Microanalysis Standards and Instrumental Calibration: Practical Improvements in Analytical Confidence

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Electron-probe microanalysis (EPMA) can in principle use a minimal set of standards to analyze diverse compounds over the entire concentration range. Careful measurement procedures result in precise analyses, and accuracy relative to a set of primary standards is evaluated through use of secondary standards. The inspection of analyses on secondary standards is the main test an analyst has to evaluate accuracy. Few studies have evaluated accuracy for multielement mineral and glass standards, but analysts quote accuracy of approximately 2-5% when questioned. Is this figure correct and how are sets of standards evaluated in an objective manner?

Certification testing of NIST SRM 481 AuAg binary alloys utilized relations between measured k and known C (where $k=(P-B)^{smp}/(P-B)^{std}$ and C is concentration) to demonstrate the internal consistency and accuracy of EPMA measurements at multiple accelerating potential (FIG 1A)[1]. K-ratio measurements on binary alloys of known composition have been used to develop correction algorithms in order to minimize the difference between measured and calculated k-ratio (FIG 1B), and these plots again demonstrate consistency in the compositional data set [2]. However, there are few if any published k-ratio data on multi-element mineral standards, and there is typically anecdotal evidence concerning estimates of accuracy for these materials.

Procedures used to evaluate the alignment of multiple x-ray spectrometers can also be used to test the agreement of microanalysis standards. All spectrometers on a properly aligned instrument should measure identical k-ratios k^{exp} relative to a set of pure element, oxide, or silicate standards. Further, these k^{exp} should equal calculated k-ratios k^{corr} obtained using correction algorithms with valid data sets (e.g., mass absorption coefficients). A plot of k^{exp}/k^{corr} vs. weight percent of each element reveals systematic errors in instrumental or compositional aspects, and the use of multiple spectrometer data simplifies detection of instrumental problems while errors in composition or correction should apply systematically to all measured values. The use of this plot thus demonstrates internal consistency of the standards used if the instrument is performing properly. This approach provides significant confidence in measurement on an instrument and has revealed systematic errors in spectrometer alignment and the composition of standards in the suite. A suite of mineral standards has been used for this purpose, and includes compositions in the Ca-Mg-Al-Si-Ti-Fe (CMASTF) compositional system (FIG 1C). This suite of standards was analyzed by both EDS and WDS methods using primary standards $CaSiO_3$, MgO, Al_2O_3, SiO_2, TiO_2, and Fe_2O_3. Measurements were made on a JEOL JXA-8200 microprobe with 5 WDS spectrometers and an E2V-Gresham SDD EDS detector, using the Probe for EPMA analysis software, and were obtained at 15 kV, 25nA, and 10-20 um defocused beam. Repeaking of the WDS spectrometer was necessary for Mg, Si, and Al for phases where a peak shift is observed due to bonding effects. All analyses were corrected using the Armstrong Φ(ρz) algorithm with "LINEMU" macs of Probe for EPMA (Henke, Henke and Ebisu, and Heinrich).

The results indicate excellent accuracy and agreement among the chosen standards for major and minor element concentrations, but for trace elements errors are observed for some standards that are well out of the range of counting statistics (FIG 2A and 2B). The accepted composition for Al in Weill glass E (nominal 8.99% Al_2O_3) is incorrect by 15% relative, when viewed with all analytical data. The accuracy of all WDS analyses expressed in 1σ percent of k^{exp}/k^{corr} ranges from 0.6-2.27% with most values less than 1%. Thus the relative accuracy of the standard analyses is as good as 1% relative. Results from SDD EDS analyses will also be presented.

