

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”

Polygonization

E.g., Ir-Si system

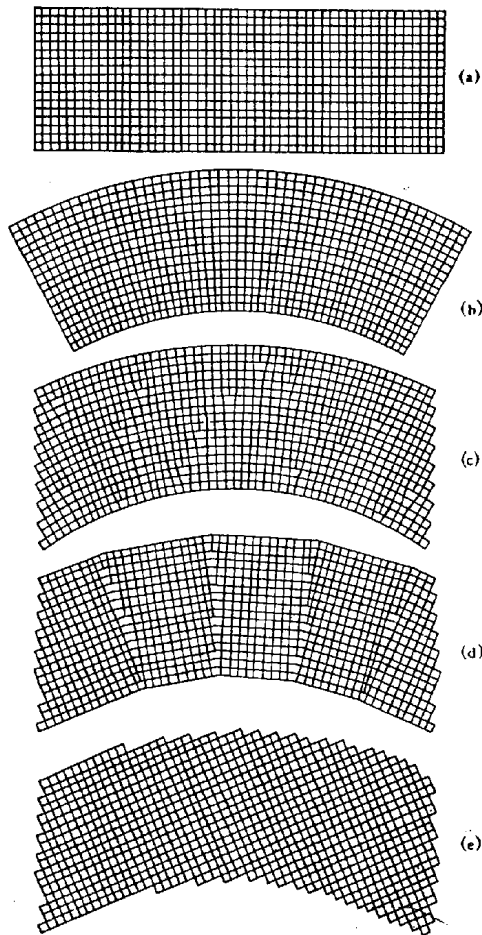
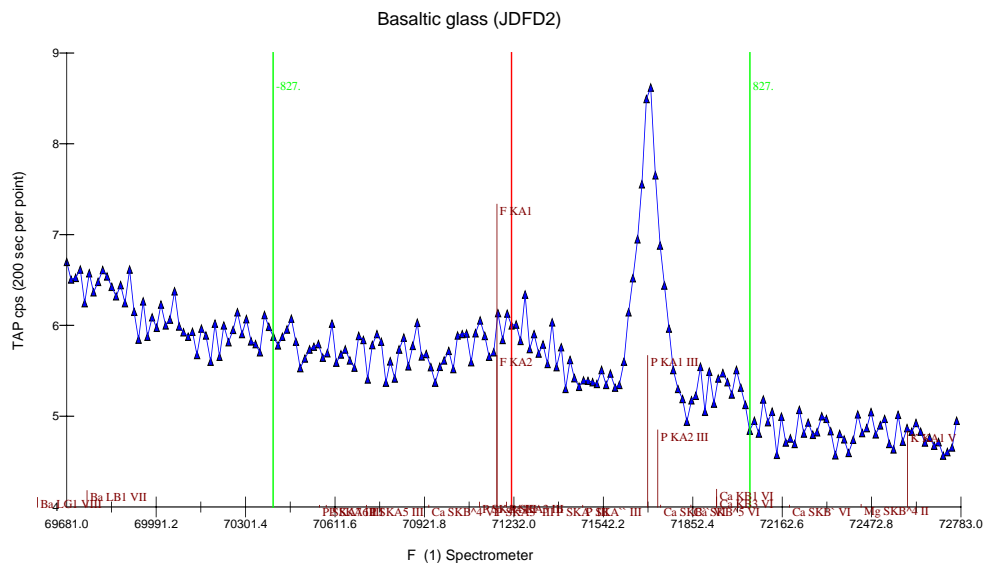
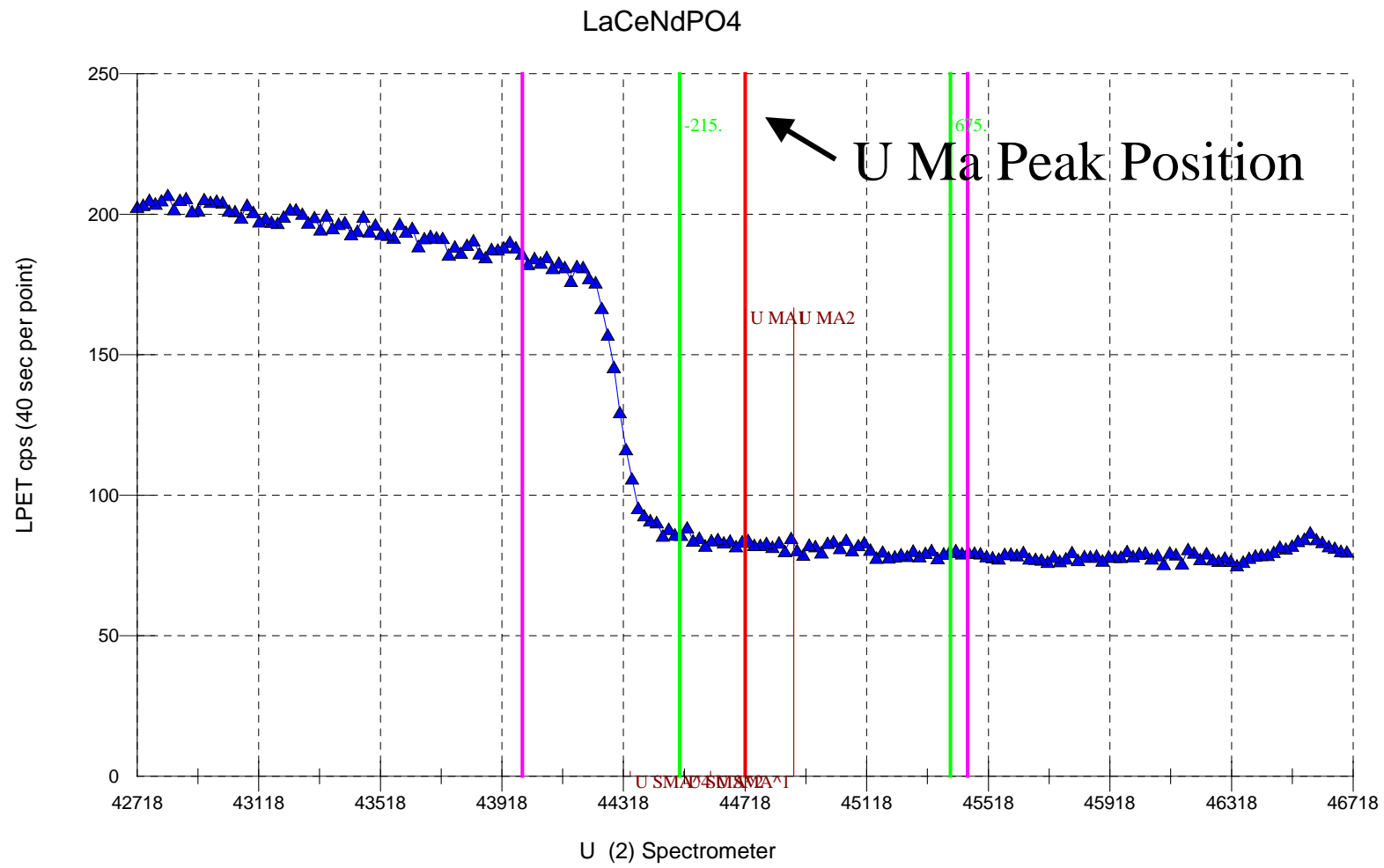


