

Study of Trace Phosphorus in Zircon (large interference from Zr La line) using both TAP and PET Bragg crystals

Conditions: 20 keV, 50 nA, 10 um beam, 300 seconds on peak count time
Samples: Synthetic ZrSiO4 and natural zircon (GRR-486, from Chi Ma)

The example below is a synthetic zircon that is presumably pure (ICPMS analysis pending). This first EPMA analysis is shown without the interference correction applied. Note the large differences in concentration between the spectrometers due to different overlap ratios due to different crystal selections (and therefore spectral resolution).

Note also use of “same-side” off-peak background corrections due to presence of large Zr la peak on low side of P ka peak and that Zr was only measured on one spectrometer for the interference correction.

ELEM:	p ka	p ka	p ka	p ka	p ka	zr la
BGD:	OFF	OFF	OFF	OFF	OFF	OFF
SPEC:	1	2	3	4	5	5
CRYST:	TAP	LPET	LPET	TAP	PET	PET
ORDER:	1	1	1	1	1	2

On and Off Peak Positions:

ONPEAK	23964.0	70392.0	70308.4	23988.0	70376.0	69398.0
OFFSET	7.46094	-4.7344	78.8672	-16.539	11.2656	-10.875
HIPEAK	25390.1	71598.0	71495.4	25239.0	71420.9	69986.2
LOPEAK	24665.4	70822.8	70691.5	24686.5	70852.6	68809.9
HI-OFF	1426.10	1205.98	1187.03	1251.04	1044.90	588.195
LO-OFF	701.357	430.758	383.094	698.463	476.578	-588.10

PHA Parameters:

ELEM:	p ka	p ka	p ka	p ka	p ka	zr la
DEAD:	3.00	3.25	3.31	2.90	2.97	2.97
BASE:	.50	.56	.50	.56	.56	.56
WINDOW	4.00	4.00	4.00	4.00	4.00	4.00
MODE:	0	0	0	0	0	0
GAIN:	1750.	1186.	1321.	1324.	963.	963.
BIAS:	1300.	1290.	1850.	1293.	1830.	1830.

Un 4 Std#257 as unknown

TakeOff = 40.0 KiloVolt = 20.0 Beam Current = 50.0 Beam Size = 10
(Magnification (analytical) = 20000), Beam Mode = Analog Spot
(Magnification (default) = 600, Magnification (imaging) = 200)
Number of Data Lines: 20 Number of 'Good' Data Lines: 20
First/Last Date-Time: 01/16/2008 07:15:30 PM to 01/16/2008 10:26:06 PM

Average Total Oxygen:	.000	Average Total Weight%:	100.343
Average Calculated Oxygen:	.000	Average Atomic Number:	24.776
Average Excess Oxygen:	.000	Average Atomic Weight:	30.525
Average ZAF Iteration:	3.00	Average Quant Iterate:	2.00

WARNING- Duplicate analyzed elements are present in the sample matrix!!

Use Aggregate Intensity option or Disable Quant feature for accurate matrix correction.

Using Conductive Coating Correction For Beam Energy Loss and Absorption: (No Coating)

