USING QUANTITATIVE ITERATION TO CORRECT "PATHOLOGICAL" SPECTRAL INTERFERENCES

Microscopy & Microanalysis, Atlanta, Georgia, July 12-16, 1998
Problem Elements and Spectrometry Problems Symposia (Invited)

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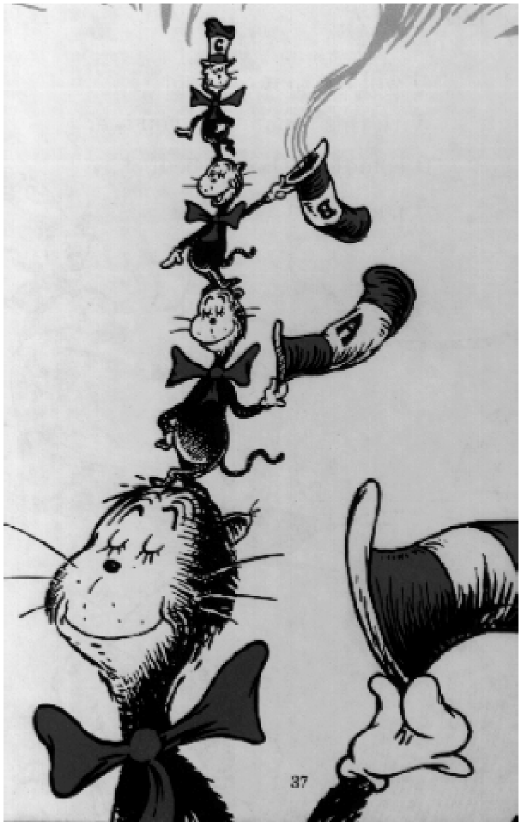
As microanalysts, working in what is commonly considered to be a "mature" field, we would like to imagine that it is possible to quantitatively analyze any sample that happens to drop into our laps, however, as we have already seen this morning, that belief is not always in accordance with reality.

For the next 30 minutes, I would like to talk about two types of spectral interferences, both of which I like to term "pathological", due to the degree of difficulty they present to the analyst, although I should mention that the methods to be described here are completely applicable to the more frequently encountered and much less difficult cases of minor spectral overlap.

Cascade
Although these two types of "pathological" interferences are related and can be treated similarly, I designate the first type as "cascade" overlaps,

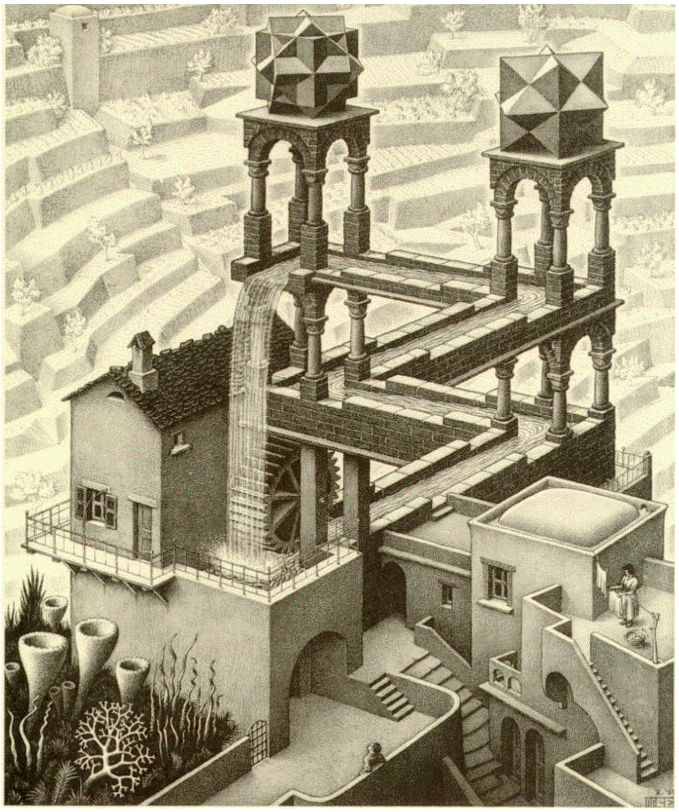


where element A interferes with element B, which in turn interferes with element C. The difficulty here of course is that one cannot correct for the interference on element C until one determines the interfering intensity contributed from element B, and one cannot determine the actual intensity contribution of element B on element C until one has determined the contribution of the interfering intensity from element A on element B.

"Self-interfering"
And the second type I designate "self-interfering" overlaps

where two primary analytical lines both interfere significantly with each other. In this case the difficulty is that since both lines are first order diffraction peaks and hence of similar energy, we cannot take advantage of pulse-height analysis (PHA) to suppress the interference, and for various other analytical reasons we might not be able to switch to an alternative emission line that avoids the interference altogether.

Of course, one can conceive of yet another type of "pathological" overlap which might consist of simultaneous "cascade" and "self-interfering" overlaps.



Although I was unable to obtain a sample that demonstrates this extreme situation, it is not altogether impossible that one could encounter such a specimen. In any case, I did some quick overlap calculations on a hypothetical composition of this type and the results can be seen in the following figure.

Table 1

```
For As ka      LiF at  1.17728 wt. %:   33.000
  Interference by Bi LA2           at  1.15560 =       .2%
  Interference by Pb SLAA          at  1.16710 =       .3%
  Interference by Pb SLAA          at  1.16790 =       .3%
  Interference by Pb SLAA          at  1.16940 =       .4%
  Interference by Pb SLA           at  1.17070 =       .5%
  Interference by Pb SLA^IX        at  1.17150 =       .5%
  Interference by Pb SLA^Y         at  1.17300 =       .6%
  Interference by Pb LA1           at  1.17520 =     64.5%
  Interference by Pb SLA1^Z        at  1.17570 =       .7%
  Interference by Pb SLAS          at  1.18230 =       .5%
  Interference by Pb LA2           at  1.18660 =      3.8%

For Pb la      LiF at  1.17518 wt. %:   33.000
  Interference by Bi SLAA          at  1.13520 =       .1%
  Interference by Bi SLA^X         at  1.13910 =       .2%
  Interference by Bi SLA^IX        at  1.14050 =       .2%
  Interference by Bi SLA'          at  1.14180 =       .2%
  Interference by Bi LA1           at  1.14410 =     25.5%
  Interference by Bi SLA1^Z        at  1.14450 =       .3%
  Interference by Bi SLAS          at  1.15150 =       .5%
  Interference by Bi LA2           at  1.15560 =      6.6%
  Interference by As SKA4          at  1.17050 =      1.0%
  Interference by As SKA3'         at  1.17140 =      1.0%
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  Interference by As SKA3           at   1.17200 =      1.0%
  Interference by As KA1            at   1.17610 =     99.9%
  Interference by As KA1,2          at   1.17740 =    150.5%
  Interference by As KA2            at   1.18010 =     49.8%

For Bi la       LiF at  1.14402 wt. %:   33.000
  Interference by Pb SLAA           at   1.16710 =       .5%
  Interference by Pb SLAA           at   1.16790 =       .4%
  Interference by Pb SLAA           at   1.16940 =       .4%
  Interference by As SKA4           at   1.17050 =       .4%
  Interference by Pb SLA            at   1.17070 =       .4%
  Interference by As SKA3'          at   1.17140 =       .3%
  Interference by Pb SLA^IX         at   1.17150 =       .3%
  Interference by As SKA3           at   1.17200 =       .3%
  Interference by Pb SLA^Y          at   1.17300 =       .3%
  Interference by Pb LA1            at   1.17520 =     25.2%
  Interference by Pb SLA1^Z         at   1.17570 =       .2%
  Interference by As KA1            at   1.17610 =     23.3%
  Interference by As KA1,2          at   1.17740 =     31.3%
  Interference by As KA2            at   1.18010 =      8.2%
  Interference by Pb SLAS           at   1.18230 =       .1%
  Interference by Pb LA2            at   1.18660 =       .9%
```

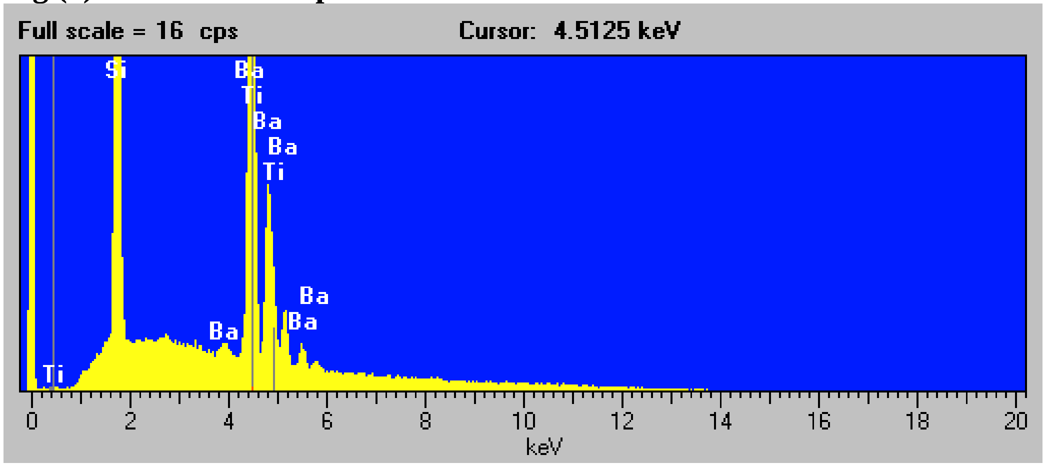
Here we have As, Pb and Bi each assumed present at 33% weight percent concentration in just such a compound. As you can see, not only are Pb and As both interfering with each other, but Bi interferes with Pb which also "self-interferes with Bi" which in turn is interfered by both As and Pb. It's almost obscene!