FIG. 1.27. Five states of a single crystal. (a) Unstrained. (b) Elastically bent. (c) Plastically bent. (d) Polygonized. (e) Recrystallized.

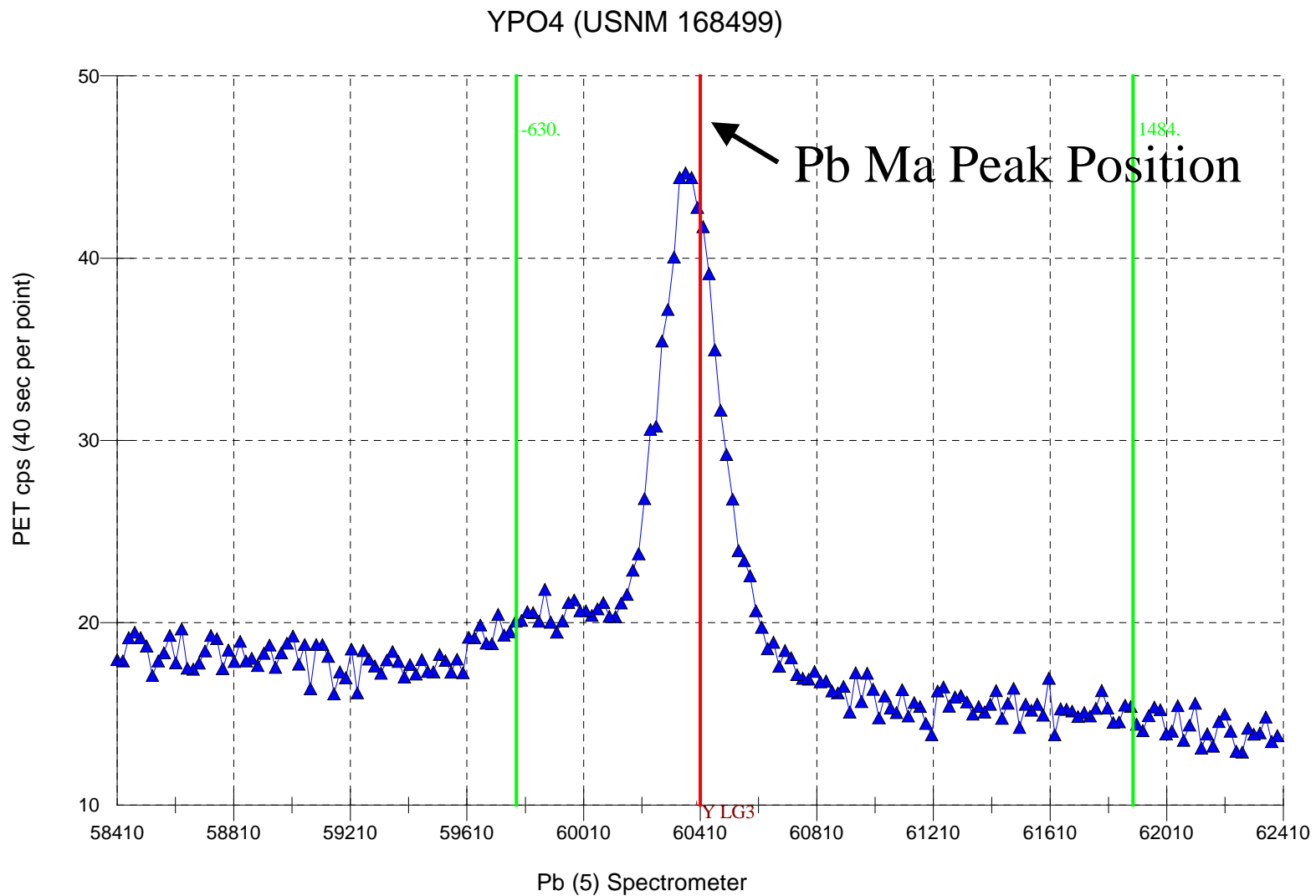
Nabarro, F.R.N. (1967) Theory of Crystal Dislocations, Oxford, 821 pp.



Detector Absorption Edges...



And Interferences...



