn will cause a reduction in the intensity diffracted by the (200) planes. Hence, when equation (1) is satisfied (for any hkl value), there will be a negative peak in the x-ray background.

As the diffraction from the analysing crystal can occur throughout 3-dimensional space, there are no general solutions for equation (1). However, for the specific geometry defined by the LiF <200> surfaces with respect to the primary beam, equation (1) is satisfied when

$$\tan\theta_1 = 2l\,/\,(h^2 + k^2 + l^2 - 2h). \tag{2}$$

The most obvious example of this situation is for the (002) planes where $\theta_1 = 45°$ as shown in Fig. 2b.

Many other combinations are possible and a list of two-theta angles at which excitation of accidental reflections will occur at the same wavelength as that diffracted by the LiF(200) planes is given in Table 1.

The size of the background hole will depend on (among other things) the number (i.e. multiplicity) and strength of the accidentally excited reflections. From Table 1 it can be seen that at a two-theta angle of 36.870° there are 6 low-order reflections excited which will cause appreciable diffraction of the primary beam. This gives rise to the anomaly in the background near the AuLα line (Fig. 1). At 90°, where the (002) and (202) reflections are excited, there are is a strong negative line observed in the background (Fig. 3).

Table 1 lists a large number of angles at which the depleted background effect should be seen. In an x-ray spectrometer the collimation of the primary beam by the Soller slits is in one plane only. That plane is normal to the surface of the analysing crystal and parallel to the plane of the two-theta traverse. Hence, sharp diffraction will only occur for the (h0l) planes. Where the accidentally diffracted reflection has a component out of this plane, that is (hkl) planes, the diffraction peak will be broad and unobservable because of the poor collimation of the primary beam. Furthermore, the reduction in background will be significant only where the accidentally excited reflections are strong, that is when the indices are small and even. In Table 1 the two-theta reflections at which (h0l) reflections are excited have been marked with an asterisk. Experimentally the holes were only observed at 2θ equals 36.87, 53.13 and 90.0°.

These observations suggest a method of overcoming the problem of background holes in WD spectrometry. If the edges of the analysing crystal are cut along surfaces that do not correspond to low-order crystallographic planes then the effect will not be seen. Indeed, a small rotation (approx. 5°) of an LiF(200) analysing crystal around an axis normal to its surface considerably reduces the depth of the background hole. The rotation also shifts the position of the negative line to a slightly lower two-theta value because of the change in diffraction geometry.
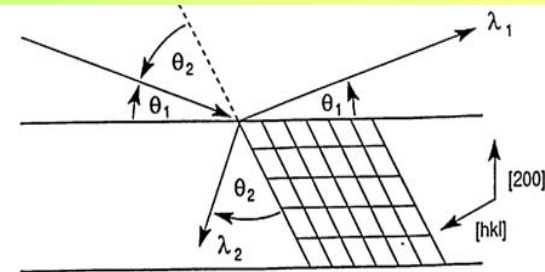
(a)
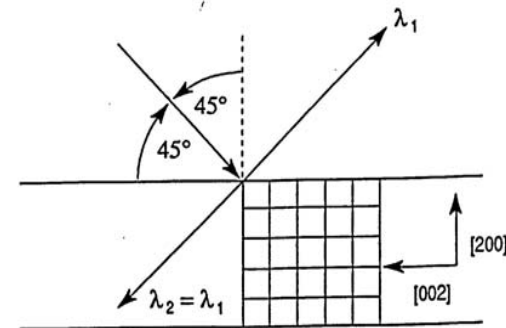
(b)

Figure 2. Geometry for the excitation of accidental diffraction reflections for a wavelength dispersive spectrometer using an LiF(200) crystal. (a) The general geometry. (b) The geometry for the accidental excitation of the (002) reflection.

The Problem...

Self, P.G., Norrish, K., Milnes, A.R., Graham, J. & Robinson, B.W. (1990): Holes in the background in XRS. *X-ray Spectrom.* 19 (2), 59-61

Reed, S.J.B. (1993) Electron Microprobe Analysis (2nd ed.). Cambridge University Press, Cambridge, UK. 326p.