Results in Elemental Weight Percents

SPEC:	Si	O					
TYPE:	SPEC	SPEC					
AVER:	15.323	34.913					
SDEV:	.000	.000					
ELEM:	P	P	P	P	P	Zr	
BGDS:	LIN	LIN	LIN	LIN	LIN	LIN	
TIME:	300.00	300.00	300.00	300.00	300.00	40.00	
ELEM:	P	P	P	P	P	Zr	SUM
XRAY:	(ka)	(ka)	(ka)	(ka)	(ka)	(la)	
119	.255	.013	.010	.171	.013	49.628	100.327
120	.259	.011	.009	.177	.013	49.804	100.509
121	.257	.016	.011	.167	.015	49.550	100.251
122	.262	.014	.015	.175	.016	49.472	100.190
123	.262	.015	.013	.177	.023	49.678	100.404
124	.259	.016	.014	.178	.028	49.402	100.132
125	.255	.016	.016	.177	.012	49.727	100.439
126	.266	.014	.016	.175	.029	49.704	100.441
127	.265	.020	.011	.177	.017	49.724	100.450
128	.265	.019	.011	.183	.024	49.626	100.364
129	.265	.016	.015	.177	.023	49.623	100.355
130	.281	.015	.012	.180	.018	49.508	100.251
131	.264	.018	.013	.168	.024	49.783	100.506
132	.252	.012	.009	.170	.000	49.773	100.452
133	.258	.014	.009	.174	.018	49.597	100.304
134	.261	.010	.013	.173	.017	49.668	100.378
135	.256	.009	.010	.174	.019	49.605	100.309
136	.261	.012	.009	.174	.016	49.548	100.255
137	.269	.016	.010	.170	.019	49.559	100.278
138	.267	.013	.010	.172	.021	49.544	100.263
AVER:	.262	.014	.012	.174	.018	49.626	100.343
SDEV:	.006	.003	.002	.004	.006	.108	
SERR:	.001	.001	.001	.001	.001	.024	
%RSD:	2.5	19.0	20.9	2.3	35.0	.2	
STDS:	285	285	285	285	285	257	
STKF:	.1619	.1619	.1619	.1619	.1619	.4109	
STCT:	10027.8	7370.5	4684.3	11200.7	1452.2	1235.3	
UNKF:	.0020	.0001	.0001	.0013	.0001	.4101	
UNCT:	121.2	4.9	2.5	90.2	1.2	1232.9	
UNBG:	63.1	16.9	12.0	69.3	5.7	27.2	
ZCOR:	1.3377	1.3377	1.3377	1.3377	1.3377	1.2101	
KRAW:	.0121	.0007	.0005	.0081	.0008	.9980	
PKBG:	2.92	1.29	1.21	2.30	1.22	46.43	

The example below is with the quantitative interference correction applied from the single Zr channel. Note that all spectrometers now report concentrations close to within statistics.

Un 4 Std#257 as unknown
 TakeOff = 40.0 KiloVolt = 20.0 Beam Current = 50.0 Beam Size = 10
 (Magnification (analytical) = 20000), Beam Mode = Analog Spot
 (Magnification (default) = 600, Magnification (imaging) = 200)
 Number of Data Lines: 20 Number of 'Good' Data Lines: 20
 First/Last Date-Time: 01/16/2008 07:15:30 PM to 01/16/2008 10:26:06 PM

Average Total Oxygen: .000 Average Total Weight%: 99.929
 Average Calculated Oxygen: .000 Average Atomic Number: 24.830
 Average Excess Oxygen: .000 Average Atomic Weight: 30.535
 Average ZAF Iteration: 3.00 Average Quant Iterate: 4.00

WARNING- Duplicate analyzed elements are present in the sample matrix!!
 Use Aggregate Intensity option or Disable Quant feature for accurate matrix
 correction.

Using Conductive Coating Correction For Beam Energy Loss and Absorption: (No
 Coating)