Sample Absorption Edges

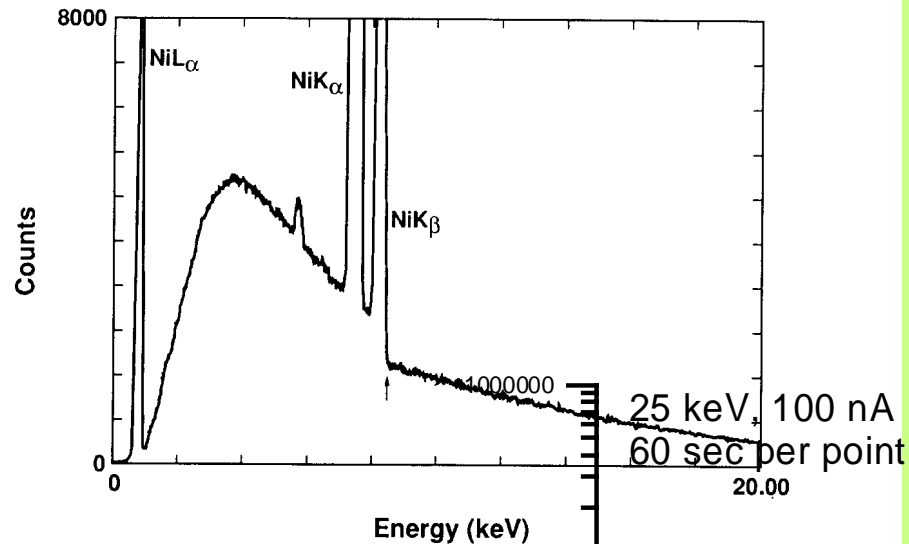
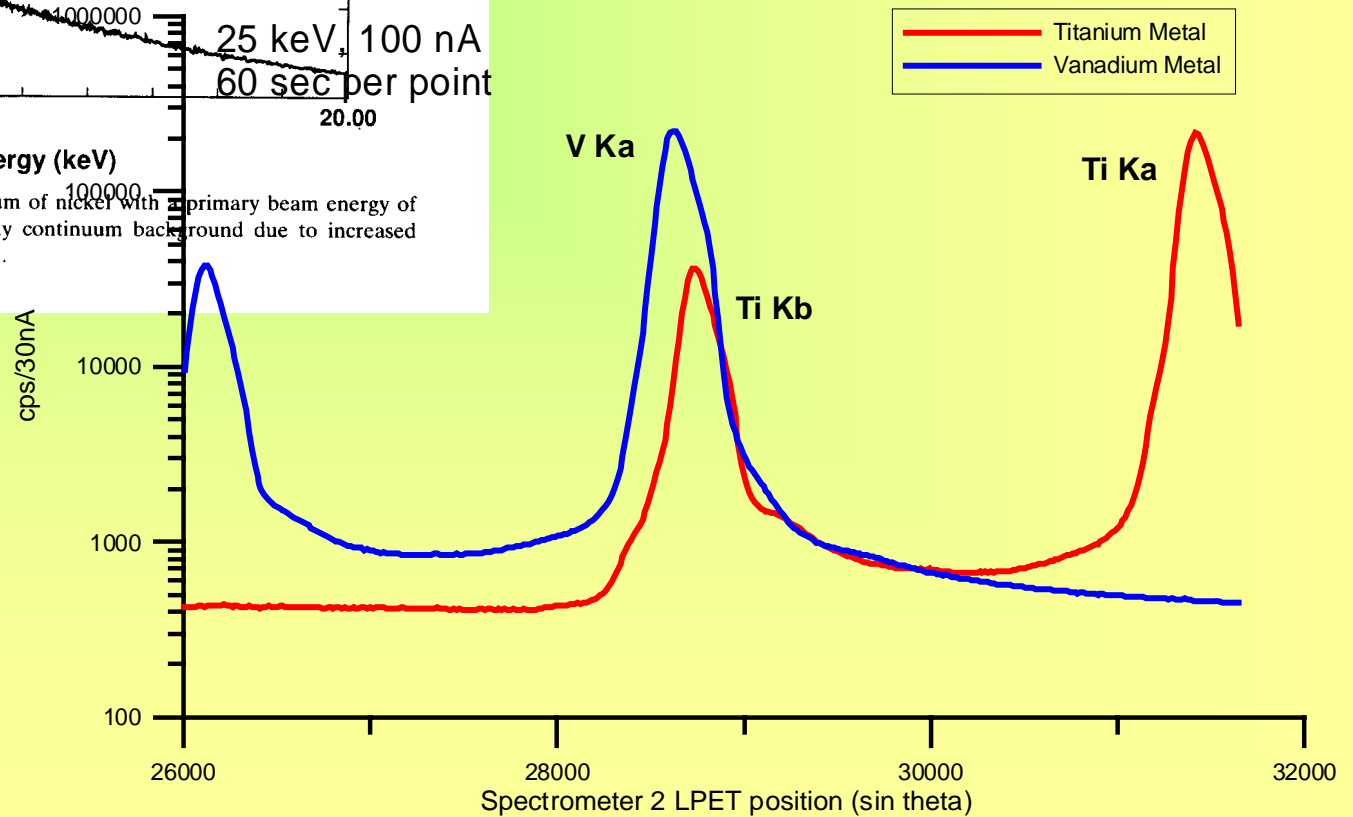


Figure 3.47. Energy-dispersive x-ray spectrum of nickel with primary beam energy of $E_0 = 40$ keV showing a sharp step in the x-ray continuum background due to increased absorption just above the Ni K absorption edge.