However, not to worry just yet, I was unable to find a Pb-As-Bi sulfide in quick look through a mineralogy text, which doesn't preclude the possibility of a synthetic material of course!

Benitoite

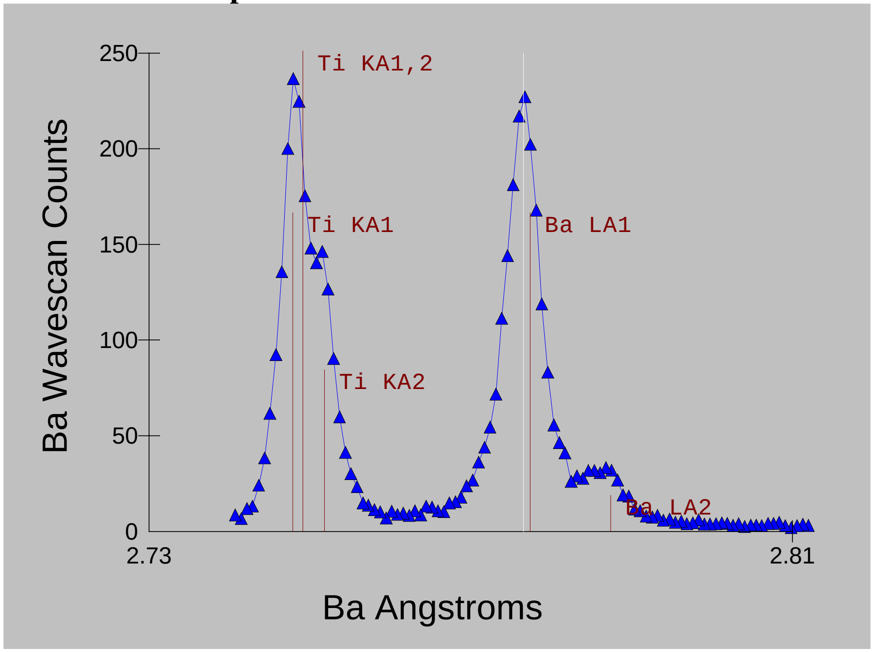
Now let's take a quick look at a more typical and benign "self-interfering" overlap, for example Ba lα and Ti kα as in the mineral Benitoite.

Fig (4) Benitoite EDS spectra



As you can see in this EDS spectra of Benitoite, although acquired at the highest pulse processing time of my system, the detector is unable to separate the Ba lα and Ti kα analytical peaks. However, the situation for the WDS acquired spectra is significantly improved using an LiF analyzing crystal under the same conditions.

Fig (5) Benitoite WDS spectra



and it is obvious that only a small amount of overlap from the peak tails is occurring.

Polygonization

Incidentally, one significant source of interferences in WDS, especially when measuring trace element concentrations, are these rather extended tails that one can detect to a great distance from the nominal emission line position. Although small in intensity, these extremely extended tails, are an artifact of the analyzer crystals used in electron microprobes. This artifact is the result of the "polygonization" process that the analyzing crystals undergo during manufacture.

Fig. (6) "Polygonization"

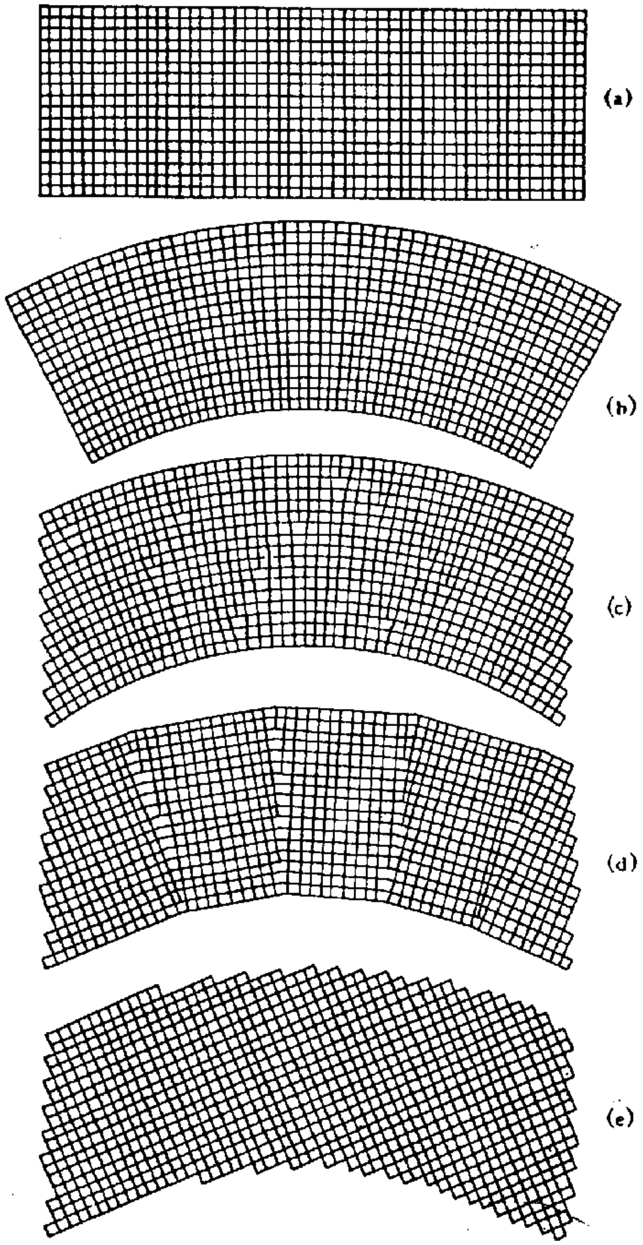


FIG. 1.27. Five states of a single crystal. (*a*) Unstrained. (*b*) Elastically bent. (*c*) Plastically bent. (*d*) Polygonized. (*e*) Recrystallized.

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

It turns out that freshly bent analyzing crystals are particularly poor in their ability to diffract x-rays due to plastic deformation that occurs when the crystals are curved to the Johann radius. To restore "reflectivity", the crystals are thermally cycled in order to partially recrystallize them, thus forming short polygon crystalline segments (and hence the term "polygonization"). However, one side effect of this process is that a certain amount of randomization is induced during the formation of these newly crystallized regions and in fact, although most segments will align themselves to the general curve of the crystal, a small fraction of them are misoriented at large angles, enough to cause x-ray diffraction at spectrometer positions far from the expected sinθ angle.

Because of polygonization induced tailing, it is best to keep in mind the words of Chuck Fiori who once said "at a sufficiently trace level, every element in the periodic table interferes with every other element in the periodic table".

Large Magnitude Self-Interfering Overlaps

Some slightly more terrifying examples of "self-interfering" overlaps can be easily found and the following is a partial list of binary pairs for large magnitude interferences of this type, calculated by assuming typical wavelength dispersive resolution, that were gleaned from a quick examination of the periodic table.

Table (2)

Interfering Pair	Wavelength Region (Å)	Approximate Overlap (% @ 50/50)
Pb Lα ↔ As Kα	1.17	150 - 65
Hg Lα ↔ Ge Kα	1.25	120 - 15
Ir Lα ↔ Ga Kα	1.34	70 - 30
Re Lα ↔ Zn Kα	1.43	140 - 60
Er Lα ↔ Co Kα	1.78	110 - 50
Eu Lα ↔ Mn Kα	2.1	15 - 5
Ba Lα ↔ Ti Kα	2.7	0.8 - 0.8
Xe Lα ↔ Sc Kα	3.0	20 - 10
In Lα ↔ K Kα	3.74	50 - 20
Th Mα ↔ Ag Lα	4.13	30 - 60
Bi Mα ↔ Tc Lα	5.1	50 - 70
Mo Lα ↔ S Kα	5.4	30 - 15

Although I cannot claim to have personally encountered all of the above combinations (for instance, I doubt that a technetium-bismuth alloy will ever find it's way into my lab), I have run into more than a few of the others and, as I'm sure many of you already know, interferences of these magnitudes can be quite troublesome to deal with.

