Trace Analysis in EPMA

M J Jercinovic¹,³, M L Williams¹, J Allaz¹, and J J Donovan²

¹Department of Geosciences, University of Massachusetts, 611 North Pleasant Street, Amherst, MA 01003, USA
²CAMCOR, University of Oregon, Eugene, OR 97403, USA

mjj@geo.umass.edu

Abstract. Trace element microanalysis has evolved steadily since the early days of EPMA, yet remains an extraordinarily challenging subject. The enhanced capabilities of modern instrumentation, including the use of spectrometers with high X-ray collection efficiencies, high brightness electron sources, and improved stability all contribute to our ability to improve detection limits and analytical spatial resolution. Along with much improved software for data acquisition and analysis, recent progress in EPMA has made the trace realm more accessible than ever. High count precision can be obtained in order to easily bring analytical sensitivity into the single ppm range, but accuracy remains the greatest struggle. With the exception of the calibration, all sources of error encountered in major element analysis are magnified in trace analysis, and other sources become apparent where high spatial resolution is needed. Beam damage and charge effects are difficult problems in high sensitivity, high spatial resolution analysis, particularly in the analysis of insulators. Software can minimize some of the resulting effects on count rates during acquisition in order to improve accuracy, and analysts can empirically evaluate the conditions of analysis (count time, voltage, current, etc.) to try to minimize these effects. Trace analysis is fundamentally an exercise in background characterization, and the acquisition and evaluation of background is a subject of developing methodology. Background curvature and interferences can result in considerable inaccuracy, but can be dealt with via detailed quantitative wavelength scanning or multi-point spectral acquisitions which allow proper regression of the background shape. In the absence of excellent quality trace element secondary standards of similar matrix to unknowns, blank testing and consistency standards can be used to test at least some aspects of the methods employed. Ultimately, the analyst must rely on accuracy evolving from application of the most rigorous protocols.

1. Introduction
Obtaining trace element concentrations by EPMA implies that the spatial context of analysis is crucial. Without this necessity, then bulk techniques employing atomic spectrometry, activation analysis, or X-ray fluorescence, which in some cases obtain limits of detection well below 1 ppb (ultra-trace concentrations), could be used (see [1] for review). It is the balance of spatial resolution and analytical sensitivity that define the critical realm occupied by microbeam techniques, each with strengths and weaknesses, ultimately providing a remarkably powerful set of tools when employed in complimentary fashion to address a particular problem. Therefore, addressing analytical sensitivity and spatial resolution remains a topical and lively subject of scientific and technological endeavour.
1.1. Perspectives
Quantitative compositional analysis at very high spatial resolution has remained an important goal since the inception of materials analysis. Today, an exceptional array of tools exist which access trace element concentrations (i.e., below 1.0 wt. %) and high spatial resolution analysis, and a number of sources attempt to address the sometimes bewildering assortment of techniques available to researchers (e.g. [2] [3]). In most cases, it can be safely stated that no single technique can address all problems, and that closing in on the most reliable result is usually the consequence of application of a number of techniques. Steady advance in both the theoretical and technological aspects of metrology continue to improve both precision and accuracy in analytical techniques, with the driving forces stemming from both the analytical needs of researchers on one end, and technologic development on the other. Furthermore, the pace of these advancements seems to be progressing at a greater rate than ever.

Trace elements are generally not essential structural constituents of materials, but they are nonetheless of great importance for tracking chemical processes and growth histories. In materials engineering, trace elements are critical for creating essential material properties (band-gap engineering in semiconductors, establishing optical transmissivity in fiber optics, etc.). Investigation of trace element concentrations and spatial variation have extraordinary power in the physical sciences and engineering, establishing the relationships between microstructures and the reactions that generate them, also allowing the evaluation of reactions at interfaces. The dilute nature of trace elements is highly advantageous in thermochemical modeling where Henry’s Law behavior can be assumed, resulting in revolutionary advances in igneous and metamorphic petrology, environmental science, paleoclimatology, economic geology, geochronology, cosmochemistry, chemical engineering, and numerous other applications involving materials in the solid state.

Natural and human engineered materials are seldom truly homogeneous, and complex compositional structures often provide exciting opportunities to tease out the details of phase relationships in space and time. Today, our ability to image at ever higher resolution has revealed remarkable complexities, and has led to a need for improved micro (and nano) - analytical capability suitable to the task. Furthermore, the need to acquire minor and trace element information from these micro- and nano- domains has added a particular impetus to improve both hardware and software in order to accomplish both the spatial and sensitivity requirements.