Results in Elemental Weight Percents

SPEC: Si O
 TYPE: SPEC SPEC

AVER: 15.3230 34.9130
 SDEV: .00000 .00000

ELEM: P P P P P Zr
 BGDS: LIN LIN LIN LIN LIN LIN
 TIME: 300.00 300.00 300.00 300.00 300.00 40.00

ELEM:	P	P	P	P	P	Zr	SUM
XRAY:	(ka)	(ka)	(ka)	(ka)	(ka)	(la)	
119	-.00501	.00395	.00134	-.00167	.00105	49.6834	99.9191
120	-.00242	.00200	.00061	.00349	.00077	49.8593	100.100
121	-.00368	.00622	.00217	-.00617	.00282	49.6058	99.8431
122	.00177	.00468	.00636	.00156	.00438	49.5269	99.7817
123	-.00009	.00519	.00457	.00295	.01096	49.7338	99.9933
124	-.00127	.00625	.00475	.00423	.01615	49.4574	99.7235
125	-.00812	.00678	.00692	.00254	.00023	49.7829	100.027
126	.00295	.00487	.00735	-.00017	.01724	49.7599	100.028
127	.00110	.01004	.00219	.00168	.00509	49.7801	100.036
128	.00171	.00902	.00162	.00793	.01195	49.6820	99.9502
129	.00064	.00677	.00586	.00195	.01061	49.6791	99.9409
130	.001751	.00555	.00248	.00470	.00619	49.5644	99.8368
131	-.00190	.00843	.00404	-.00862	.01201	49.8392	100.089
132	-.001394	.00223	-.00033	-.00658	-.01222	49.8297	100.035
133	-.00786	.00389	-.00066	-.00274	.00594	49.6531	99.8877
134	-.00542	-.00019	.00376	-.00432	.00452	49.7252	99.9595
135	-.001050	-.00038	.00082	-.00337	.00671	49.6620	99.8912
136	-.00547	.00254	-.00086	-.00354	.00364	49.6046	99.8369
137	.00189	.00584	.00092	-.00740	.00612	49.6157	99.8590
138	-.00024	.00358	.00067	-.00562	.00823	49.6009	99.8435

AVER: -.00192 .00486 .00273 -.00096 .00612 49.6823 99.9291
 SDEV: .00647 .00277 .00257 .00468 .00645 .10779
 SERR: .00145 .00062 .00057 .00105 .00144 .02410
 %RSD: -337.2 57.1 94.1 -487.8 105.4 .2
 STDS: 285 285 285 285 285 257

STKF: .1619 .1619 .1619 .1619 .1619 .4109
 STCT: 10027.8 7370.5 4684.3 11200.7 1452.2 1235.3

UNKF:	.0000	.0000	.0000	.0000	.0000	.4101
UNCT:	-.9	1.7	.6	-.5	.4	1232.9
UNBG:	63.1	16.9	12.0	69.3	5.7	27.2
ZCOR:	1.3393	1.3393	1.3393	1.3393	1.3393	1.2115
KRAW:	-.00009	.00022	.00013	-.00004	.00028	.99805
PKBG:	.98705	1.09942	1.05027	.99360	1.07590	46.4284
INT%:	-100.78	-68.88	-80.14	-100.61	-340.97	----

The example below is a natural zircon with the same corrections as above. Note that some spectrometers are systematically different by some -40 PPM to +50 PPM (as can also be observed in the synthetic specimen above). These systematic differences in the continuum shape are due to “holes” in the background from analyzing crystal defects (Donovan, et al., 2007)

Un 5 GRR-486a
 TakeOff = 40.0 KiloVolt = 20.0 Beam Current = 50.0 Beam Size = 10
 (Magnification (analytical) = 20000), Beam Mode = Analog Spot
 (Magnification (default) = 600, Magnification (imaging) = 200)
 Number of Data Lines: 20 Number of 'Good' Data Lines: 20
 First/Last Date-Time: 01/16/2008 10:36:26 PM to 01/17/2008 01:46:59 AM

Average Total Oxygen:	.000	Average Total Weight%:	99.705
Average Calculated Oxygen:	.000	Average Atomic Number:	24.796
Average Excess Oxygen:	.000	Average Atomic Weight:	30.489
Average ZAF Iteration:	3.05	Average Quant Iterate:	4.00

WARNING- Duplicate analyzed elements are present in the sample matrix!!
 Use Aggregate Intensity option or Disable Quant feature for accurate matrix correction.

