

These are the analytical routines I've set up on the University of Arizona Cameca SX100 microprobe for the analysis of silicates, oxides, and other oxy-anion minerals in my FKM thin sections. A pair of sulfide analytical routines which I only use infrequently are also included. I've also encouraged the economic geology students in our research group to use these routines as well, since it's not always obvious at the start of a microprobe project what minor elements could turn out to be important or interesting. In several cases, students have discovered unexpected trace element enrichments in their samples that have then inspired new directions in their research.

The general format here is: first, the name of the analytical routine (and the major mineral groups I use it for), followed by the spectrometer and crystal arrangement. Following that is the list of condition 1 elements. Condition 1 is the low current, short counting time condition used for what I anticipate will be major elements. I generally use a 20 kV accelerating voltage and 20 nA beam current (on the cup) for condition 1. In addition to all of the expected major elements run under condition 1, these routines also include a variety of minor and potentially significant trace elements run at a second, high-current (usually 299 nA; also 20 kV), longer counting time condition 2. Rather than attempt to measure every element of interest in every mineral (which would make these analytical routines much longer), these routines have been optimized for specific mineral groups where possible (hence separate routines for epidote, titanite, and other minerals).

For each element listed below, I include: (1) the measured X-ray line followed by the standard used, (2) the on-peak counting time at the nominal peak position, in  $10000 \cdot \sin\theta$  units (peak positions may shift a bit, and are assessed each calibration and in some cases for different matrices), (3) the positions of the (-) and (+) backgrounds relative to the main peak position, in  $10000 \cdot \sin\theta$  units (backgrounds are counted for  $\frac{1}{2}$  the peak time on each background position), and (4) Cameca's internally calculated detection limits, which seem to be derived for a  $3\sigma$  confidence interval. Through the use of differential mode to minimize higher order X-ray interferences, and the careful choice of background measurement positions, these  $3\sigma$  detection limits for many of the sought trace elements have been reduced to less than 100-150 ppm, and in some cases even lower (note that the detection limits reported here are not absolute, but vary slightly depending on the mineral analyzed, the day's operating conditions, and even sample to sample... these values should be treated as a general guideline).

These analytical routines presume that minor and trace elements occur at relatively low concentrations. I've had to make some occasional adjustments when a minor element is present in unexpectedly high concentrations. To avoid issues with dead time corrections, I've typically "promoted" an abundant condition 2 trace element to a condition 1 major element. Another consideration is that the high current portion of the analytical routines can be a bit rough on some beam-sensitive samples. For samples where I recognize the potential for beam damage, I try to use a slightly broader beam (5-10  $\mu$ , where sample size allows), or very slowly move the focused beam on samples I'm confident are sufficiently homogeneous.

A final analytical consideration is that even with extreme care, it is sometimes challenging to find X-ray lines that are entirely free from interferences. The classic example is the slight overlap of the Ti  $K\beta$  peak on the V  $K\alpha$  peak. I've discovered in the course of analyzing unusual materials that unexpected interferences pop up in places I don't initially expect them. Whenever I've discovered these, I've gone back to the standards and made calibration curves in an attempt to quantify the overlaps. Although modern microprobe software is sophisticated enough to make these corrections for you (and this might be desirable if you're doing high precision analyses... note, however, that you still have to be aware these overlaps exist and you still have to set up the corrections in the initial calibration... the software won't do all of the work for you!), I prefer the simpler approach of just correcting my raw data offline in Excel with the overlap corrections I've previously measured. One important caveat, however, is that these overlaps vary depending on the analytical current you use. So while the values I include at the end of this document work reasonably well for the particular instrument and analytical conditions used with these routines (and in a pinch might be acceptable estimates for other analytical conditions), ideally you should develop and evaluate these for the instrument and operating conditions you are likely to use.