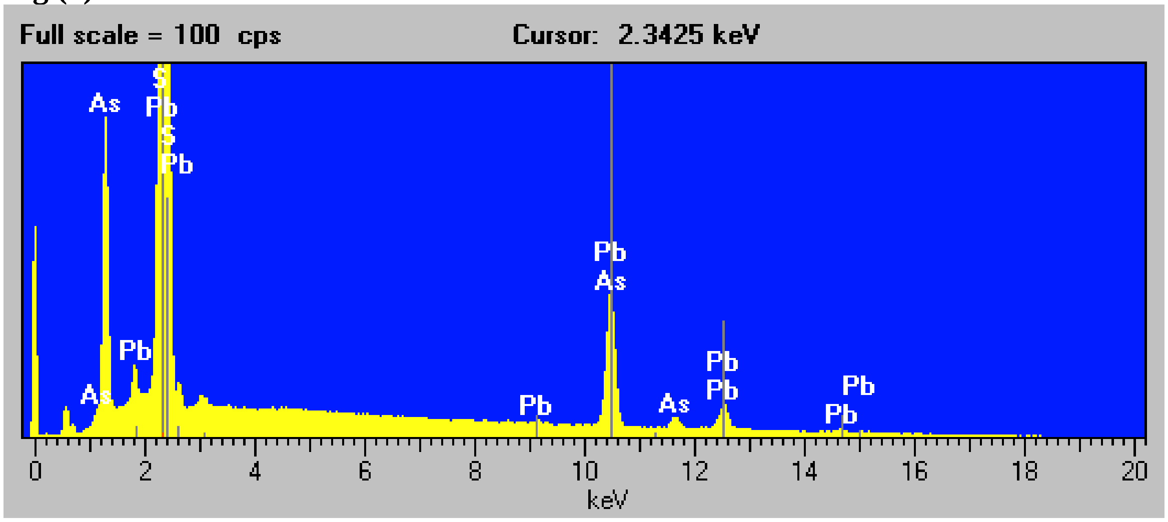
Just for comparison, I should point out that the previously discussed barium - titanium interference, also included here, is, as you can see, completely dwarfed in magnitude by the other examples in this table.

Self-interfering example

For the purposes of discussing interferences of this variety, I will concentrate on the system Pb Lα ↔ As Kα because the sulphosalt mineral family which commonly contains these elements, is often encountered in ore petrology investigations.

Let's take a quick look at some actual spectra from these types of samples, which exhibit, what I have already termed, overlaps of the "self interfering" variety. Here is an EDS spectra, of an unknown ore mineral, again acquired with a pulse processing time configured for maximum energy resolution.

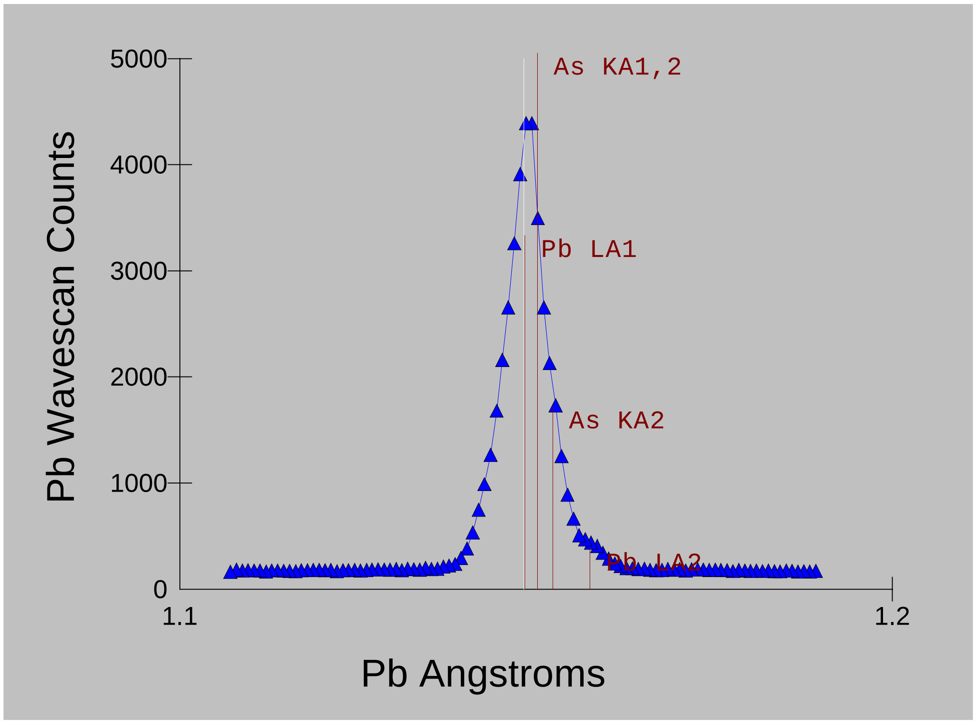
Fig (7) ore mineral



Not a very pretty picture, but it is at least evident that that As is present from the As Lα line and Pb likely present from the appearance of the secondary L lines, although S is interfered strongly by the Pb Mα line and can only be inferred by the mineralogy.

Here now we have the same ore mineral sample, and it's spectra acquired in the vicinity of the Pb Lα and As Kα lines, using a WD spectrometer equipped with an LiF analyzing crystal with an approximate energy equivalent resolution of 10 eV.

Fig (8)



Even with the kind of resolution available with WDS, we still have large overlaps that will create confusion with qualitative analysis and much difficulty when we attempt quantitative analysis.

Cascade Example

The other "pathological" interference that can also be extremely difficult for many analysts, are of course the already mentioned "cascade" interferences. This is a situation often, but not exclusively encountered in minor or trace element analysis, in which, a major element will interfere with another major or minor element, which in turn, interferes with yet another minor or trace element. The difficulty is that if one attempts to correct for the overlap on the trace element, one must know the intensity of the interfering element, however, if this interfering intensity has been significantly inflated by yet another interference, one must correct for that interference before correcting for the overlap on the trace element.

From this observation, we might surmise that the order in which the interferences are dealt with, could be important in the correction procedure, which is of course an undesirable restraint from a programmatic viewpoint.

Examples of this "cascade" interference, are readily found among the transition metals due to the Kβ interferences that are ubiquitous in that region of the periodic table for the elements V to Cu, and also from a series of Lβ interferences in the vicinity of Rh and Ag.

The following table contains some calculations regarding "cascade" overlaps for two different combinations of elements, again assuming typical WDS spectral resolution.

Table (3)

```
For  V ka      LiF at  2.50498 wt. %:   33.000

For Cr ka      LiF at  2.29113 wt. %:   33.000
  Interference by V  SKB''         at  2.27680 =       .1%
  Interference by V  KB1           at  2.28490 =      6.5%
  Interference by V  KB3           at  2.28490 =      3.3%
  Interference by V  SKB'          at  2.29040 =       .7%

For Mn ka      LiF at  2.10326 wt. %:   33.000
  Interference by Cr KB1           at  2.08510 =       .7%
  Interference by Cr KB3           at  2.08510 =       .3%
  Interference by Cr SKB'          at  2.09000 =       .2%
  Interference by Cr SKBN          at  2.11770 =       .1%
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Table (4)

```
For Rh la      PET at  4.59809 wt. %:   33.000

For Pd la      PET at  4.36830 wt. %:   33.000
  Interference by Rh SLB1^4        at  4.33610 =       .2%
  Interference by Rh SLB1'''       at  4.34420 =       .4%
  Interference by Rh SLB1''        at  4.35180 =       .7%
  Interference by Rh SLB1'         at  4.36170 =       .9%
  Interference by Rh LB1           at  4.37480 =     39.4%