1.2 Trace Element EPMA
The exciting growth of a number of analytical technologies is no less exemplified by the new capabilities introduced in EPMA over the past decade, specifically, ultra-high count rate spectrometers, implementation of high brightness cathodes (REEB₆, Schottky) and development of sophisticated and powerful software for acquisition (i.e. spectrometer integration, cycled peak-bkg acquisition [4][5], time dependent acquisition, background acquisition by regression of scan or multi-point spectral data) as well as downstream data reduction (matrix iterated interference corrections, blank correction, etc.). These developments have made the trace element micro-analysis arena more accessible than ever and have substantially revised our concepts of the “limitations” of EPMA. Although highly case-specific, the frontiers of high spatial resolution analysis at exceptional precision and accuracy are being continually pushed to new levels.

There are many splendid contributions addressing trace element EPMA, dating back to the early years of the application of the technique and steadily continuing to the present [6-13]. The precision statistics of analysis have been well characterized, and recent work has concentrated on the improvement of accuracy, particularly with regard to addressing peak interferences [13], and background curvature and other features [e.g., 13, 14, 15].

Precision and sensitivity in EPMA can always be increased by counting longer and/or increasing amperage without sacrificing spatial resolution. With this in mind however, it is best to consider the following...
“Assuming counting statistics to be the only relevant consideration, the smallest detectable peak may be defined as 3 s.d. of the background count. The probability of the background count-rate exceeding the 3 s.d. limit due to random fluctuations is 0.2%. The detection limit cannot be reduced indefinitely by accumulating more counts, however, because systematic errors in the background correction eventually become significant.”

S.J.B. Reed [16]

Here, Reed fundamentally addresses the issue of accuracy, the correctness of the analysis. Analyses performed by any technique always have an associated (and hopefully reported) estimate of precision, but the complete characterization of error (how accurate?) may be much larger, and may be far more elusive. There are certainly many sources of error, but the issue of background measurement accuracy (as alluded to above) is among the most fundamental in high spatial resolution trace element EPMA (e.g. [14 – 19] for discussions relevant to EPMA geochronology). This topic brings a number of matters to the forefront, including precision/sensitivity, and evaluation of accuracy. Both of these are firmly intertwined with the attempted spatial resolution of analysis. In trace analysis, the analyst can be reasonably assured that any difficulties known in major element analysis are magnified in the analysis of very low concentrations, and there are a few problems more specific to high spatial resolution trace element analysis.

2. Sensitivity and Spatial Resolution
The fundamental tradeoff in nearly all micro- and nano-analytical methods is precision vs. spatial resolution. Unlike ablation-based micro-analytical methods such as SIMS or LA-ICP-MS which are substantially reliant on the volume of material ablated in order to obtain higher precision, electron beam generated X-ray techniques derive precision from the number of photons counted, a result of beam current, counting time, X-ray production efficiency (fluorescence yields, ionization cross sections), and collection efficiency. Counts, and peak/bkg, can be increased by increasing overvoltage (Figure 1) which increases electron path lengths in the target and the number of ionizations per unit time. This, of course, directly compromises spatial resolution (Figure 2) as the scattering volume increases. Electron beam techniques offer some flexibility such that a number of variables can be adjusted in order to overcome apparent counting limitations in some circumstances (always sample dependent), the typical approach being to substantially increase beam current and/or counting time.

![Figure 1. Measured peak to background ratio for PbMα from pyromorphite as a function of beam accelerating potential (E₀). Measurements made using a Cameca VLPET spectrometer.](image1)

![Figure 2. Calculated relative spatial resolution and minimum detectability limit as a function of kV (From Reed[12], Fig. 1). High absorption case illustrates eventual peak intensity decrease as X-ray production volume deepens in specimen.](image2)
However, the consequential increases in systematic errors due to variations in behaviour of either the instrument or sample must always be factored in (e.g. contamination, beam current drift, compositional change in the sample due to prolonged beam exposure at high current density).

Attempting quantification of trace concentrations requires an understanding of the basic relationships controlling the precision of analysis. It is instructive, therefore, to revisit the basic relationships for the precision of X-ray emission. The variance of the raw k-ratio (net intensity sample/net intensity std.) can be expressed as follows [6][20]:

\[
\sigma_k^2 = k^2 \left[ \frac{N + N(B)}{n \left( \overline{N} - N(B) \right)^2} + \frac{N_s + N_s(B)}{n' \left( \overline{N}_s - N_s(B) \right)^2} \right]
\]

(1)

Where \( \sigma_k \) is the standard deviation, \( \overline{N} \) and \( N(B) \) are the measured mean counts for peak and background on the sample, \( \overline{N}_s \) and \( N_s(B) \) are the mean counts for peak and background on the standard, and \( n \) and \( n' \) are the number of measured points on sample and standard respectively.