**petroSILICATE** analytical routine (for general silicates and oxides):

sp1	sp2	sp3	sp4	sp5
<u>TAP</u>	<u>LPET</u>	<u>LPET</u>	<u>TAP</u>	<u>LLIF</u>
<b>condition 1: 20 kV, 20 nA</b>				
Na K $\alpha$ (albite)	Ca K $\alpha$ (anorthite)	K K $\alpha$ (orthoclase)	Mg K $\alpha$ (forsterite)	Mn K $\alpha$ (rhodonite)
10 sec at 46258	10 sec at 38382	10 sec at 42762	10 sec at 38416	10 sec at 52199
-600 +600	-800 +600	-500 +750	-525 +525	-900 +500
3 $\sigma$ DL 342 ppm	3 $\sigma$ DL 144 ppm	3 $\sigma$ DL 161 ppm	3 $\sigma$ DL 359 ppm	3 $\sigma$ DL 384 ppm
Al K $\alpha$ (anorthite)	Ba L $\alpha$ (barite)	Ti K $\alpha$ (rutile)	Si K $\alpha$ (orthoclase)	Fe K $\alpha$ (fayalite)
10 sec at 32393	10 sec at 31726	10 sec at 31413	10 sec at 27678	10 sec at 48082
-550 +550	-900 +400	-500 +1100	-670 +600	-380 +850
3 $\sigma$ DL 294 ppm	3 $\sigma$ DL 454 ppm	3 $\sigma$ DL 166 ppm	3 $\sigma$ DL 262 ppm	3 $\sigma$ DL 434 ppm
<b>condition 2: 20 kV, 299 nA</b>				
F K $\alpha$ (sellaite)	Cl K $\alpha$ (marialite)	V K $\alpha$ (V metal)	Zn L $\alpha$ (zincite)	Ni K $\alpha$ (Ni-diopside)
20 sec at 71157	10 sec at 54033	40 sec at 28613	20 sec at 47602	40 sec at 41175
-1500 +1200	-425 +700	-800 +1100	-3200 +1075	-500 +700
3 $\sigma$ DL 606 ppm	3 $\sigma$ DL 32 ppm	3 $\sigma$ DL 28 ppm	3 $\sigma$ DL 99 ppm	3 $\sigma$ DL 51 ppm

Y L $\alpha$ (YAG)	Sr L $\alpha$ (SrTiO <sub>3</sub> )	Cr K $\alpha$ (chromite)	Zr L $\alpha$ (zircon)	Co K $\alpha$ (Co-diopside)
100 sec at 25049	30 sec at 78433	40 sec at 26169	100 sec at 23580	40 sec at 44429
-275 +200	-2450 +1075	-800 +600	-500 +700	-400 +500
3 $\sigma$ DL 73 ppm	3 $\sigma$ DL 123 ppm	3 $\sigma$ DL 22 ppm	3 $\sigma$ DL 122 ppm	3 $\sigma$ DL 46 ppm
Ga L $\alpha$ (GGG)	P K $\alpha$ (apatite)	Sc K $\alpha$ (Sc-diopside)		Cu K $\alpha$ (chalcopyrite)
100 sec at 43865	40 sec at 70367	40 sec at 34640		10 sec at 38260
-620 +620	-900 +930	-550 +1730		-500 +500
3 $\sigma$ DL 108 ppm	3 $\sigma$ DL 33 ppm	3 $\sigma$ DL 22 ppm		3 $\sigma$ DL 150 ppm
	Sn L $\alpha$ (cassiterite)	S K $\alpha$ (barite)		
	40 sec at 41143	40 sec at 61399		
	-800 +675	-1900 +1550		
	3 $\sigma$ DL 61 ppm	3 $\sigma$ DL 33 ppm		

**petroTOUMALINE** analytical routine (for tourmaline), is identical to the petroSILICATE analytical routine, but with 3.2 wt% B added as an unanalyzed element (note that this added B is only used to improve the PAP corrections... nominal B is calculated from the normalization). Similar approximate B additions are made for the analysis of axinite, serendibite, grandidierite and other borosilicates.

**petroEPIDOTE** analytical routine (for epidote and allanite group minerals; also for REE-bearing vesuvianite and other REE-bearing calc-silicate minerals):