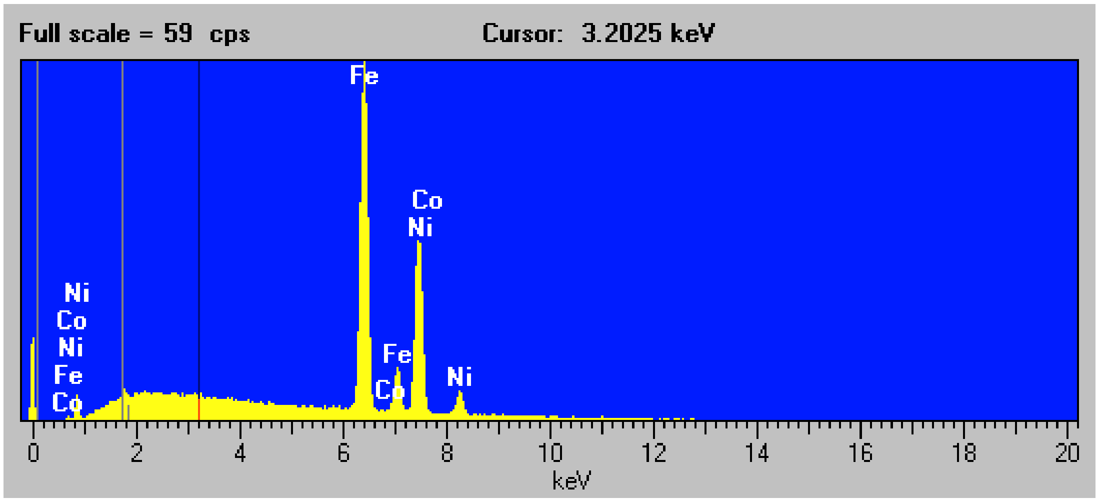
For Ag la      PET at  4.15503 wt. %:   33.000
  Interference by Pd SLB1'''       at  4.11780 =       .1%
  Interference by Rh SLB2^A        at  4.12480 =       .3%
  Interference by Pd SLB1''        at  4.12520 =       .3%
  Interference by Rh LB2           at  4.13130 =      3.8%
  Interference by Pd SLB1'         at  4.13510 =       .6%
  Interference by Pd LB1           at  4.14650 =     38.8%
```

The V-Cr-Mn interference isn't too bad, at these particular concentrations, but if one were trying to measure a trace amount of Mn, it would be much more problematic. The Rh-Pd-Ag interference is extremely large and definitely requires special handling. Note that even these large concentrations experience overlaps of 30 to 40%.

In this talk I will examine two different real world examples of "cascade" interference, the first is an interesting interference caused by the fact that the K line of a higher Z transition metal is capable of fluorescing both the Kα and Kβ lines of a slightly lower Z transition metal, which in turn can interfere with the trace analysis of another transition metal.

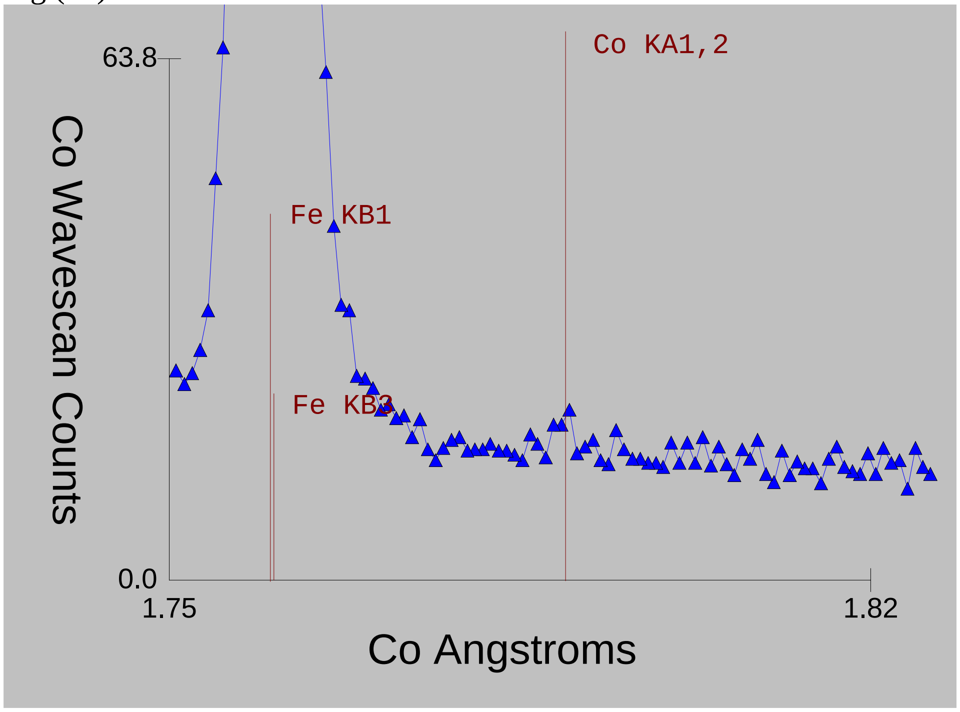
Here is the EDS spectra of a Fe-Ni alloy (NIST SRM 1159) that exhibits this "cascade" fluorescence interference.

Fig (9)



As you all know, the presence of Ni in the sample, causes a large fluorescence of both the Fe Kα and Kβ lines, of which the Fe Kβ line interferes with the Co Kα line sufficiently to cause problems when attempting to determine trace concentrations of Co in any Fe-Ni alloy. The bottom line here is: beware of any quoted Co trace concentrations in a matrix of Fe and Ni!

Fig (10)



Again, here is the corresponding WDS spectra, which even with it's intrinsically higher resolution is unable to prevent the extended tails (and satellite lines) from the Fe Kβ line from interfering with the Co Kα line.

And here is an EDS spectra of the second "cascade" interference example that I will discuss in a moment, a more typical, but still fascinating example of the perversity of the universe, in which the Kβ lines of three consecutive transition metals each in turn strongly interferes with the next transition metal element in the periodic table, in this case a Ti-V-Al alloy (NIST SRM 654b) which has the interference Ti to V to Cr. (Ti Kβ → V Kα - V Kβ → Cr Kα):

Fig (11)

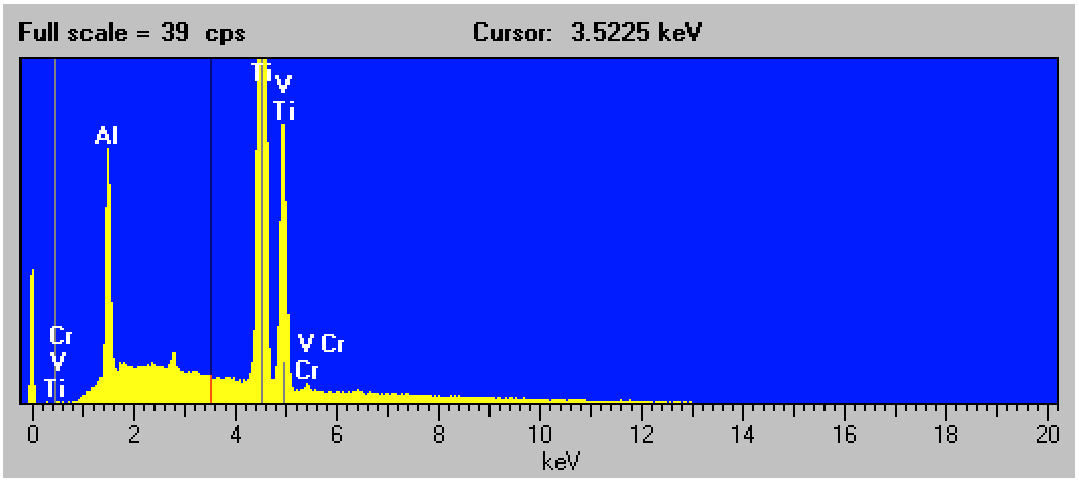
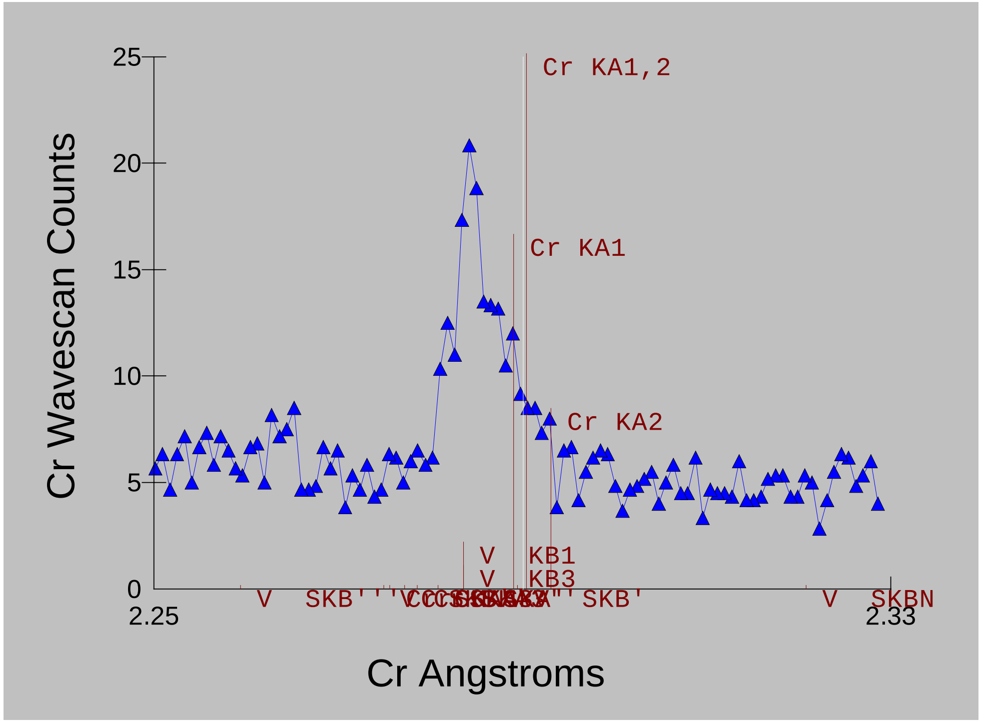


Fig (12)



And corresponding the WDS spectra of the same sample which again, even with it's intrinsically higher resolution is incapable of separating the interference of V Kβ → Cr Kα:

Technique

What I would like to discuss now, is a general procedure that can be used to deal with all types of "pathological" (and of course, minor) spectral interferences. For this, I will utilize wavelength dispersive data, since this represents the best resolution currently availble, and I will further restrict the discussion to methods based on peak intensities, as opposed to graphical methods working with complete spectra, which for WDS spectrometers, are quite time consuming, especially for trace element concentrations.

One procedure for the correction of spectral overlaps used by many analysts (typically as a “back-of-the-envelope” calculation), is based on a simple ratio of the interfering and interfered intensities.

This method will be completely inadequate for dealing with the types of interferences that we have been discussing. This can be easily understood by considering that in the case of "self-interfering" overlaps, the contribution to the interfering intensities must be solved simultaneously. A quick look at some actual measured intensities will show the magnitude of the problem:

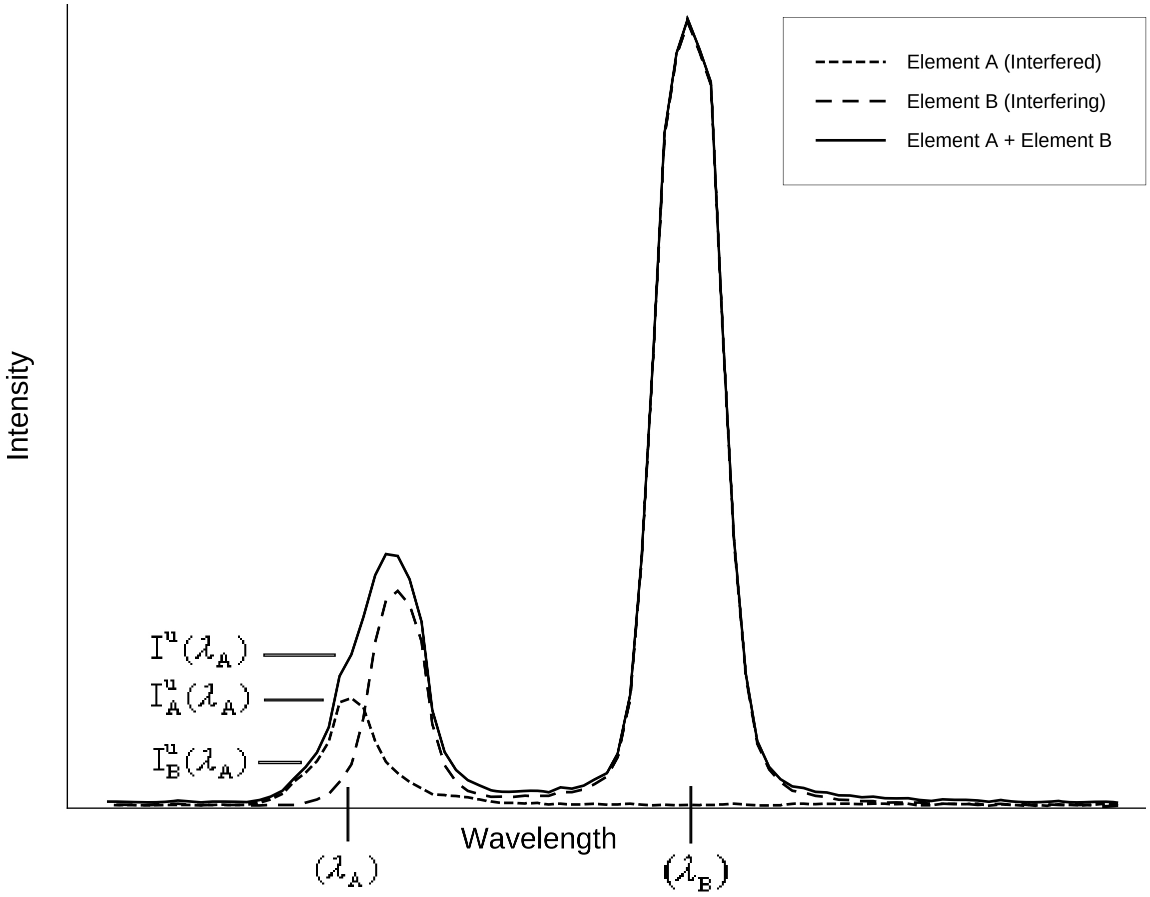
Table (5)

	Pb Lα (cps)	As Kα (cps)	S Kα (cps)
PbS	1473.3 ± 11.5	1213.0 ± 3.8	1453.3 ± 9.3
GaAs	1624.7 ± 29.9	1771.7 ± 8.2	2.5 ± 1.2
FeS	14.0 ± 3.3	13.9 ± 3.7	4986.9 ± 26.3

As you can see here, the interfering intensity from As as measured in GaAs at the emission line position for Pb Lα, is actually greater than the intensity of Pb Lα as measured in PbS due to the greater relative strength of K lines compared to L lines!

Now let us examine the interference correction procedure itself. Here I will refer to a schematic diagram of a typical interference to explain the nomenclature

Fig (13)