The variance of the concentration is then:

\[
\sigma_c^2 = C^2 \left[ \frac{N + N(B)}{n \left( \overline{N} - N(B) \right)^2} + \frac{N_s + N_s(B)}{n' \left( \overline{N}_s - N_s(B) \right)^2} \right] \times \left[ 1 - \frac{(a - 1)C}{a} \right]^2
\]

(2)

Where \( \sigma_c \) is the concentration standard deviation, \( C \) is concentration, and \( a \) is the correction factor that relates the k-ratio to the concentration. An interesting result of this relationship is that precision for trace element analysis by EPMA is highly dependent on the precision of the sample analysis, and less dependent on the precision of the standardization, presuming the standardization is performed on a material with a relatively high concentration of the element of interest (Figure 3). This is not to imply that the standardization is unimportant, but that larger errors in calibration are required in order to substantially affect trace elements compared to major elements. It is also clear that using a standard with a low concentration (and therefore low net intensity) for the element of interest will result in large errors in the final trace element analysis relative to using standards with high concentrations of the element of interest. This should be considered when assessing the errors introduced when dealing with interferences. Interference calibrations will be, in almost all cases, on peak tails with low count rates, introducing relatively large effects on the precision of the result when errors are propagated.

The accuracy question is similar, as pointed out by Robinson et al. [4]. For major element analysis, the accuracy is dominated by the peak counts for both sample and standard as Pk-Bkg is large for both (so \( C \approx f(N/N_s) \)), but at trace concentrations, the largest source of inaccuracy is the determination of net counts on the unknown (\( C \approx f(N-N(B)) \)). A theoretical example is shown in Figure 3.
With a standard net intensity of 100 cps/nA, and unknown net intensity of 0.00001 cps/nA (so about 10 ppm), 5% variation of the standard only results in inaccuracies on the order of 1 ppm in the final result.

The sensitivity of analysis can be quantified by calculation of the minimum detectability limit. This has been approached statistically in several different ways, including the simple approximation of Leibhafsky et al. [21]. Based on the Poisson statistics of X-ray emission spectrography, the precision of the counts can be estimated by $N^{1/2}$. Leibhafsky et al. [21] suggest that a peak is detectable from the background at $3 \sqrt{N_B}$, where $N_B$ is the number of background counts. The clear implication, and the basis for all trace element analysis, is that detectability is essentially a characterization of background. The concentration at the limit of detection ($C_{DL}$) can then be expressed, in simplified fashion, by [20][22]:

$$C_{DL} = \frac{3 \sqrt{N(B)}}{N_{Std} - N(B)} C_{Std}$$

(3)

Where $C_{Std}$ is the concentration of the element of interest in the standard, $N(B)$ is the background intensity, and $N_{Std}$ is the intensity in the standard.

Another simplified estimation can be made from the Ziebold [6] expression:

$$C_{DL} > 3.29a/(ntP*P/B)^{1/2}$$

(4)

Where $a$ relates composition and intensity, $n$ is the number of measurements, $t$ is the measurement time, $P$ is the count rate (pure element), and $P/B$ is the peak to background ratio (pure element).

More advanced techniques for estimating the minimum detectable concentration also take into account the chosen confidence level, and standard deviation of measurements [7]:

$$C_{DL} = [C_S/(\bar{N}_S - \bar{N}_{SB})] \cdot [2^{1/2}(t_{n-1}^{1-a}) S_c/n^{1/2}]$$

(5)

Where $C_{Std}$ is the concentration of the element in the standard, $\bar{N}_S$ and $\bar{N}_{SB}$ are the mean counts for peak and background on the standard, $n$ is the number of repetitions, $S_c$ is the standard deviation of the measurements, and $(t_{n-1}^{1-a})$ is the student factor at the selected confidence level.
Ancey, et al. [23] propose a similar approach, including two confidence factors:

\[
C_{DL} = \left( \frac{FC_{std}}{P_{std} - B_{std}} \right) \cdot \left( \frac{\lambda(\alpha, \beta)}{2t_{sam}} \right) \left[ 1 + \frac{4B_{sam}t_{sam} (1 + \frac{\alpha_{sam}^{-1}}{\alpha_{sam}})}{\lambda(\alpha, \beta)} \right]
\]  

(6)

Where \( F \) is the calculated correction factor, \( C_{std} \) is the concentration in the standard, \( P_{std} \) is the peak intensity of the standard, \( B_{std} \) is the standard background intensity, \( t_{sam} \) is the peak counting time of the sample, \( B_{sam} \) is the sample background intensity, \( \alpha_{sam} \) is a constant relating differences in peak and background acquisition time, and \( \lambda(\alpha, \beta) \) is the confidence level for the two risks (\( \alpha \), for the possibility that the conclusion is \( C > 0 \), when in fact \( C = 0 \); and \( \beta \), for the possibility that the conclusion is \( C = 0 \), when in fact \( C > 0 \)). The Ancey et al. expression [23], at the 95% confidence level is used in this paper.