sp1	sp2	sp3	sp4	sp5
<u>TAP</u>	<u>LPET</u>	<u>LPET</u>	<u>TAP</u>	<u>LLIF</u>
<b>condition 1: 20 kV, 20 nA</b>				
Na K $\alpha$ (albite)	Ca K $\alpha$ (anorthite)	Ti K $\alpha$ (rutile)	Mg K $\alpha$ (forsterite)	Mn K $\alpha$ (rhodonite)
10 sec at 46258	10 sec at 38382	10 sec at 31413	10 sec at 38416	10 sec at 52199
-600 +600	-800 +600	-500 +1100	-525 +525	-900 +500
3 $\sigma$ DL 384 ppm	3 $\sigma$ DL 185 ppm	3 $\sigma$ DL 211 ppm	3 $\sigma$ DL 283 ppm	3 $\sigma$ DL 439 ppm
Al K $\alpha$ (anorthite)			Si K $\alpha$ (orthoclase)	Fe K $\alpha$ (fayalite)
10 sec at 32393			10 sec at 27678	10 sec at 48082
-550 +550			-670 +600	-380 +850
3 $\sigma$ DL 280 ppm			3 $\sigma$ DL 246 ppm	3 $\sigma$ DL 552 ppm
<b>condition 2: 20 kV, 299 nA</b>				
F K $\alpha$ (sellaite)	Cl K $\alpha$ (marialite)	V K $\alpha$ (V metal)	Zn L $\alpha$ (zincite)	La L $\alpha$ (REE3 glass)
20 sec at 71157	10 sec at 54033	30 sec at 28613	20 sec at 47602	20 sec at 66202
-1500 +1200	-425 +700	-800 +1100	-3200 +1075	-855 +600
3 $\sigma$ DL 799 ppm	3 $\sigma$ DL 55 ppm	3 $\sigma$ DL 30 ppm	3 $\sigma$ DL 155 ppm	3 $\sigma$ DL 218 ppm

Y L $\alpha$ (YAG)	Sr L $\alpha$ (SrTiO <sub>3</sub> )	Cr K $\alpha$ (chromite)	Ga L $\alpha$ (GGG)	Ce L $\beta$ (REE3 glass)
100 sec at 25049	30 sec at 78433	30 sec at 26169	100 sec at 43865	20 sec at 58526
-275 +200	-2450 +1075	-800 +600	-620 +620	-340 +975
3 $\sigma$ DL 59 ppm	3 $\sigma$ DL 131 ppm	3 $\sigma$ DL 25 ppm	3 $\sigma$ DL 99 ppm	3 $\sigma$ DL 449 ppm
	Th M $\alpha$ (thorianite)	Sc K $\alpha$ (Sc-diopside)		Pr L $\beta$ (REE3 glass)
	40 sec at 47294	30 sec at 34640		20 sec at 56090
	-500 +500	-550 +1730		-700 +240
	3 $\sigma$ DL 108 ppm	3 $\sigma$ DL 22 ppm		3 $\sigma$ DL 407 ppm
	U M $\beta$ (uraninite)	Pb M $\alpha$ (NBS K0229)		Nd L $\beta$ (REE2 glass)
	40 sec at 42466	30 sec at 60412		20 sec at 53812
	-625 +450	-1000 +1300 (exp. fit)		-600 +420
	3 $\sigma$ DL 140 ppm	3 $\sigma$ DL 160 ppm		3 $\sigma$ DL 412 ppm
				Sm L $\beta$ (REE2 glass)
				20 sec at 49622
				-300 +345
				3 $\sigma$ DL 441 ppm

Gd L $\beta$  (REE1 glass)  
 20 sec at 45867  
 -300 +300  
 3 $\sigma$  DL 455 ppm

**petroEUDIALYTE** analytical routine (for eudialyte and related minerals), is similar to the petroEPIDOTE analytical routine, but adds to the routine Zr, Nb and K as condition 1 elements (see petroTITANITE and petroSILICATE for details), and P as an additional condition 2 element (see petroSILICATE for details).

**petroTITANITE** analytical routine (for titanite, rutile, perovskite and related minerals; sometimes I run rutile with petroSILICATE modified with added Nb):

sp1	sp2	sp3	sp4	sp5
<u>TAP</u>	<u>LPET</u>	<u>LPET</u>	<u>TAP</u>	<u>LLIF</u>
<b>condition 1: 20 kV, 20 nA</b>				
Na K $\alpha$ (albite)	Ca K $\alpha$ (anorthite)	Ti K $\alpha$ (rutile)	Si K $\alpha$ (orthoclase)	Mn K $\alpha$ (rhodonite)
10 sec at 46258	10 sec at 38382	10 sec at 31413	10 sec at 27678	10 sec at 52199
-600 +600	-800 +600	-500 +1100	-670 +600	-900 +500
3 $\sigma$ DL 376 ppm	3 $\sigma$ DL 209 ppm	3 $\sigma$ DL 267 ppm	3 $\sigma$ DL 238 ppm	3 $\sigma$ DL 427 ppm
Al K $\alpha$ (anorthite)				Fe K $\alpha$ (fayalite)
10 sec at 32393				10 sec at 48082
-550 +550				-380 +850
3 $\sigma$ DL 213 ppm				3 $\sigma$ DL 444 ppm

