

Optimizing the Dose for Energy Dispersive Electron Probe X-ray Microanalysis Measurements

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Achieving the desired measurement precision without wasting time can be a challenge. One common strategy is to collect for a duration that seems “more than long enough” to the analyst. This approach is often wasteful of time but more often it underestimates the dose requirements to achieve the desired precision. Within a single sample, the dose requirements to measure a major element ($C > 0.10$) and a minor element ($0.10 > C > 0.01$) to the same precision can easily vary by two orders-of-magnitude and often significantly more. Another approach is to make the measurement, consider the reported measurement precision and then adjust the dose to meet the desired precision goals. This depends upon actually being able to determine the measurement uncertainty, an important piece of information which all too few energy dispersive spectrometer vendor applications actually report.

A better way is to simulate dose correct spectra and to use these spectra to estimate the required dose to perform the measurement. It can be argued from basic statistics and demonstrated with measurements that, to a very good approximation, the precision of an x-ray spectroscopy measurement scales as the dose^{-1/2} where the dose is the product of the live time and the probe current. Increasing the dose by a factor of a hundred will only improve the precision ten-fold.

NIST DTSA-II makes it easy to simulate dose-correct spectra and to quantify these spectra as though they were measured spectra. However, this process is tedious. To simplify the measurement design process, NIST DTSA-II has a number of optimization tools. One aspect of these tools, the ability to optimize the selection of standard material to minimize the uncertainty due to the matrix correction, was discussed last year [1]. This year we will discuss how to use expert-mode tools to optimize the dose and thus allow you to design a measurement which will achieve your measurement goals in the minimum amount of measurement time and the minimum amount of sample exposure and possible damage.

The expert tool asks you to provide precision goals for each element and the conditions under which you intend on making the measurement. It then uses analytical model simulations of the measured standard, unknown, and reference x-ray spectra, followed by linear least squares fitting of top-hat filtered spectra to determine the measurement precision for a default dose. The measurement precision is then compared to the desired precision on an element-by-element basis and the doses for the standard, unknown and references are scaled to achieve the desired precision. The results are reported as a list of required spectra with the optimal dose. Furthermore, an estimate of the more complete uncertainty budget including terms for precision and matrix correction uncertainties is reported. This allows you to determine before the measurement is made whether the measurement will be useful for the desired purpose.

One surprising outcome is that while the standard and unknown doses are critical in determining the measurement precision, the reference doses are much less significant. This is to say that it is far better to

spend your limited laboratory time collecting the standards and unknown spectra. References matter but not nearly as much as intuition suggests.

[1] NWM Ritchie, “Designing the optimal quantitative electron probe x-ray microanalysis measurement”, *Microscopy and Microanalysis*, 19 Supplement S2, 2013, pp 1248 – 1249

Material	Dose	Transition	Reason
Unknown	6 nA·s	O K	Unknown
Al2O3	1.2 nA·s	O K	Ref against unknown for O
Unknown	2.5 nA·s	Si K	Unknown
Unknown	34 nA·s	Ti Kα	Unknown
Ti	0.8 nA·s	Ti Kα	Ref against unknown for Ti Kα
Unknown	24 nA·s	Ba Lα	Unknown
BaCl	3.4 nA·s	Ba Lα	Ref against unknown for Ba Lα
Benitoite	6 nA·s	O K	Standard
Ti	0.5 nA·s	Ti L	Ref against standard for O K
Al2O3	3.5 nA·s	O K	Ref against standard for O K
BaCl	1.2 nA·s	Ba M	Ref against standard for O K
Benitoite	3.1 nA·s	Si K	Standard
Benitoite	7.2 nA·s	Ti Kα	Standard
BaCl	1.3 nA·s	Ba Lα	Ref against standard for Ti Kα
Ti	0.8 nA·s	Ti Kα	Ref against standard for Ti Kα
Benitoite	38 nA·s	Ba Lα	Standard
BaCl	13 nA·s	Ba Lα	Ref against standard for Ba Lα
Ti	4.1 nA·s	Ti Kα	Ref against standard for Ba Lα
Ti	3.9 nA·s	Ti Kb	Ref against standard for Ba Lα

Figure 1. Optimized doses for measuring a glass with 40% Ba, 30% O, 25% Si and 5% Ti using Benitoite as a standard and Al₂O₃, BaCl and Ti as references. Depending upon its use, each material has different dose requirements. The optimal dose for each material is the minimum dose meeting all requirements.

Measurement plan

Composition	Beam Energy (keV)	Form	Preparation	Dose (nA·s)	Type
Unknown material					
Element	Mass Fraction	Mass Fraction (normalized)	Atomic Fraction		
O	0.3000	0.3000	0.5932	15.0	Bulk
Si	0.2500	0.2500	0.2816		
Ti	0.0500	0.0500	0.0330		
Ba	0.4000	0.4000	0.0921		
Al2O3					
Element	Mass Fraction	Mass Fraction (normalized)	Atomic Fraction		
O	0.4707	0.4707	0.6000	15.0	Bulk
Al	0.5293	0.5293	0.4000		
Ti					
Element	Mass Fraction	Mass Fraction (normalized)	Atomic Fraction		
Ti	1.0000	1.0000	1.0000	15.0	Reference
BaCl					
Element	Mass Fraction	Mass Fraction (normalized)	Atomic Fraction		
Cl	0.2052	0.2052	0.5000	15.0	Bulk
Ba	0.7948	0.7948	0.5000		
Benitoite					
Element	Mass Fraction	Mass Fraction (normalized)	Atomic Fraction		
O	0.3483	0.3483	0.6429	15.0	Bulk
Si	0.2038	0.2038	0.2143		
Ti	0.1158	0.1158	0.0714		
Ba	0.3322	0.3322	0.0714		

Figure 2. This report itemizes the spectra to collect and the form, preparation and dose.