The precision and sensitivity of the analysis depend on the count rate, counting time, and the number of points in the acquisition of the sampled compositional domain. Clearly the number of available analysis points will decrease as the analytical spatial resolution needs to increase, particularly in beam sensitive materials. Figure 4 shows the results of acquisitions at different count times comparing 15kV to 8kV for PbMα using integrated Very Large PET spectrometers (Cameca’s VLPET). The improvement in sensitivity is most dramatic as several points are accumulated, however, in most cases, only a few ppm of increased sensitivity are gained beyond 5 or 6 points. In fact, the detection limit improves only from 10ppm to 8ppm with an additional 45 minutes of acquisition at 15kV and 200nA. Detection limits below 10 ppm are attainable under these relatively modest conditions, and can obviously be considerably lower if more spectrometers are integrated on the same element, if higher accelerating potential is used, or if beam current or count time in increased (or, to think of it another way, just total coulombs). Increasing precision in this way (current and time) must be weighed against the potential for instrumental drift and beam damage, which raise questions of accuracy, although software now permits the cycling of peak and background measurements in order to minimize drift and damage effects. Note also that the detection limit achieved per unit time is directly related to beam accelerating potential, but that the use of relatively low voltage (below 10kV) for high spatial resolution analysis still permits excellent count rates and sensitivity if the requisite detectability limit is in the 10s of ppm. Performance is dramatically improved by the use of high intensity spectrometers which can yield count rates at 7 kV (assuming this is appropriate to the elements required in the analysis) that are similar to those attained at 15 kV with standard monochromators (Figure 5). In situations where the trace elements of interest have low critical excitation potentials, high spatial resolution analysis may be best accomplished with direct acquisition of only the trace components, using a hand-entered major element composition for matrix corrections, or performing the overall analysis with two conditions if appropriate. Note that the use of high intensity spectrometers are a great advantage in higher spatial resolution trace element analysis, and can also benefit efficiency, particularly to count for less time (or use lower current) in cases where beam damage is a significant issue.
Figure 4. Measured detection limits (95% conf.) for Pb Mα at different count times as a function of the number of acquired points. 200nA beam current, 15 and 8 kV accelerating potentials. Counts integrated from two VLPET spectrometers.

Figure 5. Intensity of PbMα as a function of beam accelerating potential comparing conventional PET to VLPET spectrometers.

In situations where high spatial resolution can be somewhat sacrificed, then the beam accelerating potential can be increased, the beam current can be increased (with expected degradation of beam diameter at ultra-high current), and the beam diameter can be increased to mitigate beam damage.
Such a situation is illustrated for Ti in quartz, or Zr in rutile, where detection limits approach the 1 ppm level without extraordinary conditions [13][24].

The spatial resolution of analysis (or analytical resolution) can be assessed from a theoretical approach which considers the X-ray emission volume, a function of the sample composition, element detected (ionization potential, emission line energy), excitation volume, beam energy, and beam diameter [15], and can be expressed by:

\[ D_{AR} = (D_{beam}^2 + D_{emission}^2)^{1/2} \]  

(7)

This is the quadrature sum of the error functions representing the beam diameter and the diameter of the emission volume (that includes 99.5% of the intensity) for the element of interest, and represents a first-order approximation as fluorescence at a distance is not considered. The dimensions of the X-ray emission volume can be obtained from Monte Carlo interaction models (i.e., CASINO [25]) and relationships can be calculated for various beam diameters. For high Z, high density materials, the analytical spatial resolution can be significantly improved by using smaller beam diameters at accelerating potentials below 15 kV (Figures 6-8). As beam voltages substantially below 7-8 kV are seldom useful for most trace element work (ionization cross sections too low at low overvoltage), practical trace element nano-analysis by EPMA is limited to the realm of 7-15 kV in heavy matrices, and where the realized beam diameter can be confined to diameters of 100-600 nm by use of high brightness cathodes (REEB6 or Schottky). Clearly, maintaining small beam diameter at beam currents useful to perform trace element analysis are necessary, typically 100-500 nA in order to attain reasonable precision in 300 to 1000 seconds. The realized analytical resolution, as measured directly in boundary tests, for Th and Pb in monazite (monoclinic LREE, actinide-bearing phosphate) at high current are shown in Figure 8. We can conclude, therefore, that trace element analysis at 500 nm spatial resolution is possible in materials of sufficiently high Z and density.
Figure 6. Spatial resolution in monazite and labradorite, illustrating Monte Carlo simulations of electron scattering as a function of beam voltage. Note red boxes indicating 5 um and 1 um dimensions.