**condition 2: 20 kV, 299 nA**

F K $\alpha$ (sellaite)	Th M $\alpha$ (thorianite)	V K $\alpha$ (V metal)	Zr L $\alpha$ (zircon)	La L $\alpha$ (REE3 glass)
20 sec at 71157	50 sec at 47294	30 sec at 28613	120 sec at 23580	20 sec at 66202
-1500 +1200	-500 +500	-800 +1100	-500 +700	-855 +600
3 $\sigma$ DL 799 ppm	3 $\sigma$ DL 108 ppm	3 $\sigma$ DL 33 ppm	3 $\sigma$ DL 64 ppm	3 $\sigma$ DL 219 ppm
Y L $\alpha$ (YAG)	U M $\beta$ (uraninite)	Nb L $\alpha$ (LiNbO <sub>3</sub> )		Ce L $\beta$ (REE3 glass)
100 sec at 25049	50 sec at 42466	90 sec at 65422		20 sec at 58526
-275 +200	-625 +450	-270 +425		-340 +975
3 $\sigma$ DL 59 ppm	3 $\sigma$ DL 140 ppm	3 $\sigma$ DL 69 ppm		3 $\sigma$ DL 428 ppm
	Sn L $\alpha$ (cassiterite)			Pr L $\beta$ (REE3 glass)
	20 sec at 41143			20 sec at 56090
	-800 +675			-700 +240
	3 $\sigma$ DL 67 ppm			3 $\sigma$ DL 368 ppm
				Nd L $\beta$ (REE2 glass)
				20 sec at 53812
				-600 +420
				3 $\sigma$ DL 386 ppm

Sm L $\beta$  (REE2 glass)

20 sec at 49622

-300 +345

3 $\sigma$  DL 388 ppm

Gd L $\beta$  (REE1 glass)

20 sec at 45867

-300 +300

3 $\sigma$  DL 429 ppm

**petroAPATITE** analytical routine (for apatite and monazite; there are no apparent dead time correction issues resulting from measuring REE L $\beta$  peaks in REE-rich minerals at 299 nA):

sp1	sp2	sp3	sp4	sp5
<u>TAP</u>	<u>LPET</u>	<u>LPET</u>	<u>TAP</u>	<u>LLIF</u>
<b>condition 1: 20 kV, 20 nA</b>				
F K $\alpha$ (apatite)	Ca K $\alpha$ (apatite)	P K $\alpha$ (apatite)		Mn K $\alpha$ (rhodonite)
20 sec at 71157	10 sec at 38382	10 sec at 70367		10 sec at 52199
-1500 +1200	-800 +600	-900 +930		-900 +500
3 $\sigma$ DL 1346 ppm	3 $\sigma$ DL 214 ppm	3 $\sigma$ DL 303 ppm		3 $\sigma$ DL 481 ppm

Na K $\alpha$  (albite)  
10 sec at 46258  
-600 +600  
3 $\sigma$  DL 407 ppm

Cl K $\alpha$  (marialite)  
10 sec at 54033  
-425 +700  
3 $\sigma$  DL 100 ppm

Fe K $\alpha$  (fayalite)  
10 sec at 48082  
-380 +850  
3 $\sigma$  DL 585 ppm

**condition 2: 20 kV, 299 nA**

Y L $\alpha$  (YAG)  
60 sec at 25049  
-275 +200  
3 $\sigma$  DL 62 ppm

Th M $\alpha$  (thorianite)  
50 sec at 47294  
-500 +500  
3 $\sigma$  DL 127 ppm

V K $\alpha$  (V metal)  
90 sec at 28613  
-800 +1100  
3 $\sigma$  DL 29 ppm

Si K $\alpha$  (orthoclase)  
10 sec at 27678  
-670 +600  
3 $\sigma$  DL 200 ppm

La L $\alpha$  (REE3 glass)  
20 sec at 66202  
-855 +600  
3 $\sigma$  DL 229 ppm