“Holes” or “negative peaks”...

HOLES IN THE BACKGROUND IN XRS

P.G. Self, K. Norrish, A.R. Milnes, J. Graham and B. Robinson.

ABSTRACT.

Sharp negative lines have been observed in wavelength-dispersive (WD) spectra. These “holes” can cause severe errors when analysing for trace elements near the lower levels of detection. This paper explains the existence of the holes in terms of diffraction from crystallographic planes other than those used in the WD analysis, and gives an overview of the theory necessary to predict the occurrence of the holes with emphasis on LiF(200) analysing crystals.

Introduction.

When determining trace element concentration by x-ray spectroscopy (XRS) or when using an electron microprobe, it is necessary to measure the background on both sides of a fluorescence line and subtract this background from the intensity at the line position to obtain the net line intensity. Thus, for accurate quantitative measurements of trace element concentration, the background must be determined with at least the same accuracy as used in measuring the fluorescent-line intensity.

Some years ago, when determining Sb concentrations in sphalerite using $SbL\alpha$ radiation with a wavelength-dispersive (WD) microprobe fitted with a $Ge(III)$ analysing crystal, we found that samples known to be free of Sb gave a significant net line intensity. Investigation showed that the anomalous result was due to a depression in intensity at one of the positions ($-2\theta = 62.5^\circ$) used to measure background. The depression was quite sharp and appeared on an intensity trace as a weak negative line.

Initially it was assumed that the effect was spurious and caused by some aberration of our equipment. However, considerable testing of the equipment did not account for the anomaly. Furthermore, it was found that a similar effect was observed with the $LiF(200)$ crystal at $2\theta = 53.1^\circ$ and this effect occurred at the same angle when using the spectrometer in the microprobe and when using the x-ray fluorescent spectrometer. We therefore concluded that we were dealing with a real phenomenon, although we could not explain it.

More recently the effect has again been observed using an electron microprobe whilst measuring gold concentration using $AuL\alpha$ with a $LiF(200)$ crystal. The $AuL\alpha$ line is at 1.277\AA ($2\theta=36.98^\circ$), and there is a distinct hole in the background at 1.273\AA ($2\theta=36.87^\circ$). The effect could again be reproduced on an x-ray spectrometer. The possibility that the effect might be related to the gas counter (perhaps to an absorption edge) was considered. However, the effect was found to be present when a scintillation counter was used.

An intensity trace from a blank sample is shown in Fig. 1. The hole in the background is very apparent in this trace and the width of the negative line is the same as the width of the $AuL\alpha$ line. The hole is approximately 9% of the background level which is significant when it is considered that it is equivalent to between 8 and 35 ppm of Au depending on operating conditions. In electron microprobe analysis the hole was approximately 11% of the background and this corresponded to 700 ppm Au.

After considerable discussion it was realized that the effect was due to multiple diffraction. That is, it was caused by the accidental excitation of diffraction reflections other than the $LiF(200)$ reflection used in the WD analysis.

LiF Analysing Crystals.

In a single crystal, diffraction can occur from any atomic plane. So that in a crystal such as LiF, there are many sets of planes that can diffract radiation. Furthermore, because of their strong cleavage, LiF crystals used in (200) orientation are usually specifically oriented with respect to the WD geometry. When a [200] LiF surface is used for WD analysis the other faces of the crystal are [020] and [002]. One of these faces is aligned parallel to the plane of two-theta traverse in the spectrometer. In the following discussion it is assumed that the (002) planes are parallel to the plane of two-theta traverse.