Figure 7. Analytical spatial resolution (AR) in monazite as a function of voltage and beam diameter (D nm). This is the quadrature sum of the beam diameter and emission volume containing 99.5% of the PbMα φ(pZ) intensity. Both radial and depth (φ(pZ)) components of analytical resolution are shown.
3. Precision and Spatial Resolution vs. Accuracy – Beam Power Density and Stability

If one of the goals of investigation is to make exceptionally precise measurements of trace elements at the highest possible analytical spatial resolution, then the other must be to ensure that the results are reasonably accurate. One aspect of such measurements concerns the analysis of insulating, beam-sensitive materials, and what, in fact, constitutes beam sensitivity. The dielectric properties of many materials present problems with accuracy simply from the deposition of charge (i.e. [26-29]). Measurements of elemental concentrations in materials such as glasses, carbonates, apatite and triplite group phosphates, or feldspar minerals are notoriously difficult, and experience significant beam damage and/or elemental instabilities at even conservative beam conditions. Trace element analysis in such materials suffers also. Other phases which may generally behave in a stable fashion during major element analysis may begin to destabilize at the high current densities necessary for high spatial resolution trace element analysis. For example, phosphorous loss is observed in monazite under high beam current density (15 kV, 200 nA) over a period of a few hundred seconds [14]. The high analytical spatial resolution permitted by the small electron scattering volumes at lower voltage in high Z, high density phases intensifies the problem. Gunn et al. [30] examined the problem of carbonate analysis, and concluded that adequate stability could only be obtained at values of beam power density (BPD) below 3μW/μm². The estimation of BPD in this case is:

\[ \text{BPD} = \frac{(I^*E_0)}{A} \]

Where \( I \) is the beam current (nA), \( E_0 \) is accelerating potential in (kV), and \( A \) is the beam area (μm²). Here, we will modify this in order to account for the volume of excitation rather than landing area, and also account for the percentage loss of beam electrons emitted from the specimen by backscattering. Note that this is still an oversimplified model as it does not account for effects such as secondary electron emission, space charge buildup in insulators (internal potential changing the landing energy and deforming the interaction volume) or coating (scattering and grounding of some charge):

\[ \text{Simple Beam Power Density} = \frac{[I-(I^*\eta)]^* E_0}{V} \]
Where $\eta$ is the backscattered electron coefficient, the fraction of beam electrons scattered out of the specimen (determined via CASINO), and $V$ is the estimated interaction volume. The interaction volume is calculated as an edge-rounded disk (a shape estimated from Monte Carlo modeling of defocused beam scattering in solids):

$$V = \frac{1}{3} \pi h (3a^2 + 3b^2 + h^2)$$

(10)

Where $a$ is the radius of the excitation volume, $b$ is the radius of the beam, and $h$ is half the total depth of beam penetration. The radius of the excitation volume is:

$$a = \sqrt{b^2 + d_s^2}$$

(11)

Where the scattering diameter ($d_s$) is estimated at beam size = 0.

Calculated results for this simplified beam power density are shown for monazite ($Z=38$) in Figure 9, and labradorite feldspar ($Z=11$) in Figure 10. Small beam diameter (below micron) at low voltage increases the electron dose in the specimen tremendously, and has the added effect of shifting the depth of charge deposition closer to the surface, increasing surface heating and charge effects, expressed as carbon deposition near the beam.

![Graph showing electron beam power density in monazite as a function of beam diameter, voltage and current. The influence of coating is not considered.](image-url)
The effects of internal charge build-up, heating, and radiation damage have to be assessed for each material to be analysed. If the measured elements are stable enough, then the analysis has a chance of being accurate. Assessing the stability of trace elements, however, is obviously not straightforward (low counting precision in stability tests). The stability of major element emission or absorbed current (Figures 11, 12 and 13) will generally have to serve as proxies, especially if the structural state of the trace elements of interest can be specified, but the effects of surface contamination build-up will also have to be assessed over the time required for a single point analysis. Figure 14 shows the percentage error for the integrated count times for GdLα in GdPO₄ at different count times and accelerating potential. The beam damage resulting from lower kV at high current is dramatic, leading to nearly 7% error in the accumulated counts over 900 seconds at 10kV. Clearly, multiple points with shorter count times are preferable, and the choice of voltage must be assessed based on the spatial requirements and error tolerance. The use of acquisition techniques such as time-dependent evaluation and extrapolation back to time = 0, and cycled peak and background during the course of the analysis [4][5][13] are important software developments in improving the accuracy of the analysis of beam sensitive materials.

Another important variable is the effectiveness of the surface conductive coating. As long as samples and standards are coated simultaneously to ensure constant thickness, either thicker carbon, or metal evaporation offer a means to mitigate charge and thermal effects to some extent. Gold, with exceptionally high electrical and thermal conductivity, is ideal for moderating beam effects [14], but has the drawbacks of high electron and X-ray absorption, as well as producing a complex emission spectrum. The use of silver was proposed by Smith [31] for carbonate analysis, and copper has been used for oxygen analysis in insulators [32]. Plasma cleaning, followed by 2-layer coating first with aluminum (200Å) then carbon (80Å) has been proposed for monazite trace element analysis [33]. The use of metals for quantitative EPMA remains interesting and subject to question, and certainly measurement of oxygen through copper has inherent inaccuracy [34]. Results for major element
analyses performed on monazite using an aluminum coat are very comparable to those done using a carbon coat.