As L $\alpha$  (NiAs)  
60 sec at 37565  
-850 +1800  
3 $\sigma$  DL 32 ppm

U M $\beta$  (uraninite)  
50 sec at 42466  
-625 +450  
3 $\sigma$  DL 156 ppm

S L $\alpha$  (barite)  
30 sec at 61399  
-1900 +1550  
3 $\sigma$  DL 29 ppm

As L $\alpha$  (NiAs)  
110 sec at 37565  
-850 +1800  
3 $\sigma$  DL 32 ppm

Ce L $\beta$  (REE3 glass)  
20 sec at 58526  
-340 +975  
3 $\sigma$  DL 493 ppm

Sr L $\alpha$  (SrTiO<sub>3</sub>)  
20 sec at 78433  
-2450 +1075  
3 $\sigma$  DL 139 ppm

Pr L $\beta$  (REE3 glass)  
20 sec at 56090  
-700 +240  
3 $\sigma$  DL 420 ppm

Nd L $\beta$  (REE2 glass)

20 sec at 53812

-600 +420

3 $\sigma$  DL 453 ppm

Sm L $\beta$  (REE2 glass)

20 sec at 49622

-300 +345

3 $\sigma$  DL 465 ppm

Gd L $\beta$  (REE1 glass)

20 sec at 45867

-300 +300

3 $\sigma$  DL 471 ppm

**quickSULFIDE** analytical routine (for triage of Cu-(Fe)-S minerals, and determining non-trace levels of Co, Ni and As in Fe-(Ni)-S minerals; a variation of this routine optimized for pyrite uses pyrite as the standard for S and Fe, and sometimes also transfers Co, Ni and As to a 299 nA second condition for lower DL):

sp1	sp2	sp3	sp4	sp5
<u>TAP</u>	<u>LPET</u>	<u>LPET</u>	<u>TAP</u>	<u>LLIF</u>
<b>condition 1: 20 kV, 20 nA</b>				
As L $\alpha$ (NiAs)	S K $\alpha$ (troilite)			Fe K $\alpha$ (toilite)
40 sec at 37565	20 sec at 61399			10 sec at 48082
-850 +1800	-500 +1550			-1100 +850
3 $\sigma$ DL 366 ppm	3 $\sigma$ DL 329 ppm			3 $\sigma$ DL 493 ppm
				Ni K $\alpha$ (Ni metal)
				10 sec at 41175
				-650 +750
				3 $\sigma$ DL 570 ppm
				Co K $\alpha$ (Co metal)
				10 sec at 44429
				-400 +1000
				3 $\sigma$ DL 620 ppm

Cu K $\alpha$  (chalcopyrite)  
 10 sec at 38260  
 -700 +500  
 3 $\sigma$  DL 704 ppm

**petroSULFIDE** analytical routine (for general sulfides and sulfosalts; note that in lieu of crystal flipping, this analytical routine would not be run during the same analytical session as the previous routines, due to the use of different crystals on sp4 and sp5. petroSULFIDE has only been tested a limited number of times, and the backgrounds, potential interferences, detection limits and elements sought may evolve as this routine is tested more. This routine should be considered a "beta" version. Elements in gray were not included in the earlier testing but are planned for the next iteration of this routine):

sp1	sp2	sp3	sp4	sp5
<u>TAP</u>	<u>LPET</u>	<u>LPET</u>	<u>LIF</u>	<u>LPET</u>
<b>condition 1: 20 kV, 100 nA</b>				
Zn L $\alpha$ (ZnS)	Ag L $\alpha$ (matildite)	Bi M $\alpha$ (matildite)	Fe K $\alpha$ (troilite)	S K $\alpha$ (troilite)
10 sec at 47602	20 sec at 47481	50 sec at 58490	10 sec at 48082	10 sec at 61399
-725 +500	-750 +850	-300 +555	-1100 +850	-500 +1550
3 $\sigma$ DL 338 ppm	3 $\sigma$ DL 161 ppm	3 $\sigma$ DL 279 ppm	3 $\sigma$ DL 322 ppm	3 $\sigma$ DL 114 ppm