B.W. Robinson, N.G. Ware and D.G.W. Smith, 1998. "Modern Electron-Microprobe Trace-Element Analysis in Mineralogy". In Cabri, L.J. and Vaughan, D.J., Eds. "Modern Approaches to Ore and Environmental Mineralogy", Short Course 27. Mineralogical Association of Canada, Ottawa 153-180

Remond, G., Myklebust, R. Fialin, M. Nockolds, C. Phillips, M. Roques-Carmes, C. "Decomposition of Wavelength Dispersive X-ray Spectra", Journal of Research of the National Institute of Standards and Technology (J. Res. Natl. Inst. Stand. Technol., v. 107, 509-529 (2002)
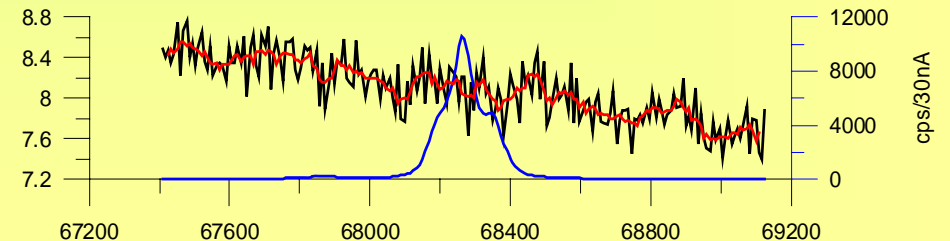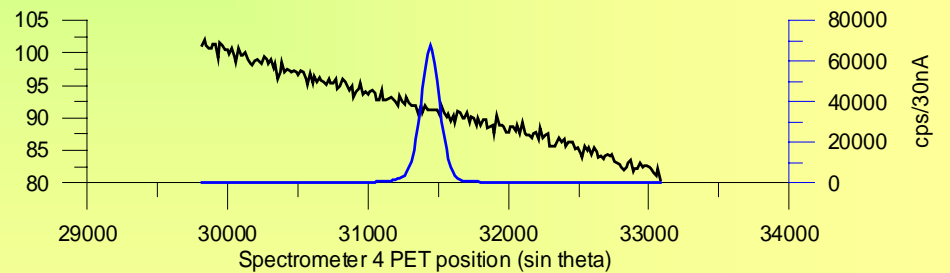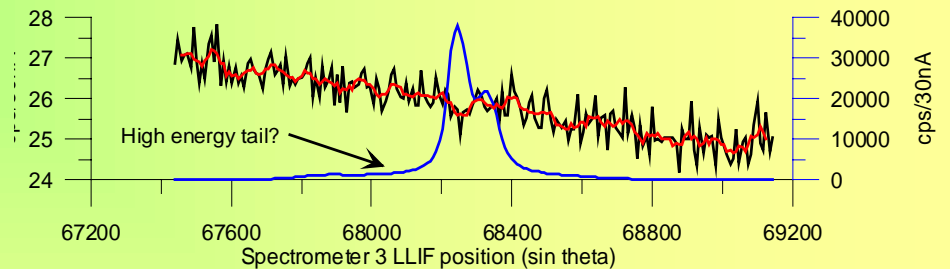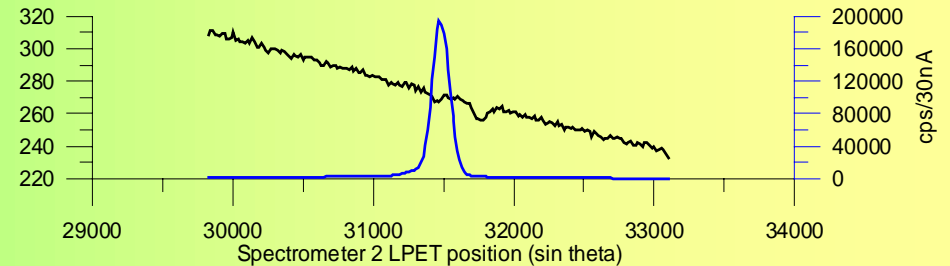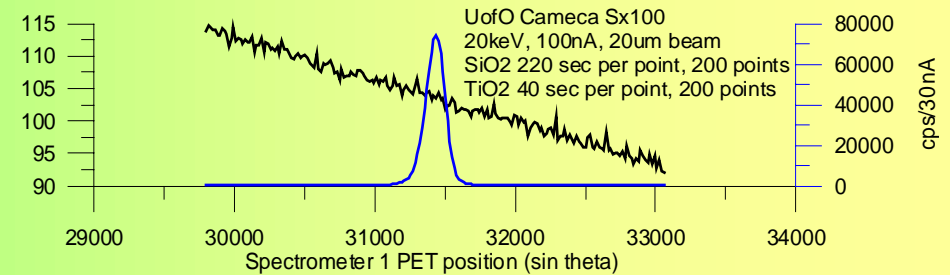
Accuracy: Which Result is Correct?

```
Un     4 SiO2 synthetic
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 100.  Beam Size =    20


Results in Elemental Weight Percents
ELEM:      Ti       Ti       Ti       Ti       Ti      Si        O
TYPE:    ANAL     ANAL     ANAL     ANAL     ANAL     SPEC     CALC
BGDS:     LIN      LIN      LIN      LIN      LIN
TIME:  200.00   200.00   200.00   200.00   200.00


ELEM:      Ti       Ti       Ti       Ti       Ti      Si        O    SUM
XRAY:    (ka)     (ka)     (ka)     (ka)     (ka)      ()       ()
   421 -.00121  .00064 -.00184  .00266  .00165 46.7430 53.2583 100.003
   422 -.00185 -.00063 -.00145 -.00118  .00245 46.7430 53.2552 99.9956