**Figure 11.** Ca Kα intensity with time in CaCO3 (20 μm beam diameter, 200nA, 15 kV), and absorbed current measured simultaneously. The resulting inaccuracy during integrated measurement will be large after 1 minute, but lower (compared to time = 0) after 10 minutes.

**Figure 12.** Absorbed current measured in GdPO4 at varying accelerating potential (focused beam, 100 nA, coating: 200Å Al and 80Å C) vs. time (measurement interval is 3 sec.). Instability in absorbed current is expressed analytically as increased counts over time (Figure 13).
4. Accuracy, Contributions to Error, and the Blank Test

Williams et al. [19] have described the basic contributions to error in trace element analysis applied to EPMA in terms of (1) short-term random errors (counting uncertainty); (2) short-term systematic error (session to session, beyond a single set of analyses: background, sample coating and calibration effects); and (3) long-term systematic errors affecting accuracy (effects stemming from quality of standards, evolving algorithms for interferences, background regression, dead-time corrections, ZAF factors). They stress population sampling as a means to developing a statistical basis for reporting overall error, and also advocate the analysis of trace element “consistency standards”, e.g., some
material which is analysed before, during and after sessions in order to assess the cumulative effects of systematic error. This is a critical and simple test which allows the analyst to know that something significant has changed, perhaps very subtle at the major element level, but substantial at the trace level. Assessing the accuracy of analysis based on secondary standards is exceptionally difficult in the trace element realm, primarily due to a lack of materials appropriate to the unknowns and with a reliable, homogeneous trace element concentration of the element or elements of interest. Illustrating accuracy at 2 wt.% may not translate at all to accuracy at 200ppm, and illustrating accuracy for 300 ppm Pb in glass may not translate to accuracy at 300 ppm in a complex phosphate (different interferences, background curvature, etc.). To date, the best approach is to do the analysis by addressing the known sources of error as rigorously as possible. For trace analysis, interferences on peaks and background, and background shape contribute immensely to analytical error (see [15], and Figure 15). The key concept is in understanding that the percentage error stems from the error on the net intensity (Pk – Bkg), such that at very low net intensity values, even the smallest perturbation in the background estimate results in very large accuracy errors (Figure 16).

Although it remains difficult to create standards with very small amounts of something, making them with none of the element of interest can be done more reliably. This gives rise to the blank test [4][13]. You should be able to analyze an appropriate blank and get a zero concentration result. Any other result, either positive or negative, indicates that there are problems to be addressed before proceeding to unknowns. Minor inaccuracies from unknown sources can actually be corrected using a blank correction scheme in software [13]. Careful characterization and analysis of synthetic GdPO₄ (synthesized using the Pb free method of J.-M. Montel) serves to illustrate several points (Figures 17-20), as described herewith.

Characterization of background is paramount in trace analysis (as Pk/Bkg approaches 1). In many respects, accurate trace analysis can be considered to be a measurement of background and what can be distinguished from it. Features within the spectral region of interest which can significantly affect the net intensity must be accounted for. This implies that the background spectrum must be evaluated at similar precision to the peak measurement. WDS scanning is essential for this evaluation, to note, in particular, where any interferences may exist, where absorption edges from major elements become significant, and the shape of the background, e.g., curvature. Noting where potential interference may exist is an important exercise, but neglects the extent to which unexpected lines can occur as a result of fluorescence at a distance, the presence of elements which should not be in the structure, but in fact are, or where catalogued positions may be in error or are incomplete. In addition, high order line positions can vary significantly depending on monochromator d-spacing variation or spectrometer focus – even very slight tuning can measurably shift positions.

Strong absorption edge effects can cause considerable inaccuracy in situations such as Co measurement in Fe, Pb measurement in sulfides, or in a number of measurement of interference corrections such as that for Th on UMβ, S on PbMβ, or Fe on CoKα. The proper scaling of edge effects with concentration could potentially be corrected in software.

As background curvature is dependent on the Bremsstrahlung emission characteristics of the sample, as well as the collection efficiency and X-ray focusing characteristics of individual spectrometers, the curvature must be established routinely as part of the general protocol. Quantitative WDS scanning and regression analysis is advocated [14][15] in order to compute the curvature and correctly estimate the background intensity under the peak of interest. In this case, the error on the background is the error of the regression (r.m.s. error). Although such acquisitions are lengthy, this is a rigorous approach which allows features in the background to be accounted for, and for curvature to be calculated directly from the scan. An important step in the process is separating signal (features) from noise (count statistics). This is aided considerably by use of a low pass filter such as the Savitsky-Golay smoothing algorithm [35] which employs local polynomial regression over user-specified data windows. Care must be exercised in setting both the window width (i.e., percent of scan points included for local regression) and the polynomial order such that background features are seen, but noise is still adequately reduced. Regression of the Savitsky-Golay fit data can then be
performed to obtain the true background under the peak of interest, and the error can be estimated via evaluation of residuals (r.m.s. error) or by Monte-Carlo methods.