Ga L $\alpha$ (GaAs)	In L $\alpha$ (InP)	Sn L $\alpha$ (Sn metal)	Cu K $\alpha$ (enargite)	Pb M $\alpha$ (galena)
20 sec at 43865	40 sec at 43110	0 sec at 41143	10 sec at 38260	10 sec at 60412
-1250 +570	-1200 +850	-1250 +730	-700 +500	-1300 +500
3 $\sigma$ DL 248 ppm	3 $\sigma$ DL 115 ppm	3 $\sigma$ DL ? ppm	3 $\sigma$ DL 524 ppm	3 $\sigma$ DL 632 ppm
Ge L $\alpha$ (Ge metal)	Te L $\alpha$ (ZnTe)	Hg M $\alpha$ (cinnabar)	Co K $\alpha$ (Co metal)	Sb L $\alpha$ (stibnite)
20 sec at 40538	40 sec at 37592	50 sec at 64513	40 sec at 44429	20 sec at 39309
-1000 +600	-970 +800	-600 +1100	-400 +1000	-450 +550
3 $\sigma$ DL 210 ppm	3 $\sigma$ DL 101 ppm	3 $\sigma$ DL 275 ppm	3 $\sigma$ DL 170 ppm	3 $\sigma$ DL 165 ppm
As L $\alpha$ (NiAs)	Tl M $\alpha$ (none at present)	V K $\alpha$ (V metal)	Ni K $\alpha$ (NiAs)	Cd L $\alpha$ (Cd metal)
20 sec at 37565	0 sec at 62405	0 sec at 28613	40 sec at 41175	0 sec at 45217
-1150 +200	not determined	not determined in sulfides	-650 +750	-500 +870
3 $\sigma$ DL 266 ppm	3 $\sigma$ DL ? ppm	3 $\sigma$ DL ? ppm	3 $\sigma$ DL 180 ppm	3 $\sigma$ DL ? ppm
Se L $\alpha$ (ZnSe)	Cl K $\alpha$ (marialite)			Mn K $\alpha$ (Mn metal)
30 sec at 34920	0 sec at 54033			0 sec at 24022
-500 +675	not determined in sulfides			-550 +800
3 $\sigma$ DL 183 ppm	3 $\sigma$ DL ? ppm			3 $\sigma$ DL ? ppm

## Overlap corrections (done offline in Excel)

The following overlap corrections are the ones I've incorporated into my mineral normalization routines. These corrections assume that the interfered element is treated as a trace element and run at 299 nA (unless otherwise noted). If the interfered element is run at a lower current, the overlap will be less (since all the peaks will be less intense). Although I assume the full concentration range of the interfering element contributes to spurious counts for the element of interest (and thus I always apply a simple linear correction, regardless of the interfering element concentration), in reality the correction is likely a more complex function, with probably little to no correction necessary if the interfering element is low abundance and its peak is small. I also do not make any adjustments to the PAP calculations applied to the other elements due to any small amounts of a particular spurious element. For high precision work on low trace elements concentrations, one would probably want to use the built-in peak overlap correction software available on the microprobe to address these potential complexities. Note that this list is not exhaustive; these interferences are the only ones that I've encountered so far in the particular non-sulfide matrices I've looked at. As I run across other overlap interferences, I will update this document. Check out my "Setting up mineral normalizations in Excel" PDF to see how I incorporate these formulas in my spreadsheets (with appropriate "if" statements to avoid nonsensical negative weight percents).

Ce M $\alpha$  overlap on F K $\alpha$  on TAP:

$$F_{(\text{nominal})} = F_{(\text{measured})} - 0.013 * Ce_{(\text{measured})}$$

Zn L $\beta$  overlap on Na K $\alpha$  on TAP (Na measured at 20 nA):

$$Na_{(\text{nominal})} = Na_{(\text{measured})} - 0.0351 * Zn_{(\text{measured})}$$

Ca K $\beta$  overlap on Sc K $\alpha$  on LPET:

$$Sc_{(\text{nominal})} = Sc_{(\text{measured})} - 0.0007 * Ca_{(\text{measured})}$$

P K $\alpha$  (2<sup>nd</sup> order) overlap on Zn L $\alpha$  on TAP:

$$Zn_{(\text{nominal})} = Zn_{(\text{measured})} - 0.0395 * P_{(\text{measured})}$$

Mg K $\beta$  overlap on As L $\alpha$  on TAP:

$$As_{(\text{nominal})} = As_{(\text{measured})} - 0.0166 * Mg_{(\text{measured})}$$

Cr K $\alpha$  (3<sup>rd</sup> order) overlap on Sr L $\alpha$  on PET:

$$Sr_{(\text{nominal})} = Sr_{(\text{measured})} - 0.0099 * Cr_{(\text{measured})}$$

P K $\alpha$  overlap on Zr L $\alpha$  on TAP:

$$Zr_{(\text{nominal})} = Zr_{(\text{measured})} - 0.043 * P_{(\text{measured})}$$

