Electron Microprobe Quantitative Mapping vs. Defocused Beam Analysis

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ABSTRACT

Despite consensus within the electron microprobe community that broad or defocused beam analyses (DBA) provide erroneous results [1-4], the technique still remains in use [5-7]. Analytical errors associated with this practice are usually attributable to heterogeneous interaction volumes, caused by the presence of multiple phases. Traditional matrix corrections used in EPMA assume that the interaction volume is homogeneous; therefore, when phase boundaries are encountered, elemental concentrations are often inappropriately corrected. Because x-ray absorption dominates the matrix correction, average compositions are typically overcorrected for the emission lines of interest, thus resulting in high totals. Attempts have been made to improve the accuracy of these analyses by weighting the abundances of each element and phase present [1,8], as well as the density of each component [2,9]. While such corrections appear to yield more accurate results, they require additional knowledge of the sample (modal abundances and phase compositions) and do not seem to be as rigorous as other methods of determining bulk compositions [3,4].

In this study quantitative x-ray maps were used to show the magnitude of error that can be associated with DBA and to highlight analytical methods that can be used to avoid the use of complicated correction factors. Two maps along the diffusion zone of an Al-$Mg_{95}Gd_5$ diffusion couple were acquired using Probe Image with a focused beam, one larger area (Area A, Fig. 1A) and one smaller area within the most heterogeneous portion of the diffusion boundary (Area B, Fig. 1B). Both maps were acquired at 15 keV and 30 nA. On- and off-peak maps of Mg, Sn, Gd, Al, and O were collected for both areas; both high and low off-peak maps were acquired for Area A, while only high off-peak maps was acquired for Area B. The on- and off-peak maps were then utilized to create quantitative element maps using CalcImage. Using Golden Software's Surfer® program, each elemental map was then averaged in horizontal strips two different ways to show the effects of performing DBA: one with the weight percent for each individual point in the strip averaged, weight percent determined from the intensity measured for that point; one with the intensities for all points in a strip averaged, with that average then converted into a weight percent (simulating DBA). 1 μm and 8 μm wide strips were averaged across 64 μm Area A and 256 μm in Area B.

As shown in Fig. 1C and 1D, the simulated DBA data often deviates from the averaged weight percent data for the same strip. Mg showed large variations in weight percent between the two methods, however, not every element analyzed exhibited these incongruities; the nature and concentration of each element is likely responsible for some of this effect. Differences of up to ~4 wt. % absolute can be seen between the defocused beam and average weight percent for Mg (Fig. 1C and1D). The non-uniformity of the disparities, over and under correcting by varying amounts, underscores the importance of using a more reliable method for determining the bulk composition of a heterogeneous material. Since the composition for each pixel can be determined and then averaged across any size area desired, utilizing these quantitative x-ray maps appears to be a more accurate method to determine average areal compositions. While there is some decrease in precision due to shorter counting times per point, for major elements this seems to be an advantageous tradeoff for the increased accuracy obtained. Subsequently, these quantitative concentration maps can also be clustered statistically to determine the phases present and, with user-specified densities, the modal mass abundance of each phase.

REFERENCES

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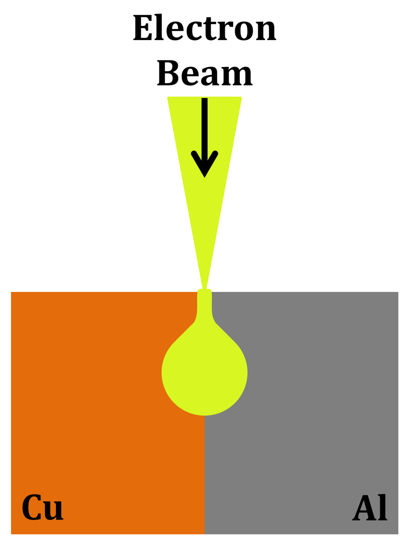
DEFOCUSED BEAM ANALYSIS

- **What is DBA?** Defocusing the beam of electrons to encompass a relatively large area in order to measure the average composition of that region
- **How can it lead to inaccurate results?** If the beam is spread over multiple phases, then the interaction volume is no longer a homogenous material; conventional matrix corrections assume homogeneity and, consequently, can improperly correct elemental concentrations in a heterogeneous material
- **Example:** Cu and Al alloy
  - If a 50% Cu and 50% Al alloy is examined with DBA analysis, with the beam spread across both phases, and it were a satisfactory way to determine the bulk composition then it should be able to correctly resolve this composition
  - Al Kα has an energy of 1.487 keV, while Cu Kα has an energy of 8.047 keV; as a result, Cu is able to absorb Al x-rays. Using traditional matrix corrections, the amount of Al will be artificially high in the heterogeneous interaction volume described because it is applying a correction where there is not one
    - Small ZAF correction on $Al_{99}Cu_1$ (1.0109)
    - Large ZAF correction on $Al_{50}Cu_{50}$ (1.5994)
  - Location of detector relative to boundary can also have an effect, since photons travel in straight lines