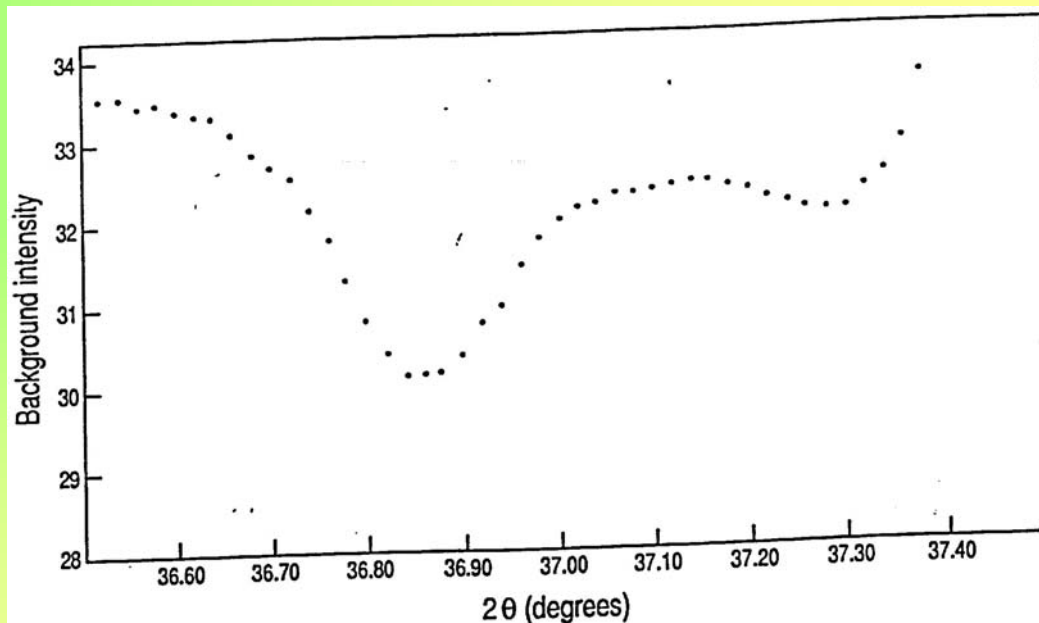


Figure 1. Intensity trace showing a distinct negative line at a two-theta value of around 36.8° . This angle is just below that for $AuL\alpha$ radiation.

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

$$2 d(200) \sin \theta_1 = 2 d(hkl) \sin \theta_2. \quad (1)$$

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

$$\tan \theta_1 = 2l / (h^2 + k^2 + l^2 - 2h). \quad (2)$$

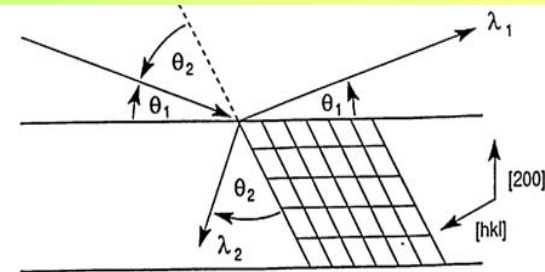
The most obvious example of this situation is for the (002) planes where $\theta_1 = 45^\circ$ as shown in Fig. 2b.

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.

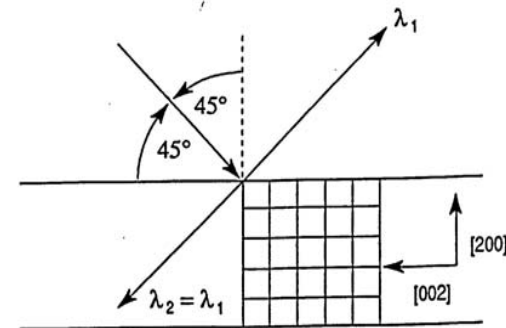
The size of the background hole will depend on (among other things) the number (i.e. multiplicity) and strength of the accidentally excited reflections. From Table 1 it can be seen that at a two-theta angle of 36.870° there are 6 low-order reflections excited which will cause appreciable diffraction of the primary beam. This gives rise to the anomaly in the background near the $AuL\alpha$ 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.