Using Conductive Coating Correction For Beam Energy Loss and Absorption: (No Coating)

Results in Elemental Weight Percents

SPEC:	Si	O
TYPE:	SPEC	SPEC
AVER:	15.3230	34.9130
SDEV:	.00000	.00000

ELEM:	P	P	P	P	P	Zr
BGDS:	LIN	LIN	LIN	LIN	LIN	LIN
TIME:	300.00	300.00	300.00	300.00	300.00	40.00

ELEM:	P	P	P	P	P	Zr	SUM
XRAY:	(ka)	(ka)	(ka)	(ka)	(ka)	(la)	
139	-.00368	.00541	.00631	-.00072	-.00519	49.5431	99.7812
140	-.00783	.00465	.00087	.00784	.00063	49.6480	99.8902
141	-.01202	.00131	.00322	.00736	.00458	49.7448	99.9853
142	-.00404	.00709	.00258	.00698	.00054	49.7513	100.000
143	-.00187	.00519	-.00025	-.00054	-.00007	49.5262	99.7646
144	-.00830	.00423	.00178	.00399	-.00455	49.4077	99.6408
145	-.00669	.00653	.00115	-.00224	.00980	49.6913	99.9358
146	-.00302	.00527	.00342	.00333	.01761	49.1763	99.4389
147	-.00328	.00397	.00149	-.00109	-.00100	49.4837	99.7198
148	-.00835	.00410	.00321	.00356	.00609	49.5081	99.7527
149	-.00429	.00327	.00125	-.00146	.00699	49.5204	99.7622

150	-.00312	.00831	.00634	.00639	.00245	49.3972	99.6536
151	-.00241	.00592	.00312	.00139	.00069	49.4046	99.6493
152	-.00596	.00566	.00372	.00472	.00923	49.3880	99.6413
153	-.00354	.00584	.00289	.00398	.00764	49.0152	99.2680
154	-.00294	.00248	.00563	.00420	.00217	49.3563	99.6038
155	-.00294	.00677	.00222	-.00243	.00678	49.3424	99.5888
156	-.00093	.00420	.00718	.00727	.00649	49.2913	99.5515
157	-.00195	.00635	.00212	.00268	.00926	49.6351	99.8896
158	-.00338	.00495	.00202	.00304	.00128	49.3477	99.5916
AVER:	-.00453	.00507	.00301	.00291	.00407	49.4589	99.7055
SDEV:	.00279	.00164	.00199	.00338	.00544	.18669	
SERR:	.00062	.00037	.00044	.00076	.00122	.04174	
%RSD:	-61.6	32.3	66.0	116.1	133.5	.4	
STDS:	285	285	285	285	285	257	
STKF:	.1619	.1619	.1619	.1619	.1619	.4109	
STCT:	9653.6	7097.3	4482.0	10759.3	1396.6	1234.1	
UNKF:	.0000	.0000	.0000	.0000	.0000	.4081	
UNCT:	-2.0	1.7	.6	1.4	.3	1225.7	
UNBG:	63.5	16.7	11.9	69.6	5.8	27.7	
ZCOR:	1.3398	1.3398	1.3398	1.3398	1.3398	1.2120	
KRAW:	-.00021	.00023	.00014	.00013	.00019	.99314	
PKBG:	.96828	1.09983	1.05363	1.02121	1.04804	45.2855	
INT%:	-101.71	-67.28	-78.55	-98.44	-85.08	----	

The example below is the same natural zircon sample but this time with the “iterated blank correction” applied to correct for systematic differences in the continuum shape due to “holes” in the background. Note that all spectrometers now report values within statistics and the results now range from -26 to +38 PPM, an improved result due to the accuracy of the blank correction.

Un 5 GRR-486a
 TakeOff = 40.0 KiloVolt = 20.0 Beam Current = 50.0 Beam Size = 10
 (Magnification (analytical) = 20000), Beam Mode = Analog Spot
 (Magnification (default) = 600, Magnification (imaging) = 200)
 Number of Data Lines: 20 Number of 'Good' Data Lines: 20
 First/Last Date-Time: 01/16/2008 10:36:26 PM to 01/17/2008 01:46:59 AM
 WARNING- Using Blank Trace Correction

Average Total Oxygen:	.000	Average Total Weight%:	99.696
Average Calculated Oxygen:	.000	Average Atomic Number:	24.798
Average Excess Oxygen:	.000	Average Atomic Weight:	30.490
Average ZAF Iteration:	3.00	Average Quant Iterate:	4.00

WARNING- Duplicate analyzed elements are present in the sample matrix!!
 Use Aggregate Intensity option or Disable Quant feature for accurate matrix correction.