   423 -.00125 -.00024 -.00115  .00049  .00428 46.7430 53.2584 100.004
   424 -.00035 -.00183 -.00204 -.00348  .00197 46.7430 53.2532 99.9904
   425 -.00081  .00041 -.00226  .00279  .00226 46.7430 53.2586 100.004
   426 -.00146  .00015 -.00208  .00066  .00215 46.7430 53.2566 99.9990
   427 -.00223  .00069 -.00163  .00273  .00031 46.7430 53.2569 99.9998
   428 -.00260 -.00038 -.00128 -.00148  .00188 46.7430 53.2544 99.9936
   429 -.00225 -.00040 -.00184 -.00016  .00315 46.7430 53.2560 99.9975
   430 -.00179 -.00023 -.00217  .00003  .00393 46.7430 53.2569 99.9996
   431 -.00093 -.00056 -.00211 -.00105  .00368 46.7430 53.2564 99.9984
   432 -.00081 -.00131 -.00174 -.00043  .00116 46.7430 53.2549 99.9948

AVER:  -.00146 -.00031 -.00180  .00013  .00240 46.7430 53.2563 99.9983
SDEV:   .00069  .00075  .00036  .00190  .00117  .00000  .00168
SERR:   .00020  .00022  .00010  .00055  .00034  .00000  .00048
%RSD:    -47.4   -243.9    -20.0  1446.7    48.7      .0       .0

STKF:    .5878    .5878    .5878    .5878    .5878   .0000    .0000
STCT: 58006.2 22135.3 69567.4  3196.7 20203.5      .0       .0
UNCT:     -1.2      -.1     -1.8      .0      .7      .0       .0
UNBG:     81.1     30.8    105.1     2.4    27.7      .0       .0

ZCOR:   1.1969   1.1969   1.1969   1.1969   1.1969   .0000    .0000
KRAW:  -.00002  .00000 -.00003  .00000  .00003  .00000  .00000
PKBG:   .98516   .99692   .98305 1.00325 1.02500  .00000  .00000
```