References

[1] Heinrich KFJ et al. NBS Special Publication 260-28. 1971.
[2] Pouchou, JL, and Pichoir, F. in Electron Probe Quantitation, KFJ Heinrich and DE Newbury, eds. Plenum, New York, 1991.
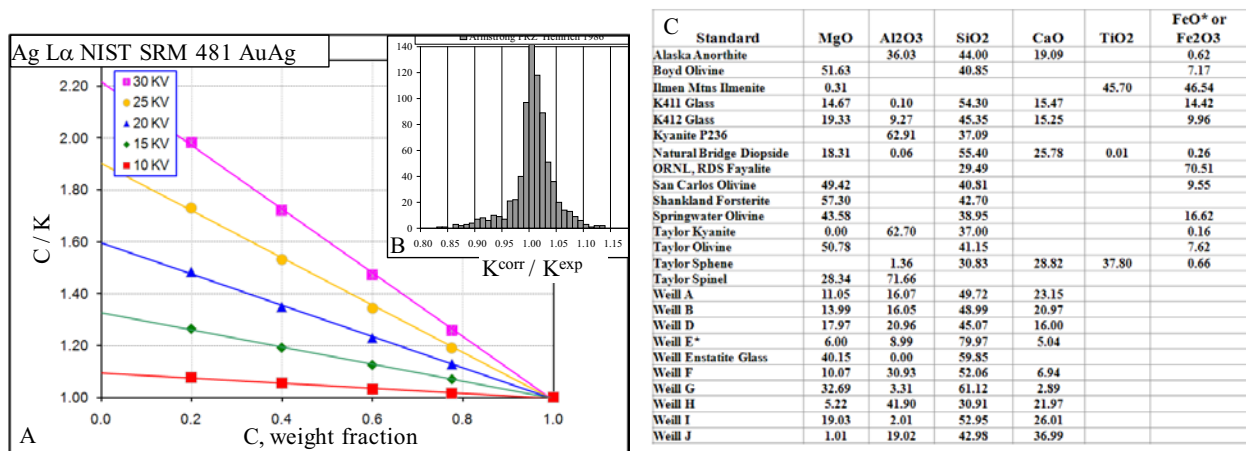
C Standard	MgO	Al2O3	SiO2	CaO	TiO2	FeO* or Fe2O3
Alaska Anorthite		36.03	44.00	19.09		0.62
Boyd Olivine	51.63		40.85			7.17
Ilmen Mtns Ilmenite	0.31				45.70	46.54
K411 Glass	14.67	0.10	54.30	15.47		14.42
K412 Glass	19.33	9.27	45.35	15.25		9.96
Kyanite P236		62.91	37.09			
Natural Bridge Diopside	18.31	0.06	55.40	25.78	0.01	0.26
ORNL, RDS Fayalite			29.49			70.51
San Carlos Olivine	49.42		40.81			9.55
Shankland Forsterite	57.30		42.70			
Springwater Olivine	43.58		38.95			16.62
Taylor Kyanite	0.00	62.70	37.00			0.16
Taylor Olivine	50.78		41.15			7.62
Taylor Sphene		1.36	30.83	28.82	37.80	0.66
Taylor Spinel	28.34	71.66				
Weill A	11.05	16.07	49.72	23.15		
Weill B	13.99	16.05	48.99	20.97		
Weill D	17.97	20.96	45.07	16.00		
Weill E*	6.00	8.99	79.97	5.04		
Weill Enstatite Glass	40.15	0.00	59.85			
Weill F	10.07	30.93	52.06	6.94		
Weill G	32.69	3.31	61.12	2.89		
Weill H	5.22	41.90	30.91	21.97		
Weill I	19.03	2.01	52.95	26.01		
Weill J	1.01	19.02	42.98	36.99		

FIG 1 A K-ratio data for Ag Lα in NIST SRM 418 AuAg alloys at 40 degree takeoff angle. Plots demonstrate internal consistency of experimental measurements and confirm AuAg concentrations. **B** Histogram of calculated k-ratios relative to experimental k-ratios for Pouchou binary alloy set (n=900), corrected using Armstrong $\Phi(\rho z)$ algorithm and Heinrich 1986 macs. **C** Composition of standards used in Ca-Mg-Al-Si-Ti-Fe suite.

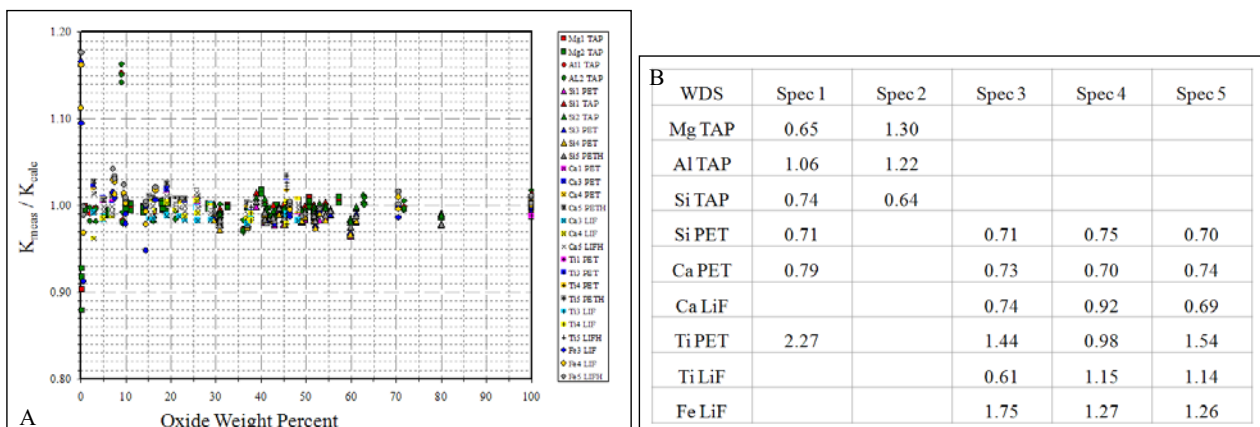| B WDS	Spec 1	Spec 2	Spec 3	Spec 4	Spec 5
Mg TAP	0.65	1.30			
Al TAP	1.06	1.22			
Si TAP	0.74	0.64			
Si PET	0.71		0.71	0.75	0.70
Ca PET	0.79		0.73	0.70	0.74
Ca LiF			0.74	0.92	0.69
Ti PET	2.27		1.44	0.98	1.54
Ti LiF			0.61	1.15	1.14
Fe LiF			1.75	1.27	1.26

FIG 2 A Plot of K^{exp} / K^{corr} vs. oxide weight percent for all WDS measurements on CMASTF standards data set. Note outlier for Al in glass Weill E is clearly incorrect in comparison to all analyses. **B** Accuracy of WDS analyses of CMASTF standards set, expressed in 1σ relative % in error of K^{exp} / K^{corr}.