In this diagram, element A is the interfered element, whose spectra is shown by the short dashed line, measured at it's analytical line position, (λ_A), element B is the interfering element shown by the long dashed line, measured at it's normal analytical line position, (λ_B), and the actual spectra, in a sample containing both elements, as measured by the analyst, is shown by the solid line. Therefore, the actual intensity of interfered element, is found by subtracting the interfering intensity, contributed by the interfering element from the overall measured intensity.

The expression seen here (*e.g.*, Gilfrich, *et al.*, 1978), for the determination of the interfering intensity contributed by element B, is often utilized,

Eq (1)

$$I_B^u(\lambda_A) \approx \frac{I_B^{\bar{s}}(\lambda_A)}{C_B^{\bar{s}}} \; \frac{I_B^u(\lambda_B)}{I_B^s(\lambda_B)} \; C_B^s$$

where the notation shown in the previous schematic, been adopted. What is being done here, is essentially calculating an approximate concentration for the presence of the interfering element in the unknown times it's fractional overlap coefficient at the analytical position for the interfered element.

The interfering element intensity, is then, as noted before, simply subtracted from the measured intensity, to obtain the approximate intensity of the interfered element.

Shortcomings of the commonly utilized method

As previously mentioned, this procedure fails for the more problematic "cascade" and "self-interfering" spectral overlaps, where the intensity of the interfering element is affected by an additional interference and even in cases of minor overlap where differences in composition between the unknown and the standard used for the interference calibration may significantly affect the interfering intensity.

However, since in all cases of overlap, the degree of spectral interference is actually not directly dependent on the intensity of the interfering element, but is rather, *compositionally* dependent on the concentration of the interfering element, we can accurately determine the interfering intensity once we have accurately determined the concentration of the interfering element. Therefore, to perform a rigorous correction for interference, two important modifications to eq. (1) are required.

Improved Interference Correction

First, it is necessary to quantitatively correct for the matrix effects on the interfering intensity in the interference standard matrix relative to the unknown, as seen here,

Eq (2)

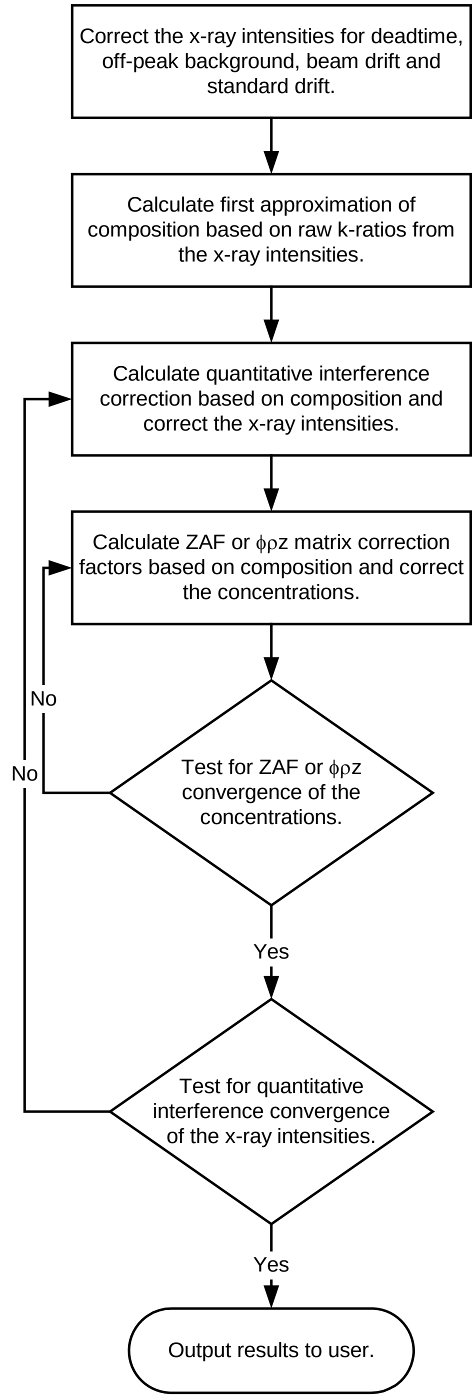
$$I_B^u(\lambda_A) = \frac{[ZAF]_{\lambda_A}^{\bar{s}}}{C_B^{\bar{s}}} \frac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^{\bar{s}}(\lambda_A)$$

where the ZAF term is the ZAF or ϕρz matrix correction factor for the element in the matrix. This not an entirely new idea, Myklebust included a correction for absorption with his overlap coefficient method in FRAME C.

Second, because the concentrations of elements will vary as the interference correction is applied, the full matrix adjusted interference correction expression shown above, must be enclosed inside an additional iteration loop to allow the interference correction to be recalculated after the concentration of each interfered element is subsequently determined.

Fig (15) Flow Chart of the iteration procedure

Flow Diagram of the Quantitative Iterated Interference Correction



As you can see, this loop here is the typical ZAF or phi-rho-z iteration loop and surrounding it, the quantitative interference correction iteration loop.

It may seem at first, that the addition of an extra iteration loop is somewhat overkill for the calculation of the matrix effects of the interference correction, and in many cases it is, but it is exactly this additional iteration loop that allows us to not only calculate for "self interfering" overlaps, but also to correct for "cascade" overlaps without regard to the order of the interferences.

One small consideration is that this additional iteration loop would increase the number of computations by the square of the iterations, but thanks to Moore's Law, which posulates that the speed of microprocessors doubles every 18 months, we have absolutely no cause for concern there.

An Approximation

Eq (3)

$$C_A^u = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I^u(\lambda_A) - \frac{[ZAF]_{\lambda_A}^{\bar{s}}}{C_B^{\bar{s}}} \frac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^{\bar{s}}(\lambda_A)}{I_A^s(\lambda_A)}$$

.

The full expression for the correction of interferences, along with the normal matrix correction for the concentration of the interfered element is shown here. As you can see, the term in the upper left, is the previously shown interference correction for the unknown intensity, after which the normal matrix correction procedure is applied.

