

EPMA Standards: The Good, the Bad, and the Ugly

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The technique of electron-probe microanalysis (EPMA) is remarkable because a set of primary calibration standards allows accurate microanalysis in multiple phases over a wide range of concentration. Other analytical techniques require calibration curves and characterization of secondary standards which have limited applicability outside of the calibration range. Significant advances in microprobe instrumentation and correction algorithms over the past 50 years have resulted in the ability to better perform quantitative analysis of materials. EPMA depends fundamentally on primary calibration standards and verification of accuracy by analysis of secondary standards. Standards should be homogeneous on the micron scale, well characterized, widely available to international laboratories, and similar in composition to typical samples in order to minimize reliance on correction algorithms. Most standards fail to satisfy one or more of these criteria, and indeed, the technique of EPMA is deficient with respect to diverse standards.

Eugene Jarosewich, a meteorite analytical chemist, made an impressive contribution to EPMA by characterizing a suite of mineral standards that have been extensively used in the international community. These standards were analyzed by classical wet chemistry techniques and EPMA measurements were made to establish intergrain variation via sigma ratios, and an additional study evaluated interlaboratory accuracy of EPMA [1,2]. These standards, in addition to NIST SRM's, are materials that have analytical pedigree not dependent on EPMA analysis alone and serve as a framework for comparison of EPMA to other techniques. These standards are "the Good". A comparison of wet chemistry and EPMA data for San Carlos olivine is shown in Figure 1, which uses the same EPMA measurements processed with ZAF and $\Phi(\rho z)$ algorithms and old vs. new mass absorption coefficient data sets to demonstrate the improvement in analytical accuracy with time and internal consistency of synthetic and natural olivine standards.

Many analysts use pure elements, oxides, and stoichiometric materials of assumed composition (e.g., Al_2O_3 , Al_2SiO_5) as EPMA standards. Many samples represent compositional systems not covered by these standards and out of necessity one must use materials that have a comparatively inferior pedigree. Standards derived from small master fragments cannot practically be analyzed by techniques other than EPMA, so their working analyses are a function of accuracy issues of the microprobe technique. Commercially available standard mounts are available to the international environment, and must be generated using large fragments from well-stocked supplies of standard materials as the customer prefers 1 mm chunks to 10 μm grains. The Taylor standard mounts used in many laboratories contain standards whose origin is undocumented and have analyses that presumably include several techniques. Other mounts contain minerals of intermediate composition and materials that are a multiphase intergrowth. Thus, all materials with assumed composition, uncertain origin, calibration solely by EPMA, or homogeneity problems, must be viewed as deficient. These standards are "the Bad". Many standards fall into this category, but this problem can be partly remedied simply by improving the characterization database.

A number of laboratories use standard mounts which contain pure element and oxide standards. These mounts were typically purchased long ago and have never been repolished or recoated. Many pure elements form a native oxide layer with time, and proper maintenance requires storage in a

vacuum or inert atmosphere, with periodic repolishing and recoating. Reliance on these as the sole primary standard results in systematic underestimation of those elements in samples. Figure 2 shows the effect of a native oxide layer on emitted x-ray intensity for Mg, Al, Fe, Cd, and U. These standards become a multilayer thin film material, and with thickening of the layer a significant portion of the x-ray signal originates in the oxide layer rather than the substrate. Due to their degradation these standards are “the Ugly”, and represent the most serious problem with respect to EPMA accuracy and interlaboratory comparison. The remedy requires careful repolishing.

References

- [1] Jarosewich et al., Geostandards Newsletter, Vol 4, no. 1, pp43-47, 1980.
- [2] Jarosewich, et al., Smithsonian Contrib. Earth Sci., 22:53–67, 1979.

Oxide	Wet Chem	PDR	PAPF-1	Arm-1	PAPF-2	Arm-2	PAPF-3	Arm-3
Oxide	Wet Chem	PDR Ox / H66	PAPF-1 Ox / H86	Arm-1 Ox / H86	PAPF-2 Ol / H86	Arm-2 Ol / H86	PAPF-3 Ol / FF	Arm-3 Ol / FF
MgO	49.42	50.10	50.04	49.82	49.44	49.44	48.98	49.00
SiO ₂	40.81	40.74	40.66	40.07	40.56	40.58	40.34	40.69
FeO*	9.55	10.13	10.08	9.89	9.89	9.89	9.89	9.74
Total	100.29	101.66	101.47	100.47	100.60	100.60	99.90	100.12
Σ M ²⁺	2.005	2.025	2.025	2.034	2.016	2.016	2.014	2.003
Si	0.997	0.986	0.986	0.982	0.991	0.991	0.992	0.997
Mg/(Mg+Fe)	0.902	0.898	0.899	0.900	0.899	0.901	0.898	0.900

PDR: Philibert-Duncumb-Reed ZAF, oxide standards, Heinrich 1966 macs
 PAPF-1 and Arm-1: Φ(ρz) algorithms, oxide standards, Heinrich 1986 macs
 PAPF-2 and Arm-2: synthetic olivine standards, Heinrich 1986 macs
 PAPF-3 and Arm-3: synthetic olivine standards, FFAST macs
 Same k-ratios, n=4, CaO 0.09, Cr₂O₃ 0.06, MnO 0.14, NiO 0.37 (wt %)
 Olivine Formula: M²⁺₂SiO₄

Figure 1 EPMA analyses of San Carlos olivine compared to wet chemistry of Jarosewich et al. [1]. Historical improvement in accuracy is summarized beginning with ZAF using oxide standards and ending with Φ(ρz) using synthetic forsterite and fayalite standards and current mac data set.

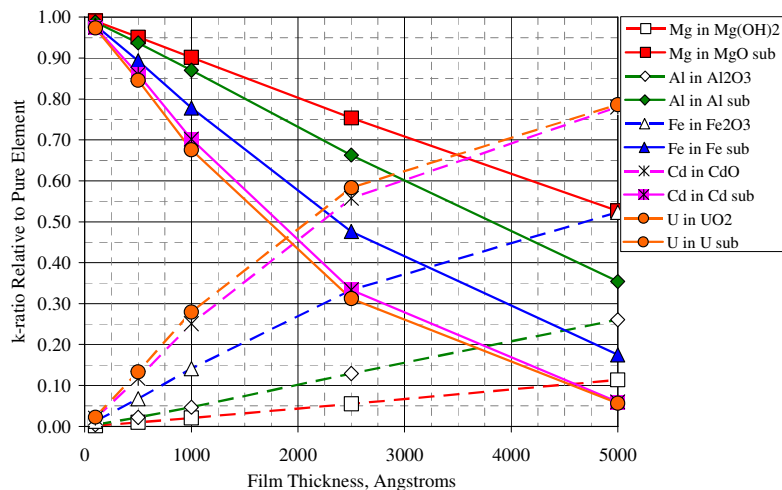


Figure 2 Effect of oxide layer on pure element standards. GMR thin-film used to calculate x-ray intensity relative to pure element for oxide layer of 100-5000 Angstroms. For higher Z materials the x-ray signal is intensified due to backscattering from the substrate. For all materials, percent level loss of substrate signal is observed for oxide layer of 100 A thickness.