Figure 15. WDS scans of the Th M region of PET. (a) Thorium as major element, high Pk./Bkg., minor errors on background are inconsequential. (b) Same as above except now scaled appropriate to trace element analysis. If the background positions shown in (a) are used, the error on the net intensity for the LHO6 example (1700 ppm) will be 20% too low from background interference alone. Red vertical bars are major potential REE interferences, the black vertical bars are minor REE interferences.
Figure 16. Background error comparing linear interpolation of PbMα background intensity using typical high and low λ positions, and exponential background from GdPO4 data. Separate errors can be estimated for the case of curvature only (lower dashed line), and curvature plus interference (upper dashed line). (a) Error (%) on net intensity with decreasing net intensity (peak cps/nA−background cps/nA) for Pb Mα when using linear 2-point background interpolation (neglecting curvature) and adding the observed background interference at lowest intensity region between Pb Mα and Pb Mβ for monazite [15]. The interference portion of the error is concentration dependent (Th/LREE). (b) Detail of region below net intensity of 0.2, corresponding to concentrations below about 500 ppm for VLPET and PETH.

Figure 17. Detailed WDS scan data from GdPO4, PbMα-PbMβ region of PET. Raw scan data comparing standard PET (scaled 5x intensity) and VLPET. Noise reduction via Savitsky-Golay filter improves accuracy of background and illustrates true features. Smoothed curves for 3%, 6.5%, 10% and 15% data widths (percent of scan in each polynomial fit window) are shown.
Figure 18. Detail of PbMα portion of figure 17 illustrating peak recognition (at .59900 and .41400 sinθ) and effect of varying Savitsky-Golay parameters. 3% window width includes too much noise, 15% window width broadening peak tails. Note that peak positions and true background intensities do not change as window size increases.

Figure 19. GdPO4 scan illustrating background positions selected for quantitative blank analysis of PbMα, with results shown in Figure 20.
Figure 20. Blank test for Pb (should be zero) in synthetic GdPO4. Quantitative results of trace element analysis done at 15kV, 200nA, for 500 sec. using linear background interpolation of varying positions (see Figure 19 for positions). Concentration results vs. total wavelength offset for background positions are listed in table to the right.

Although daunting with complex spectra in actinide-REE bearing phases (see Figure 15, what part of the scan actually does represent true background?), the quantitative scanning approach can yield good results, as illustrated on the GdPO4 blank which has several interesting features. GdPO4 is selected as a good test for Pb blank measurement relevant to monazite as there are no major peaks from this synthetic material which interfere with Pb, and that the average atomic number and density are quite close to typical monazite ($Z=38$, $\rho = 6g/cm^3$). Pb, Th, and LREE rich monazite will have numerous peaks in this region, so this is an excellent evaluation to determine if the background curve fitting and overall zero (Pb) result are accurate, particularly under the high beam current conditions used for trace element analysis.

As the precision of the scan is increased, certain unexpected features become apparent. Noise filtering reveals two unexpected peaks in the spectrum. One, arising from the 3rd order GdLβ2 line. At 7.1 keV, this line would be expected to be filtered out with the tight pulse height analysis (PHA) window used in this acquisition as the Pb Mα line is at 2.34 keV. This is the result of the fact that high energy photons still enter the counter, producing an escape peak in the PHA spectrum which extends to much lower energy [17]. The other very minor peak in the spectrum is from SKα. The presence of sulfur is completely unexpected in this case (although it can exist in natural monazite). This was traced to the carbon coat by analysis of the carbon rods used for coating in this instance. These peaks can be avoided in background analysis if you know they are there. And the correct background can be regressed from the scan data. If the analyst is unaware, and choses instead to do 2-point background interpolation, then background positions for Pb Mα analysis may be selected improperly and large errors can be incurred (Figures 16 and 20). A background inadvertently obtained on the exceptionally minor (invisible with rapid scan) S Kα peak would ramp out the PbMα measured intensity, resulting in a concentration that is 80 ppm underestimated. Likewise, background measurement including the 3rd – order GdLβ2 line would result in a concentration 40 ppm too low.
Curvature alone will result in errors if 2-point linear interpolation is used, and that error increases as the background offset increases. Large background offsets result from avoidance of interferences in the background spectrum, a situation that is well illustrated by the measurement of Pb Mα (or Mβ) in monazite [15].