However, there is one practical difficulty with eq. (3). It turns out that it is slightly difficult to estimate the fluorescence terms, here in the interference correction, because knowledge of the identity of all the excited lines would be required. Fortunately, except in some unusual cases, these fluorescence terms are generally near unity and can be neglected. Consequently, I have approximated equation (3) with

Eq. (4)

$$\mathrm{C}_\mathrm{A}^\mathrm{u} \approx \frac{\mathrm{C}_\mathrm{A}^\mathrm{s}}{[\mathrm{ZAF}]_{\lambda_\mathrm{A}}^\mathrm{s}} [\mathrm{ZAF}]_{\lambda_\mathrm{A}}^\mathrm{u} \frac{\mathrm{I}^\mathrm{u}(\lambda_\mathrm{A}) - \frac{[\mathrm{ZA}]_{\lambda_\mathrm{A}}^{\bar{\mathrm{s}}}}{\mathrm{C}_\mathrm{B}^{\bar{\mathrm{s}}}} \frac{\mathrm{C}_\mathrm{B}^\mathrm{u}}{[\mathrm{ZA}]_{\lambda_\mathrm{A}}^\mathrm{u}} \mathrm{I}_\mathrm{B}^{\bar{\mathrm{s}}}(\lambda_\mathrm{A})}{\mathrm{I}_\mathrm{A}^\mathrm{s}(\lambda_\mathrm{A})},$$

and it is this expression that I will be using in the following data reductions.

Cascade Analyses

Starting with the "cascade" interferences, let's perform some actual analyses on our old friends, the NBS SRM alloys for which we have already seen some spectra for. In table (6) we can see that equation (1), using the simple interfering intensity ratio, significantly over estimates the interference due to the secondary fluorescence of Fe Kα by Ni and hence the interference of the trace quantity of Co in the sample. On the other hand, eq. (2), using the quantitative expression for the interfering element, produces a result which calls to mind the phrase coined by Joe Michael of "spurious accuracy".

And in the other case, the Ti to V to Cr (Ti Kβ → V Kα - V Kβ → Cr Kα) “cascade” interference in SRM 654b causes eq. (1) to actually calculate a "negative" concentration. On the other hand, equation (2) using the quantitative iteration, handles the situation quite reasonably.

Table (6), Analyses exhibiting interferences of the “cascade” variety.

	wt. % (nominal)	wt. % (uncorrected)	wt. % (Eq. 1)	wt. % (Eq. 2)
Ni K ⇒ Fe Kα Fe Kβ → Co Kα	Co 0.022[1]	0.089 ± 0.008	0.010	0.022 ± 0.008
Ti Kβ → V Kα V Kβ → Cr Kα	Cr 0.025[2]	0.268 ± 0.01	-0.020	0.021 ± 0.010

[1] SRM 1159 includes : Ni 48.2, Fe 51.0, C 0.007, Mn 0.30, P 0.003, S 0.003, Si 0.32, Cu 0.038, Cr 0.06, Mo 0.01

[2] SRM 654b includes : Ti 88.974, Al 6.34, V 4.31, Fe 0.23, Si 0.045, Ni 0.028, Sn 0.023, Cu 0.004, Mo 0.013, Zr 0.008

Self-Interfering Analyses

Table (7) Analyses exhibiting interferences of the “self-interfering” variety.

	wt. % (nominal)	wt. % (uncorrected)	wt. % (Eq. 1)	wt. % (Eq. 2)
Ba Lα ↔ Ti Kα (PET)	Ba 33.15[3] Ti 11.69	33.26 ± 0.18 11.71 ± 0.08	33.08 11.59	33.08 ± 0.18 11.59 ± 0.08
Pb Lα ↔ As Kα	Pb 59.69[4] As 21.58	106.20 ± 0.33 41.38 ± 0.27	19.64 6.60	61.25 ± 1.97 22.15 ± 1.04

[3] Benitoite (BaTiSi3O9) is assumed stoichiometric : Si 20.38, Ba 33.15, Ti 11.69, O 34.896

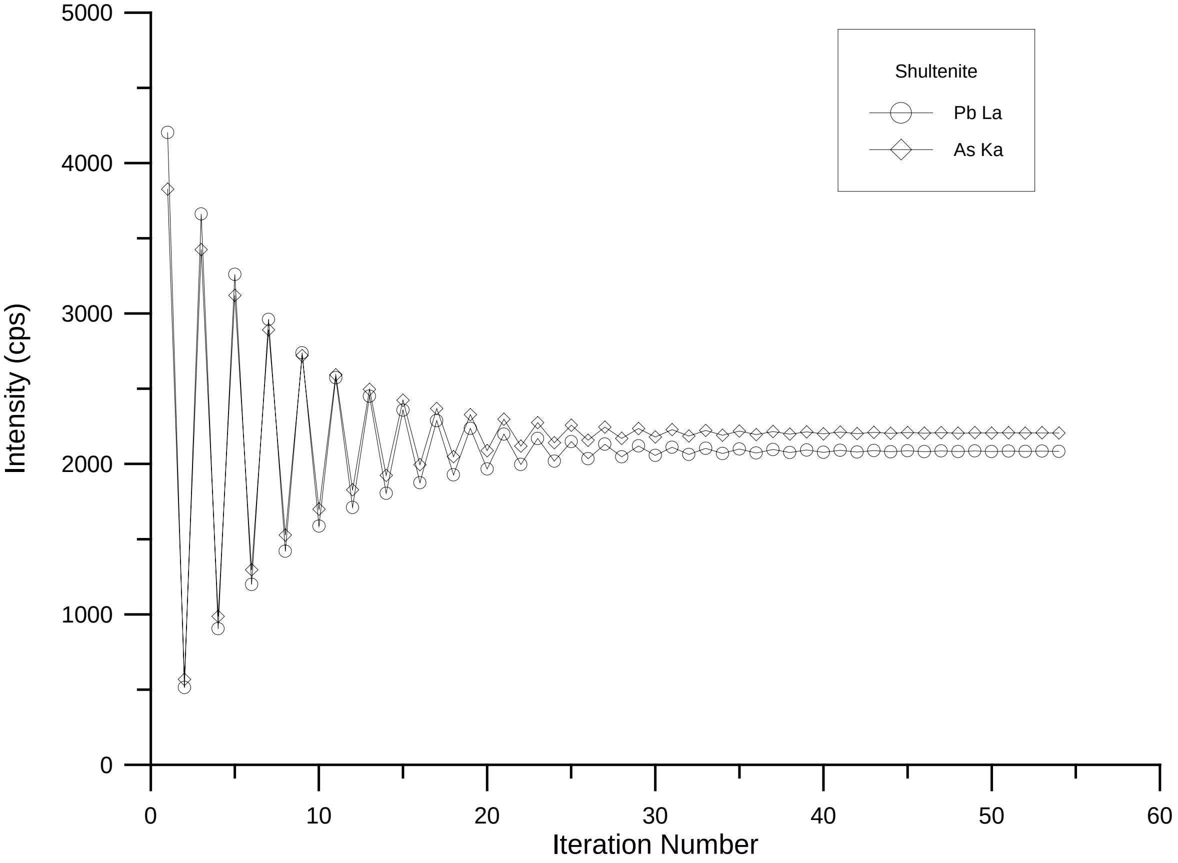
[4] Shultenite ($HAsPbO_4$) is assumed stoichiometric : Pb 59.69, As 21.58, O 18.44. The oxygen concentration was measured at 19.8 wt. % and included in the matrix correction calculations.

In the case of “self-interfering” interferences, we can see in table (7), that small interferences, such as the Ba Lα ↔ Ti Kα system in the mineral Benitoite, are not difficult to deal with, even using equation (1). In fact, eq. (1) and (2) give exactly the same result within the precision of the analysis. This is because the matrix correction effect of the interfering line is negligible with this degree of overlap.

However, in the next example, a sample of Shultenite, with the ideal formulation $HAsPbO_4$, which contains the Pb Lα ↔ As Kα interference, the use of eq. (1) is obviously untenable, while equation (2) provides quite usable results in spite of a prolonged iteration procedure of approximately 50 iterations.

To show the difficulty of the convergence during the procedure, here in fig (16), I have graphed the change in the corrected intensity of Pb and As in the previously seen Shultenite calculation. As you can see, the iteration is extremely fierce but does eventually converge after some 50 or so iterations. Although I have not yet attempted it, it is likely that a hyperbolic iteration would converge somewhat more quickly.

Fig (16) Iteration of corrected intensities using the quantitative interference correction



However, in spite of the instability of the iteration, the analysis is good enough to at least confirm the identification as shown the table (8), where the results and calculated formula based on 4 O atoms of the previous Shultenite analysis is shown.

Table (8) Shultenite $HPbAsO_4$