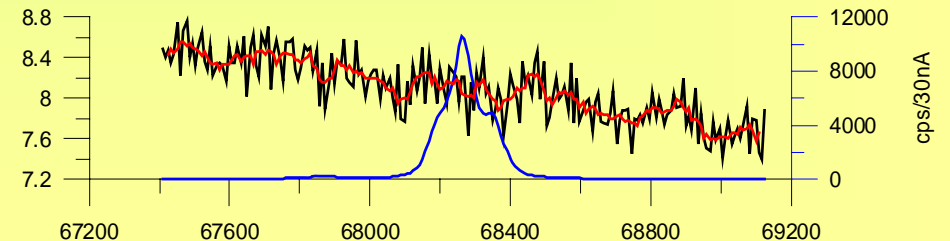
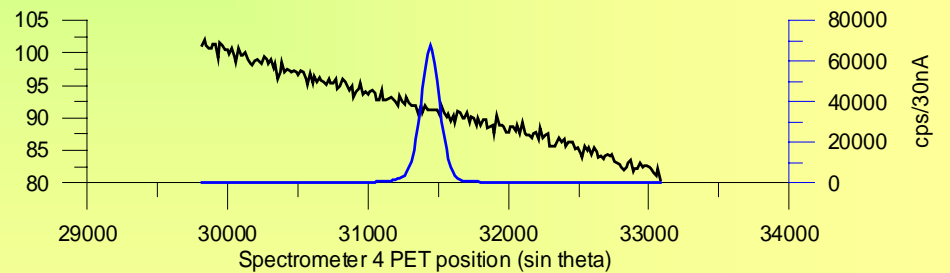
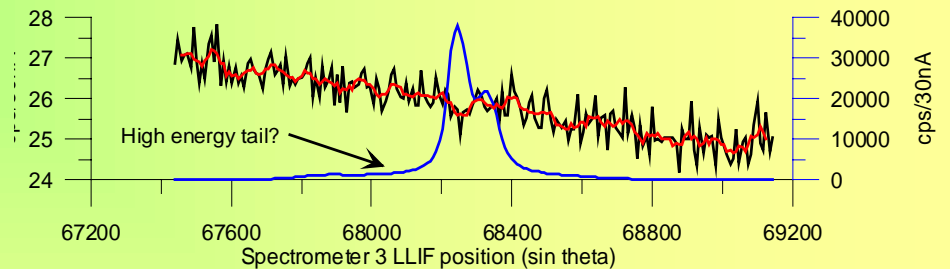
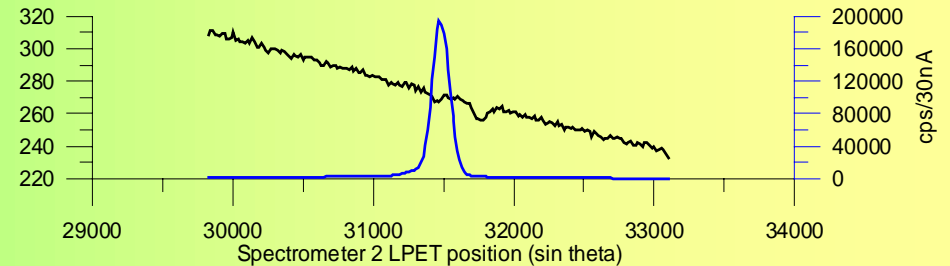
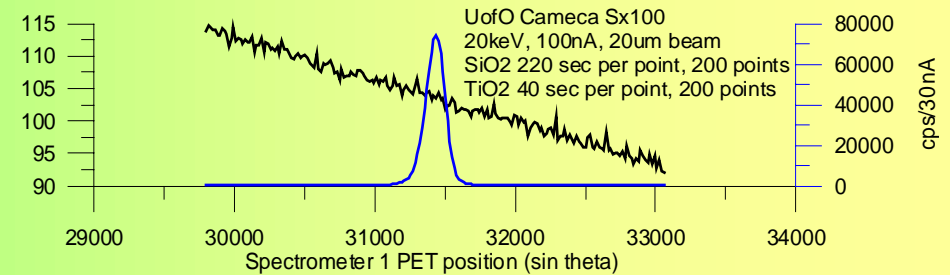
The Problem...

