

CALCZAF, TRYZAF and CITZAF: The Use of Multi-Correction-Algorithm Programs for Estimating Uncertainties and Improving Quantitative X-ray Analysis of Difficult Specimens

John T. Armstrong¹, John J. Donovan² and Paul C. Carpenter³

¹. Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA.

². CAMCOR, University of Oregon, Eugene, OR, USA.

³. Dept. of Earth and Planetary Sciences, McDonnell Center for the Space Sciences, Washington University, Saint Louis, MO, USA.

Much work has been done in the last 50 years in developing comprehensive correction algorithms for quantitative electron microbeam analysis. A number of correction methods – both theoretically and empirically based – have been used, incorporating or parameterizing various compilations of physical constants like mass absorption coefficients and mean ionization potentials. There is no single, universally accepted correction method used for microbeam analysis and the correction programs employed by the commercial instrument manufacturers give different results for the same input data.

In the 1990's efforts were made to standardize and codify the various correction models currently in use [e.g., 1] and a computer program, CITZAF, was developed to allow comparison of these different algorithms [2]. Over the years, this program has morphed and expanded in different versions [e.g., 3], and now the most versatile and sophisticated of these, CalcZAF, is available as freeware on the internet [4]. The program continues to evolve using numerical integration and Monte Carlo methods to enable analysis under non-standard conditions. It calculates fitting parameters, such as polynomial α -factors [e.g., 5] helpful in evaluating correction behaviour in extended analytical systems.

Figure 1 shows plots of calculated α -factors vs. concentration for a binary alloy system, Pt-Si, comprised of a high-Z and a low-Z element. The variation in the position, shape and direction of slope of these curves shows the disparity in compositional determination by the various correction procedures and sets of mass absorption coefficients. Table 1 shows the predicted variation in calculated composition for the analysis of PtSi using pure metal standards at high and low beam energies. There is over a 15% relative variation in the calculated concentration of Si depending on which correction is used. Lowering the beam energy does not improve the analytical uncertainty. Reducing the uncertainty in this case would require finding a standard closer in composition to the sample than the pure metals. Programs like CalcZAF are useful both in predicting analytical uncertainty and in seeing under what circumstances individual correction methods cease to produce accurate results. Further developments planned for this program include continued efforts at more realistic modeling of x-ray fluorescence effects and more extensive integration of modern Monte Carlo simulation procedures in bulk, thin film and particle corrections.

References:

- [1] "Electron Probe Quantitation", ed. K. Heinrich and D. Newbury, Plenum Press, New York (1991).
- [2] J. Armstrong, *Microbeam Analysis* **4** (1995), p. 177.
- [3] J. Donovan, et al., *Am. Mineral.* **77** (1992), p. 444.
- [4] <http://epmalab.uoregon.edu/calczaf.htm>
- [5] J. Armstrong, *Microscopy and Microanalysis* **12** (suppl. 2) (2006), p. 183.

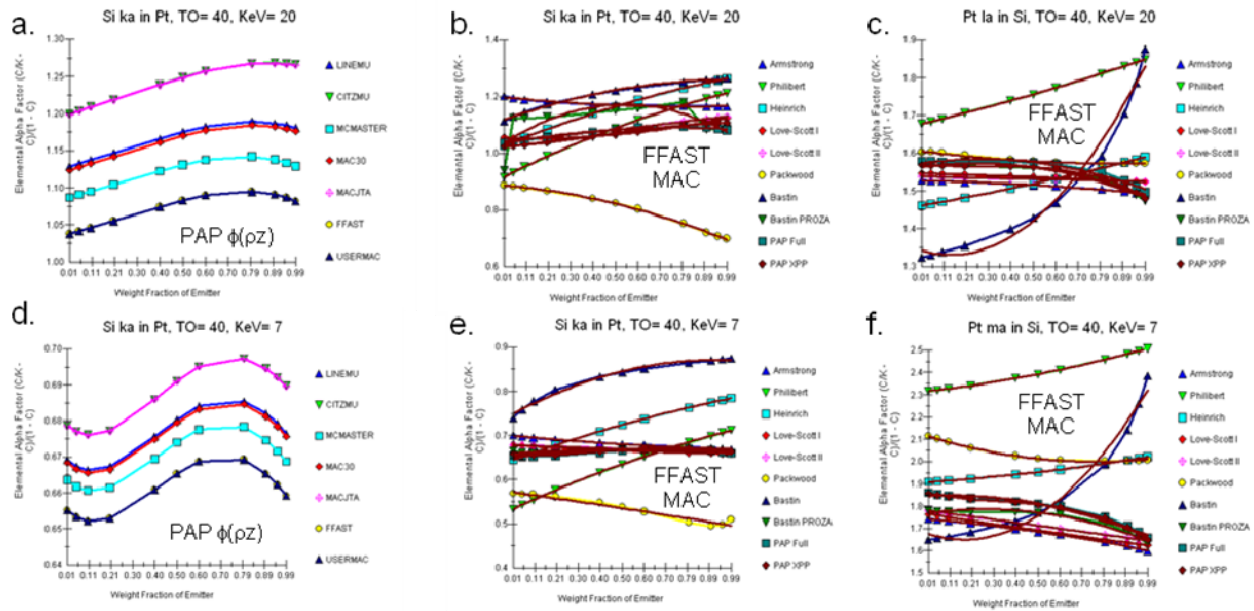


Figure 1. Plots of α -factor $[(C/k - C) / (1 - C)]$ vs. C for Si in Pt and Pt in Si at 20 and 7 keV. (a) and (d) show the difference in calculated α 's for the same correction procedure and different mass absorption coefficients. (b), (c), (e), and (f) show the differences for the same mass absorption coefficients but different correction algorithms.