```
Results in Elemental Weight Percents (Overlap Corrected)
Includes 0.312 H Calculated by Stoichiometry to O

ELEM:       Pb      As       O   SUM
    20  63.283  21.132  20.129 104.861
    21  59.046  23.467  19.811 102.636
    22  60.169  22.475  19.583 102.535
    23  62.504  21.539  19.624 103.977

AVER:   61.250  22.153  19.787 103.502
SDEV:    1.977   1.041    .249
```

```
Results Based on 4 Atoms of O
ELEM:       Pb      As       O   SUM
    20    .971    .897   4.000   6.868
    21    .921   1.012   4.000   6.933
    22    .949    .980   4.000   6.929
    23    .984    .938   4.000   6.921

AVER:     .956    .957   4.000   6.913
SDEV:     .028    .050    .000
```

Now, how well will this iteration technique work for the real world analysis of the previously mentioned sulphosalt ore minerals? For this, I obtained several specimens of Pb-As sulfides that were claimed to be Rathite, Jordanite, and Baumhauerite, each with a distinctive Pb-As ratio.

Table (9)

Rathite	$(PbS)_3$ (As2S3)$_2$
Jordanite	$(PbS)_4$ (As2S3)
Baumhauerite	$(PbS)_4$ (As2S3)$_3$

Jordanite

I first performed qualitative analysis on the specimens and from the acquired spectra, it was immediately apparent that the Rathite specimen was only a simple Fe sulfide and was therefore discarded. The Jordanite sample, however, gave the following intriguing analysis after correcting for interference using eq. (2).

Table (10) Jordanite (?) $(PbS)_4$ (As2S3)

```
Results in Elemental Weight Percents (Overlap Corrected)
ELEM:       Pb      As       S   SUM
    46  68.487  12.433  20.072 100.992
    47  69.599  11.729  19.256 100.584
    48  70.781  11.620  19.759 102.160
    49  64.479  13.488  19.848  97.815
    50  73.699   9.375  19.250 102.323
    51  72.970   9.540  19.279 101.789
    52  67.115  13.301  20.061 100.476
    53  66.667  13.553  19.741  99.960

AVER:   69.225  11.880  19.658 100.762
SDEV:    3.177   1.671    .350

Results Based on 4 Atoms of Pb
ELEM:       Pb      As       S   SUM
    46   4.000   2.008   7.575  13.583
    47   4.000   1.864   7.151  13.015
    48   4.000   1.816   7.215  13.031
    49   4.000   2.314   7.956  14.270
    50   4.000   1.407   6.751  12.158
    51   4.000   1.446   6.829  12.275
    52   4.000   2.192   7.726  13.918
    53   4.000   2.249   7.654  13.902

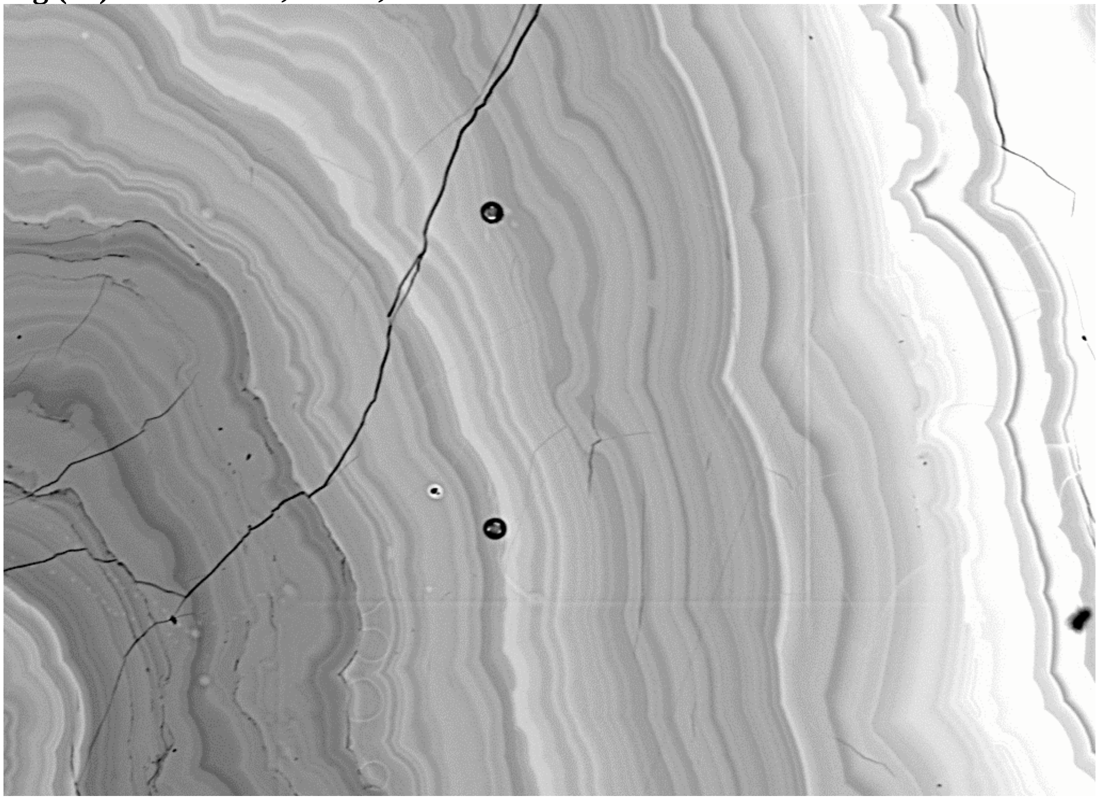
AVER:    4.000   1.912   7.357  13.269
SDEV:     .000    .348    .437
```

Since the ideal formula for Jordanite is 2 As and 7 S per 4 Pb atoms, the identification is reasonable, despite the obvious instability and resulting large standard deviations in the analysis.

Baumhauerite ?

The qualitative analysis of the alleged Baumhauerite was also performed, and immediately, it was discovered that the sample was just "slightly" inhomogeneous as seen in the following backscatter image.

Fig (17) BSE 20 keV, 20 nA, 1000x



However, I decided to continue and attempt to analyze the region near the rim of the material, since it seemed to be somewhat more homogeneous than the rest of the sample and could possibly contain a high Z element such as Pb as indicated by the higher BSE intensity. For this I was rewarded by the following quite reasonable analysis.

Table (11) Baumhauerite (?) $(PbS)_4$ $(As2S3)_3$

```
Results in Elemental Weight Percents (Overlap Corrected)
ELEM:       Pb      As       S   SUM
   990  38.244  32.544  25.930  96.718
   991  43.676  29.847  25.220  98.743
   992  46.014  28.958  24.809  99.781
   993  36.710  33.744  26.094  96.548
   994  46.770  29.248  25.152 101.170
   995  43.240  29.969  25.392  98.601
   996  41.550  31.464  26.367  99.381
   997  41.248  31.365  25.739  98.352
```

```
AVER:   42.182  30.892  25.588  98.662
SDEV:    3.501   1.682    .531

Based on 4 Pb atoms
ELEM:       Pb      As       S   SUM
   990   4.000   9.413  17.524  30.937
   991   4.000   7.559  14.925  26.484
   992   4.000   6.961  13.936  24.897
   993   4.000  10.168  18.372  32.540
   994   4.000   6.918  13.900  24.817
   995   4.000   7.667  15.178  26.845
   996   4.000   8.376  16.402  28.778
   997   4.000   8.411  16.128  28.540

AVER:    4.000   8.184  15.796  27.980
SDEV:     .000   1.152   1.617
```

However, something was still not quite right, as you can see by the formula calculation. Baumhauerite should have 6 As atoms and 13 S atoms for every 4 Pb atoms. On a hunch, I recalculated the formula based on 1 Pb atom as shown in this next table. Although the specimen is definitely not Baumhauerite, my money is on an identification of Sartorite, another Pb-As sulfide, which has an ideal formula of 2 As atoms and 4 S atoms per Pb atom.

Table (12) Sartorite (?!) (PbS) (As2S3)

```
Based on 1 Pb atoms
ELEM:       Pb      As       S   SUM
   990   1.000   2.353   4.381   7.734
   991   1.000   1.890   3.731   6.621
   992   1.000   1.740   3.484   6.224
   993   1.000   2.542   4.593   8.135
   994   1.000   1.729   3.475   6.204
   995   1.000   1.917   3.794   6.711
   996   1.000   2.094   4.100   7.195
   997   1.000   2.103   4.032   7.135
AVER:    1.000   2.046   3.949   6.995
SDEV:     .000    .288    .404
```

Timing

Finally, just in case anyone here has any doubts that pathological interferences can happen to you, I would like to share with you something that walked right into my lab only two weeks ago. In fact, just after I had these slides made. Perfect timing I must say.