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

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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	.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	

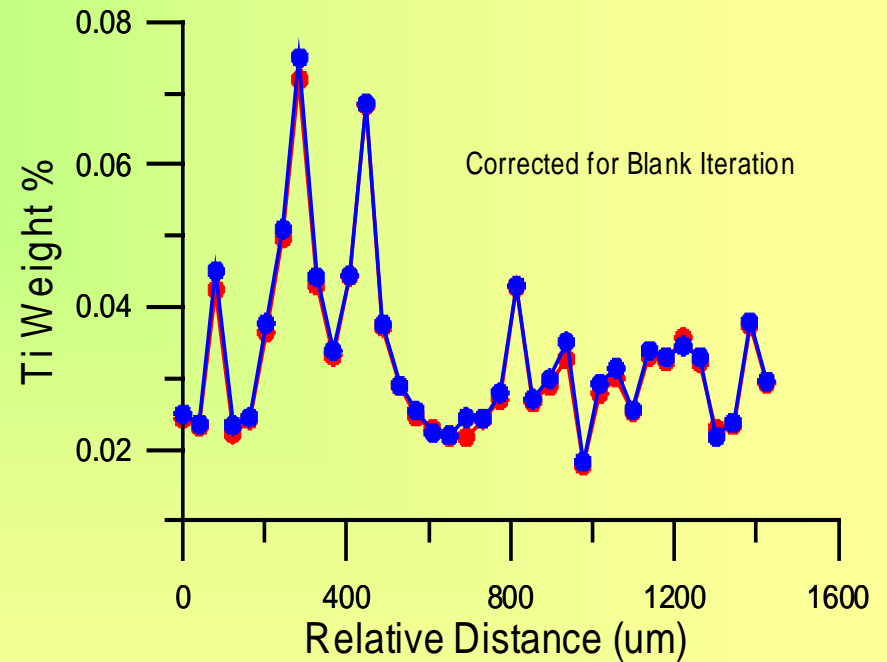
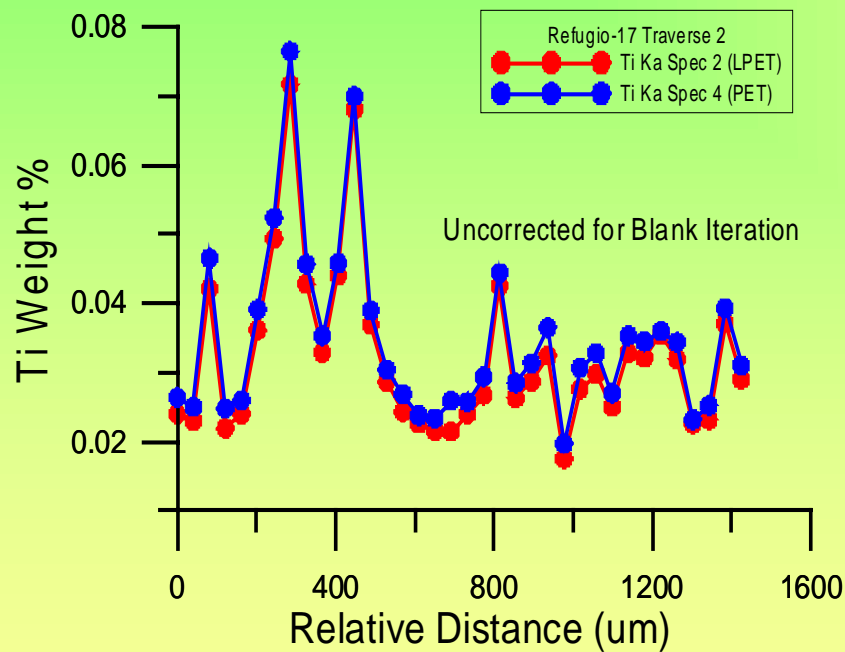
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PKBG:	1.00000	.00000	.00000	.00000	.00000	.00000	.00000	
BLNK#:	4	4	4	4	4	----	----	
BLNKL:	.000000	.000000	.000000	.000000	.000000	----	----	
BLNKV:	-.00093	.000000	.000000	.000000	.000000	----	----	

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

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?





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