Analysis of pure synthetic SiO2. Note that different spectrometers give systematically different values for this "blank" measurement ranging from -18 to + 24 PPM. Channels 1 and 3 are spectrometers 2 and 3 with LPET crystals and which have the holes under the Ti peak and yield negative concentrations as expected.

The T-test sensitivity is about 6 to 9 PPM for individual spectrometers, but the systematic (accuracy) differences in the different spectrometers are significantly larger.

The Blank Correction Itself

$$I_{corr} = I_{unk} - I_{std} * \frac{(C_{meas} - C_{level})}{C_{std}} * \frac{[ZAF]_{std}}{[ZAF]_{unk}}$$

Note: Blank level (C_{level}) can be non-zero

Blank Correction Applied to Blank Standard

```
Un     4 SiO2 synthetic
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 100.  Beam Size =   20


Results in Elemental Weight Percents
ELEM:       Ti        Ti        Ti        Ti        Ti        Si         O
TIME:   200.00    200.00    200.00    200.00    200.00


ELEM:       Ti        Ti        Ti        Ti        Ti        Si         O     SUM
XRAY:     (ka)      (ka)      (ka)      (ka)      (ka)       ()        ()
   421  .00025    .00095  -.00004   .00253  -.00076 46.7430 53.2590 100.005
   422 -.00039   -.00032   .00035  -.00131   .00005 46.7430 53.2559 99.9973
   423  .00021    .00006   .00065   .00036   .00187 46.7430 53.2591 100.005
   424  .00111   -.00153  -.00024  -.00362  -.00044 46.7430 53.2539 99.9922
   425  .00065    .00072  -.00045   .00266  -.00015 46.7430 53.2593 100.006
   426  .00000    .00045  -.00028   .00053  -.00026 46.7430 53.2573 100.001
   427 -.00077    .00100   .00017   .00260  -.00210 46.7430 53.2576 100.001
   428 -.00114   -.00007   .00052  -.00161  -.00052 46.7430 53.2551 99.9953
   429 -.00079   -.00009  -.00004  -.00030   .00074 46.7430 53.2567 99.9992
   430 -.00033    .00008  -.00037  -.00010   .00153 46.7430 53.2575 100.001
   431  .00053   -.00025  -.00031  -.00118   .00128 46.7430 53.2570 100.000
   432  .00065   -.00100   .00006  -.00056  -.00125 46.7430 53.2556 99.9965


AVER:    .00000    .00000    .00000    .00000    .00000 46.7430 53.2570 100.000
SDEV:    .00069    .00075    .00036    .00190    .00117   .00000   .00168
SERR:    .00020    .00022    .00010    .00055    .00034   .00000   .00048
%RSD:      ----      ----      ----      ----      ----        .0        .0


KRAW:    .00000    .00000    .00000    .00000    .00000   .00000   .00000
PKBG:  1.00002   1.00004   1.00000   1.00079   1.00007   .00000   .00000
BLNK#:        4         4         4         4         4      ----      ----
BLNKL: .000000   .000000   .000000   .000000   .000000      ----      ----
BLNKV: -.00146   -.00031   -.00180   .000132   .002405      ----      ----


Detection Limit in Elemental Weight Percent (Average of Sample):
ELEM:       Ti        Ti        Ti        Ti        Ti
  60ci  .00019    .00021    .00013    .00025    .00021
  80ci  .00029    .00032    .00020    .00039    .00033
  90ci  .00038    .00042    .00027    .00052    .00043
  95ci  .00047    .00052    .00033    .00063    .00053
  99ci  .00066    .00073    .00046    .00090    .00075
```

The "blank" correction is applied iteratively to improve the accuracy of the background calibration within the matrix correction so that the k-ratios and P/B are properly calculated.