```
St   17 Zn-ReSCN
TakeOff = 40  KiloVolts = 15
Elemental Composition

Elemental Wt. % Total:  100.000     Average Total Oxygen:     .000
Average Calcu. Oxygen:     .000    Average Excess Oxygen:     .000
Average Atomic Weight:   49.900    Average Atomic Number:   54.873

ELEM:       Re      Zn       S       O       N       C       H
XRAY:       la      ka      ka      ka      ka      ka
ELWT:   65.850   7.706  15.119   1.886   4.954   4.248    .238
KFAC:    .5426   .0847   .1091   .0047   .0104   .0067   .0024
ZCOR:   1.2135   .9102  1.3854  4.0163  4.7817  6.3580   .0000
```

```
ATWT:   17.647   5.882  23.529   5.882  17.647  17.647  11.765

On Peak Interferences for : St   17 Zn-ReSCN

For Re la      LiF at  1.43298 wt. %:   65.850
  Interference by Zn SKA3          at  1.42990 =       .1%
  Interference by Zn SKA'          at  1.43050 =       .1%
  Interference by Zn KA1           at  1.43550 =     11.1%
  Interference by Zn KA1,2         at  1.43680 =     15.8%
  Interference by Zn KA2           at  1.43930 =      4.4%

For Zn ka      LiF at  1.43652 wt. %:    7.706
  Interference by Re SLA^X         at  1.42690 =      2.8%
  Interference by Re SLA^IX        at  1.42960 =      3.9%
  Interference by Re SLA'          at  1.43020 =      4.2%
  Interference by Re LA1           at  1.43310 =    519.8%
  Interference by Re SLAS          at  1.43800 =      5.6%
  Interference by Re LA2           at  1.44420 =     40.7%

For  S ka      PET at  5.37386 wt. %:   15.119

For  O ka   NiCrBN at  24.0041 wt. %:    1.886
  Interference by Zn LB1      II   at  23.9800 =     34.7%
  Interference by Zn LA1      II   at  24.5020 =      1.0%
  Interference by Zn LA2      II   at  24.5020 =       .1%

For  N ka   NiCrBN at  32.1138 wt. %:    4.954

For  C ka   NiCrBN at  45.4269 wt. %:    4.248
```

As you can see from this nominal composition, the substance is some sort of an organic cyanide and according to the student it contains clusters of rhenium and sulfur atoms, ideally in the ratio of 6 rheniums to 9 sulfurs. However, the problem is that this substance also contains significant zinc, which not only interferes with the rhenium but is in turn interfered by the rhenium itself. A classic case of self interference, and as you can see from this calculation, the estimated interference will substantially affect the analysis.

Anyway, here is the analysis of the substance without any interference correction. As you can see the interference is indeed quite severe.

```
Un   10 Zn-ReSCN gr2
TakeOff = 40  KiloVolts = 20  Beam Current = 20  Beam Size = 0

Elemental Wt. % Total:  123.137     Average Total Oxygen:     .000
Average Atomic Weight:   54.342    Average Atomic Number:   53.229
Average ZAF Iteration:     4.00    Average MAN Iteration:     2.00

Results in Elemental Weight Percents

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.900   5.000   4.200    .200
SDEV:     .000    .000    .000    .000

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000  19.463  74.142  17.309    .000 122.214
```

```
    55    .000    .007  20.459  74.986  16.357    .000 123.108
    56    .000    .019  19.578  75.195  17.997    .000 124.089

AVER:     .000    .009  19.833  74.774  17.221    .000 123.137
SDEV:     .000    .010    .545    .558    .824    .000
SERR:     .000    .006    .314    .322    .476    .000
%RSD:       .1   113.3     2.7      .7     4.8      .1
STDS:      834     730     660     575     730     660

STKF:    .5968   .4279   .5007  1.0000   .4736   .5158
STCT:    627.1  3670.9  3712.9  3672.8  4423.1  1315.9

UNKF:    .0000   .0001   .2103   .6516   .0947   .0000
UNCT:     -2.7      .3  1559.2  2393.0   884.3    -3.2
UNBG:     11.6    28.0    67.3    61.5     6.6    64.0

ZCOR:   1.2061   .9201   .9433  1.1476  1.8189  1.0216
KRAW:   -.0043   .0001   .4199   .6516   .1999  -.0024
PKBG:      .77    1.01   24.18   40.00  135.89     .95

Results Based on 6 Atoms of re

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.774   5.334   5.225   2.965
SDEV:     .013    .040    .039    .022

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000   4.486   6.000   8.134    .000  34.048
    55    .000    .002   4.663   6.000   7.600    .000  33.518
    56    .000    .005   4.450   6.000   8.339    .000  34.005

AVER:     .000    .002   4.533   6.000   8.025    .000  33.857
SDEV:     .000    .003    .114    .000    .382    .000
SERR:     .000    .001    .066    .000    .220    .000
%RSD:       .8   113.2     2.5      .0     4.8      .8
```

And after utilizing the iterated quantitative interference correction, the results are almost acceptable, especially for an analysis performed by a student. As you can see the ratio of rhenium to sulfur is close to predicted.

```
Un   10 Zn-ReSCN gr2
TakeOff = 40  KiloVolts = 20  Beam Current = 20  Beam Size = 0

Elemental Wt. % Total:  101.134     Average Total Oxygen:      .000
Average Atomic Weight:   50.129    Average Atomic Number:   54.345
Average ZAF Iteration:     4.00    Average MAN Iteration:    14.33

Results in Elemental Weight Percents

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.900   5.000   4.200    .200
SDEV:     .000    .000    .000    .000

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
```

```
    53    .000    .000   6.325  65.726  17.333    .000 100.683
    55    .000    .007   7.471  65.113  16.343    .000 100.233
    56    .000    .019   6.188  66.949  18.029    .000 102.486

AVER:     .000    .009   6.661  65.929  17.235    .000 101.134
SDEV:     .000    .010    .704    .935    .848    .000
SERR:     .000    .006    .407    .540    .489    .000
%RSD:       .1   113.3    10.6     1.4     4.9      .0
STDS:      834     730     660     575     730     660

STKF:    .5968   .4279   .5007  1.0000   .4736   .5158
STCT:    627.1  3670.9  3712.9  3672.8  4423.1  1315.9

UNKF:    .0000   .0001   .0704   .5727   .0947   .0000
UNCT:     -2.7      .3   522.0  2103.2   884.3    -3.2
UNBG:     11.6    28.0    67.3    61.5     6.6    64.0

ZCOR:   1.2207   .9322   .9463  1.1513  1.8203  1.0207
KRAW:   -.0043   .0001   .1406   .5727   .1999  -.0024
PKBG:      .77    1.01    8.75   35.26  135.89     .95
INT%:      .00     .00  -66.57  -12.11     .00     .00

Results Based on 6 Atoms of re

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    2.013   6.050   5.926   3.363
SDEV:     .028    .085    .084    .047

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000   1.645   6.000   9.189    .000  34.236
    55    .000    .002   1.961   6.000   8.745    .000  34.274
    56    .000    .006   1.580   6.000   9.383    .000  34.053

AVER:     .000    .003   1.728   6.000   9.106    .000  34.188
SDEV:     .000    .003    .204    .000    .327    .000
SERR:     .000    .002    .118    .000    .189    .000
%RSD:      1.3   112.3    11.8      .0     3.6     1.4
```

Final slide (Escher)

In conclusion, I’d just like to say that, the use of a quantitatively iterated interference correction is an essential tool for WDS microanalysis. Because implementation of this algorithm is simple, it is desirable that this capability be available to the general EPMA community, not only for situations involving extreme and multiple overlaps, but even for the less severe and and more commonly encountered cases of minor spectral interferences.

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