The quantitative WDS scan approach is adequate to the task of background evaluation in the above situation, and has proven to give reasonable results in very complex situations [32][36][37]. However, the balancing of scan resolution (precision) with acquisition time remains problematic. Typical scan acquisitions require a considerable time investment in background acquisition in the overall analysis of a single compositional domain (30 minutes or more for the scan). In order to resolve very minor background features, even more beam exposure time or intensity is required, never quite attaining the precision of the peak measurement, especially in the low ppm sensitivity range. An alternative approach, the multi-point background acquisition, has recently been developed (Probe Software, Inc [38]). This method (Figure 21) allows the user to set up to 24 points in the wavelength region around the peak of interest for automatic acquisition, statistical evaluation, and regression (see Allaz, et al., this meeting). The advantage is that obvious minor peaks in the background (or holes) will be immediately flagged for exclusion from the background regression and calculation of intensity. Very high background precision is possible with this technique in less time than required for the full, high precision, WDS scan of the same region.

![Figure 21. Spectrum (PET) of Pb-Ma region in monazite illustrating new multi-point acquisition procedure. User-selected positions are automatically acquired, and resulting data are regressed and optimized to find true background. Points with residual values are eliminated and the line regressed again (for example, the point between PbMα and PbMβ will be removed). Curvature and interferences are appropriately accounted for.](image)

Of particular significance to high spatial resolution trace element EPMA, are the effects of fluorescence at a distance. Even in situations where the analyst has taken great care to generate an appropriately small activation volume at a current and voltage that will still allow an apparently accurate analysis at sufficient sensitivity, critical elements may be fluoresced from boundary phases or
compositional domains which compromise the analysis. There are many possible cases, and one such example is the fluorescence of Th from high Th material near low Th monazite (Figure 22). The high concentration of light REEs in monazite results in high intensity REE-L emission, and fluorescence of Th (or Pb, or U) from the adjacent domain [15]. This is not a hopeless situation, however, as empirical corrections can be applied, or theoretical correction may be possible where the geometry can be modelled, using PENEPEMA [39]. An example is the analysis of Ti in zircon near FeTiO$_3$ [40].

![Figure 22. Boundary fluorescence test showing apparent Th concentration in synthetic monazite (Th-free), next to natural Moacyr monazite [15]. Each point represents an average of 6 measurements at that distance. Individual point analyses were performed at 15 kV, 200 nA (LaB$_6$ cathode), 500 s count time and VLPET spectrometer.]

5. Conclusions
Trace analysis by EPMA has many interesting challenges, and new developments in instrumentation and software are resulting in improved potential analytical spatial resolution, detectability limits, and accuracy. Precision, although critical, is not the biggest obstacle, especially as modern instruments offer much higher collection efficiency along with stable high beam current output to enable lengthy acquisitions. Accuracy, however, remains the great challenge. With great care, the analyst can obtain meaningful results for a number of elements, in some cases approaching the single ppm level in regions below 1 micron in size. Among the most challenging is the situation in which very high spatial resolution, along with high sensitivity are required. Beam damage, internal charge effects, and surface contamination compromise results, and must be considered when setting up the conditions of analysis, and in interpreting results.

The spatial resolution of analysis can extend to well below one micron in low voltage (below 15 kV) analysis of high average atomic number phases. However the use of high current and/or lengthy beam exposure time in order to achieve highly sensitive analyses exacerbates damage and charge effects, particularly in insulating materials, bringing accuracy into question. Higher voltage mitigates some of this, and increases count rates, but the obvious tradeoffs are spatial resolution and high matrix corrections. Possible work-arounds involve the use of metallic coatings, and software which cycles peak and background measurements, and can correct for systematic changes in count rates during the analysis.

Trace analysis by EPMA is fundamentally a characterization and measurement of background, and even minor inaccuracies in the background determination produce extremely large errors in net intensity as increased sensitivity is attempted. Therefore, just extending the protocols for major
element analysis into the trace realm is unsatisfactory. Detailed wavelength scanning is critical, and must be performed at a precision determined by the expected net counts at the peak. Such scans can be acquired quantitatively (and accurately smoothed, i.e., Savitsky-Golay) in order to regress background curvature for more accurate background intensity determination. Background curvature and interferences render simple 2-point linear interpolation inadequate (especially in complex materials), potentially resulting in 10s to 100s of ppm errors, but use of quantitative scanning or the new multi-point regression technique offers both high precision and improved accuracy for trace element work.

Blank testing is a useful method for evaluating at least some aspects of the analytical method, and remains one of the few reliable measures in the absence of appropriately low concentration secondary standards. The use of consistency standards offers a method to monitor short term systematic error. Neither of these insures accuracy in the analysis of unknowns, but they do offer a means to monitor performance and test basic protocols. The existence of interferences on peak and background remain critical as even extremely minor features can result in large errors in the trace realm. For peak acquisition, accurate matrix-iterated interference corrections are absolutely necessary. Careful consideration of analysis near phase or compositional domain boundaries where fluorescence from outside of the primary excitation volume can occur is imperative. These are critical techniques in gaining confidence in trace element analysis.

References
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