Aggregate Intensities for Improved Sensitivity

```
Un     4 SiO2 synthetic
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 100.  Beam Size =    20


Results in Elemental Weight Percents
ELEM:       Ti        Ti        Ti        Ti        Ti        Si         O
TIME:   1000.00       .00       .00       .00       .00

ELEM:       Ti        Ti        Ti        Ti        Ti        Si         O    SUM
XRAY:      (ka)      (ka)      (ka)      (ka)      (ka)       ()        ()
   421   .00014    .00000    .00000    .00000    .00000 46.7430 53.2571 100.000
   422  -.00005    .00000    .00000    .00000    .00000 46.7430 53.2570 99.9999
   423   .00054    .00000    .00000    .00000    .00000 46.7430 53.2574 100.001
   424  -.00003    .00000    .00000    .00000    .00000 46.7430 53.2570 99.9999
   425   .00015    .00000    .00000    .00000    .00000 46.7430 53.2571 100.000
   426  -.00007    .00000    .00000    .00000    .00000 46.7430 53.2570 99.9999
   427  -.00025    .00000    .00000    .00000    .00000 46.7430 53.2568 99.9996
   428  -.00026    .00000    .00000    .00000    .00000 46.7430 53.2568 99.9996
   429  -.00020    .00000    .00000    .00000    .00000 46.7430 53.2569 99.9997
   430  -.00007    .00000    .00000    .00000    .00000 46.7430 53.2570 99.9999
   431   .00014    .00000    .00000    .00000    .00000 46.7430 53.2571 100.000
   432  -.00004    .00000    .00000    .00000    .00000 46.7430 53.2570 99.9999


AVER:    .00000    .00000    .00000    .00000    .00000 46.7430 53.2570 100.000
SDEV:    .00022    .00000    .00000    .00000    .00000   .00000   .00015
SERR:    .00006    .00000    .00000    .00000    .00000   .00000   .00004
%RSD:      ----        .0        .0        .0        .0       .0        .0


KRAW:    .00000    .00000    .00000    .00000    .00000   .00000   .00000
PKBG:   1.00000    .00000    .00000    .00000    .00000   .00000   .00000
BLNK#:        4         4         4         4         4      ----      ----
BLNKL: .000000   .000000   .000000   .000000   .000000     ----      ----
BLNKV: -.00093   .000000   .000000   .000000   .000000     ----      ----


Detection Limit in Elemental Weight Percent (Average of Sample):
ELEM:       Ti        Ti        Ti        Ti        Ti
  60ci   .00006    .00000    .00000    .00000    .00000
  80ci   .00010    .00000    .00000    .00000    .00000
  90ci   .00013    .00000    .00000    .00000    .00000
  95ci   .00016    .00000    .00000    .00000    .00000
  99ci   .00022    .00000    .00000    .00000    .00000
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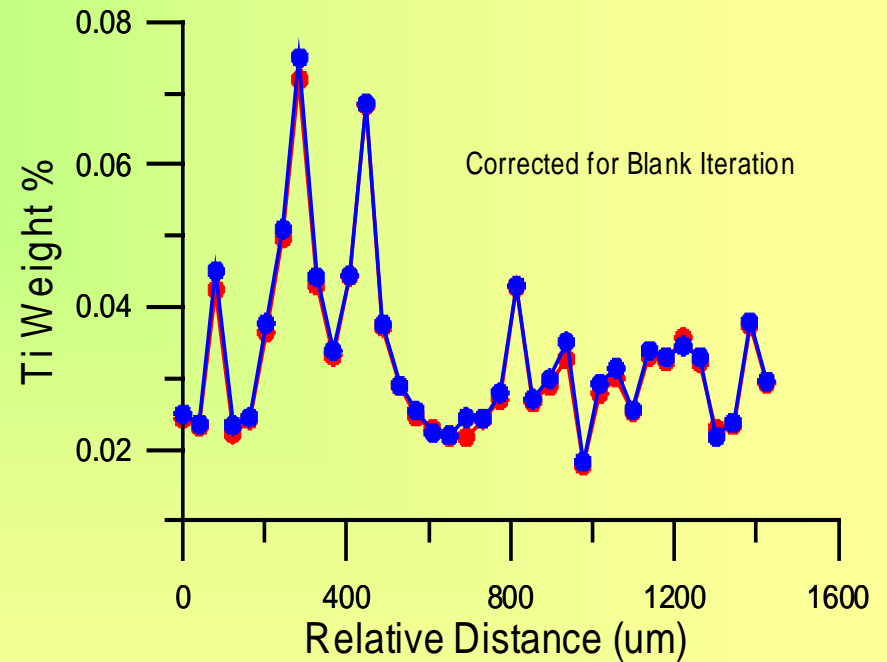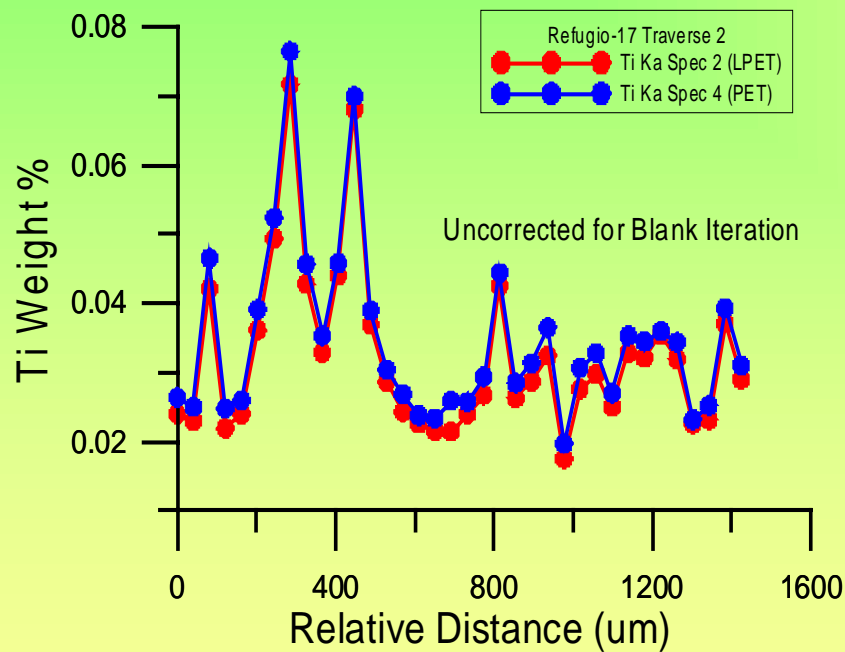
Using the blank correction combined with the aggregate intensity calculation option where duplicate elements on multiple spectrometers are combined for even better sensitivity we now get 2.2 PPM detection at 99% confidence and 0.6 PPM at 60% confidence!

Accuracy at the 400 PPM Level?

CAMCOR

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