Results in Elemental Weight Percents

SPEC:	Si	O				
TYPE:	SPEC	SPEC				
AVER:	15.3230	34.9130				
SDEV:	.00000	.00000				
ELEM:	P	P	P	P	P	Zr
BGDS:	LIN	LIN	LIN	LIN	LIN	LIN

TIME: 300.00 300.00 300.00 300.00 300.00 40.00							
ELEM:	P	P	P	P	P	Zr	SUM
XRAY:	(ka)	(ka)	(ka)	(ka)	(ka)	(la)	
139	-.00176	.00054	.00357	.00024	-.01130	49.5443	99.7716
140	-.00591	-.00022	-.00185	.00879	-.00549	49.6493	99.8806
141	-.01009	-.00355	.00049	.00831	-.00154	49.7461	99.9757
142	-.00212	.00222	-.00014	.00793	-.00558	49.7525	99.9908
143	.00005	.00033	-.00298	.00042	-.00618	49.5274	99.7550
144	-.00637	-.00063	-.00095	.00494	-.01066	49.4089	99.6312
145	-.00477	.00167	-.00158	-.00128	.00368	49.6926	99.9263
146	-.00110	.00041	.00069	.00428	.01149	49.1865	99.4383
147	-.00136	-.00089	-.00124	-.00013	-.00711	49.4849	99.7102
148	-.00643	-.00076	.00048	.00452	-.00003	49.5094	99.7431
149	-.00237	-.00159	-.00148	-.00050	.00087	49.5217	99.7526
150	-.00120	.00344	.00361	.00734	-.00367	49.3984	99.6440
151	-.00049	.00105	.00039	.00235	-.00542	49.4058	99.6397
152	-.00404	.00080	.00099	.00567	.00311	49.3892	99.6317
153	-.00162	.00098	.00016	.00494	.00152	49.0164	99.2584
154	-.00102	-.00238	.00290	.00516	-.00394	49.3575	99.5943
155	-.00102	.00191	-.00051	-.00147	.00066	49.3436	99.5791
156	.00099	-.00066	.00445	.00822	.00037	49.2925	99.5419
157	-.00003	.00148	-.00061	.00364	.00314	49.6364	99.8800
158	-.00146	.00009	-.00071	.00399	-.00484	49.3489	99.5820
AVER:	-.00261	.00021	.00028	.00387	-.00205	49.4606	99.6963
SDEV:	.00279	.00164	.00199	.00338	.00543	.18600	
SERR:	.00062	.00037	.00044	.00076	.00121	.04159	
%RSD:	-106.9	770.4	697.4	87.3	-265.4	.4	
STDS:	285	285	285	285	285	257	
STKF:	.1620	.1620	.1620	.1620	.1620	.4110	
STCT:	9653.6	7097.3	4482.0	10759.3	1396.6	1234.1	
UNKF:	.0000	.0000	.0000	.0000	.0000	.4082	
UNCT:	-1.2	.1	.1	1.9	-.1	1225.7	
UNBG:	63.5	16.7	11.9	69.6	5.8	27.7	
ZCOR:	1.3382	1.3382	1.3382	1.3382	1.3382	1.2117	
KRAW:	-.00012	.00001	.00001	.00018	-.00009	.99314	
PKBG:	.98173	1.00473	1.00602	1.02805	.98014	45.2855	
INT%:	-101.71	-67.28	-78.55	-98.44	-85.08	----	
BLNK#:	4	4	4	4	4	----	
BLNKL:	.000000	.000000	.000000	.000000	.000000	----	
BLNKV:	-.00192	.004858	.002727	-.00096	.006114	----	

J. J. Donovan and D. A. Wark and M. J. Jercinovic, "Improved EPMA Trace Element Accuracy Using A Matrix Iterated Quantitative Blank Correction", *Microscopy and Microanalysis*, 2007