Pt L, Si K 20 keV							Pt M, Si K 7 keV							
Elemental Weight Percents:			Atomic Percents:			Correction Procedure Used:	Elemental Weight Percents:			Atomic Percents:				
ELEM:	Pt	Si	TOTAL	Pt	Si	TOTAL	(all with LINEMU (Henke) MACs)	ELEM:	Pt	Si	TOTAL	Pt	Si	TOTAL
1	87.57	14.08	101.65	47.25	52.75	100	Armstrong/Love Scott	1	86.69	13.28	99.96	48.45	51.55	100
2	89.64	11.48	101.12	52.92	47.08	100	Philibert/Duncumb-Reed	2	92.68	10.87	103.55	55.12	44.88	100
3	87.80	12.59	100.39	50.11	49.89	100	Heinrich/Duncumb-Reed	3	90.15	12.75	102.90	50.45	49.55	100
4	87.35	12.56	99.91	50.04	49.96	100	Love-Scott I	4	86.80	12.93	99.72	49.16	50.84	100
5	87.33	12.54	99.88	50.06	49.94	100	Love-Scott II	5	87.04	12.94	99.98	49.19	50.81	100
6	87.09	10.88	97.97	53.55	46.45	100	Packwood Phi(pz)	6	88.97	11.14	100.11	53.48	46.52	100
7	89.13	13.74	102.87	48.28	51.72	100	Bastin (original) Phi(pz)	7	91.94	14.78	106.72	47.25	52.75	100
8	87.52	13.45	100.97	48.37	51.64	100	Bastin PROZA Phi(pz)	8	87.17	12.73	99.90	49.65	50.35	100
9	87.41	12.59	100.00	50.00	50.00	100	Pouchou and Pichoir (PAP)	9	87.42	12.59	100.00	50.00	50.00	100
10	87.17	12.37	99.54	50.36	49.64	100	Pouchou and Pichoir (XPP)	10	87.36	12.63	99.99	49.90	50.10	100
AVER:	87.80	12.63	100.43	50.09	49.91	100		AVER:	88.62	12.66	101.28	50.26	49.74	100
SDEV:	0.86	0.97	1.32	1.95	1.95	0		Std Dev:	2.23	1.08	2.35	2.34	2.34	0
% RSD	1.0%	7.7%	1.3%	3.9%	3.9%			% RSD	2.5%	8.6%	2.3%	4.7%	4.7%	
MIN:	87.09	10.88	97.97	47.25	44.88	100		MIN:	86.69	10.87	99.72	47.25	44.88	100
MAX:	89.64	14.08	102.87	55.12	52.75	100		MAX:	92.68	14.78	106.72	55.12	52.75	100
Mass Absorption Coefficients Used:							Mass Absorption Coefficients Used:							
ELEM:	Pt	Si	TOTAL	Pt	Si	TOTAL	(all with Pouchou and Pichoir-PAP)	ELEM:	Pt	Si	TOTAL	Pt	Si	TOTAL
9a	87.41	12.59	100.00	50.00	50.00	100	LINEMU (Henke) MACs	9a	87.42	12.59	100.00	50.00	50.00	100
9b	87.42	12.54	99.96	50.09	49.91	100	MAC30 (Heinrich '88) MACs	9b	87.46	12.57	100.04	50.04	49.96	100
9c	87.12	11.69	98.81	51.76	48.24	100	FFAST (Chantler/NIST) MACs	9c	87.51	12.35	99.86	50.50	49.50	100
AVER:	87.32	12.27	99.59	50.62	49.38			AVER:	87.46	12.50	99.97	50.18	49.82	
SDEV:	0.17	0.51	0.68	0.99	0.99			SDEV:	0.05	0.13	0.09	0.28	0.28	
% RSD	0.2%	4.1%	0.7%	2.0%	2.0%			% RSD	0.1%	1.0%	0.1%	0.5%	0.6%	

Table 1. Results of CalcZAF calculations of the compositional variation produced by varying the correction procedures and values of the mass absorption coefficients (MACs) used by the program. The k-ratios (intensities relative to the pure elements) input into the program were those calculated for platinum silicide (PtSi: Pt 87.41 wt. %, Si: 12.59 wt. %) using the Pouchou and Pichoir PAP correction procedure with Henke MACs. The calculations were done for Pt L and Si K at 20 keV and for Pt M and Si K at 7 keV. In this case, lowering the accelerating potential does not reduce analytical uncertainty.