This next pair is complicated by the fact that both the Ba L $\alpha$  and Ti K $\alpha$  lines are commonly sought, and each interfere with the other. In common Ti-rich minerals with little to no anticipated Ba (e.g. rutile, titanite), and in common Ba minerals with little to no anticipated Ti (e.g. barite, celsian), the "correction to the correction" is probably insignificant. For minerals with both Ba and Ti but in relatively small amounts (e.g. in particular, some micas), the circular corrections may also be relatively insignificant. For those less common minerals with major quantities of both Ba and Ti (i.e. benitoite, taramellite, lamprophyllite), one either has to use an iterative approach to ascertain the nominal Ba and Ti counts, or select different X-ray lines or analyzing crystals. Note that due to the differing intensities of the L and K lines, the Ti interference on Ba appears to be ~4X more problematic than the Ba interference on Ti.

Ba L $\alpha$  overlap on Ti K $\alpha$  on PET (Ti measured at 20 nA):

$$Ti_{(nominal)} = Ti_{(measured)} - 0.0051 * Ba_{(measured)}$$

Ti K $\alpha$  overlap on Ba L $\alpha$  on PET (Ba measured at 20 nA):

$$Ba_{(nominal)} = Ba_{(measured)} - 0.019 * Ti_{(measured)}$$

V K $\alpha$  suffers interferences not only from well-known Ti K $\beta$ , but also from various L lines of Ba and several LREE elements. The REE corrections are especially relevant to determine the wakefieldite component of monazite or the mukhinite component of allanite. The precise determination of low levels of V in a mineral with major Ba, Ti, and REE (e.g. joaquinite) would be challenging. Note that measured Ti and Ba are not used for the correction, because these may in part be spurious themselves, and the spurious components would not contribute to erroneous V; nominal (or "corrected") Ti and Ba are used.

Ti K $\beta$  overlap on V K $\alpha$  on PET:

$$V_{(nominal)} = V_{(measured)} - 0.054 * Ti_{(nominal, \text{ after Ba correction})}$$

Ba L $\beta$ 3 overlap on V K $\alpha$  on PET:

$$V_{(nominal)} = V_{(measured)} - 0.0106 * Ba_{(nominal, \text{ after Ti correction})}$$

La L $\beta$  overlap on V K $\alpha$  on PET:

$$V_{(nominal)} = V_{(measured)} - 0.0xx * La_{(measured)} \text{ (correction recognized but not yet calibrated)}$$

Ce L $\alpha$  overlap on V K $\alpha$  on PET:

$$V_{(nominal)} = V_{(measured)} - 0.0021 * Ce_{(measured)}$$

Pr Ln overlap on V K $\alpha$  on PET:

$$V_{(nominal)} = V_{(measured)} - 0.0xx * Pr_{(measured)} \text{ (correction recognized but not yet calibrated)}$$

This next pair of overlap corrections shows the difference between treating an interfered element as a trace element (measured at 299 nA) or treating it as a major element (measured at 20 nA), and thus demonstrates how the overlap correction is also current-dependent. As in the previous example with the Ti and Ba overlap on V, here also only real V contributes to spurious Cr.

V K $\beta$  overlap on Cr K $\alpha$  on PET (Cr measured at 299 nA):

$$Cr_{(nominal)} = Cr_{(measured)} - 0.103 * V_{(nominal, \text{ after Ti, Ba and REE corrections})}$$

V K $\beta$  overlap on Cr K $\alpha$  on PET (Cr measured at 20 nA):

$$Cr_{(nominal)} = Cr_{(measured)} - 0.072 * V_{(nominal, \text{ after Ti, Ba and REE corrections})}$$

The following overlap corrections are the ones so far observed in the more extensive petroSULFIDE routine. This routine has been little used so far, and so it's possible these overlaps could be reduced or eliminated by selecting different analytical lines. Conversely, it's also likely that other interferences will be discovered once a wider selection of diverse sulfides and sulfosalts are tested.

Zn L $\beta$ 4 overlap on Ga L $\alpha$  on TAP:

$$Ga_{(\text{nominal})} = Ga_{(\text{measured})} - 0.0017 * Zn_{(\text{measured})}$$

As L $\beta$ 4 overlap on Se L $\alpha$  on TAP:

$$Se_{(\text{nominal})} = Se_{(\text{measured})} - 0.0023 * As_{(\text{measured})}$$