X-RAY MAPS

- **Acquisition**
  - X-ray maps across a diffusion zone of an Al-Mg95Gd5 diffusion couple were obtained using Probe Image
  - Instrument conditions: focused beam at 15 keV and 30 nA
  - Two areas, about 200μm apart and across the same diffusion zone, were mapped; one map being smaller and focused on the most heterogeneous area of the zone
  - On- and off-peak maps of Mg, Sn, Gd, Sn, Al, and O were collected (only high off-peak maps were acquired for the smaller map)
- **Simulating DBA:**
  - In order to compare the bulk composition that would be ascertained by DBA to that acquired by averaging quantified x-ray maps, the same initial x-ray intensity data was utilized for both
  - For quantitative maps, the on and off-peak intensity maps were quantified into weight percent using CalcImage. All of the weight percent data points in each strip were then averaged, to give the bulk composition of that area
  - For DBA, the on- and off-peak intensity maps were first averaged in strips, then these average intensities were quantified into weight percent with CalcImage to yield the bulk composition for each strip

AUTOMATION

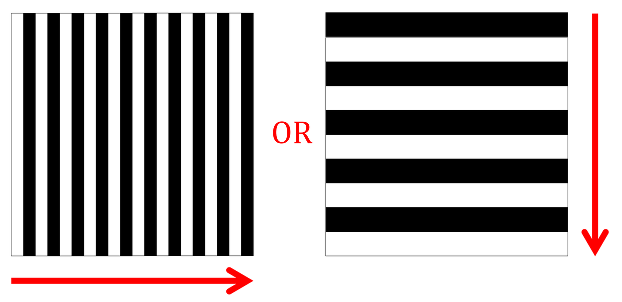
- An average strips script discussed here can be created from CalcImage
- Other data processing scripts that can be implemented through CalcImage:
  - Average polygon → average the Z values of a chosen area
  - Cross section → graph the Z values along a chosen path
  - Plot traverse data → graphs Z values of points along a traverse

CODE APPLICATION

Golden Software's Scriptor application for Surfer® and Grapher® was employed for this work. It utilizes a Visual BASIC-like programming language; this quality makes it very accessible to anyone already acquainted with BASIC, and also provides a pre-existing database of knowledge for troubleshooting. Additionally, Grapher® comes equipped with a script recorder that automatically generate a script mimicking the actions you make in the regular graphing software.

- **Averaging Strips Script**
  - Determines the average z value across a horizontal or vertical strip of a chosen width, and then plots those averages along with an image map of the original data
  - Can vary the width and direction strips are averaged

```
StripIncrement! = 1    ' in MICRONS
StripIncrement! = StripIncrement!  * 0.001    ' convert to mm

StripDirection% = 2    ' 1 = vertical, 2 = horizontal
If StripDirection% = 1 Then
StripType$ = "Vertical"
ElseIf StripDirection% = 2 Then
StripType$ = "Horizontal"
End If
```



  - Creates Excel spreadsheet with boundaries of each strip, the distance traveled along the x or y axis, strip averages and their standard deviations
  - Creates PDF or JPEG's of each strip averages graph and image maps
  - Quickly analyzes and graphs thousands of data points
  - Difficulties encountered:
    - Initial way in which the grid file data was read was time prohibitive → had it parse it into a string and average data from there, dramatically reduced script runtime

```
'Open the file to read through
   TempFileNumber% = 1
   Open ConvertedGridFile$ For Input As #TempFileNumber%
'Loop through data in the range
   Do Until EOF(TempFileNumber%)
      'Read the converted blanked file (space delimited) and change the delimiting character
         achar$ = Chr$(32)
         Line Input #TempFileNumber%, astring$
         Call MiscParseStringToStringA(astring$, achar$, bstring$)
         XPos! = Val(bstring$)
         Call MiscParseStringToStringA(astring$, achar$, bstring$)
         YPos! = Val(bstring$)
         Call MiscParseStringToStringA(astring$, achar$, bstring$)
         ZVal! = Val(bstring$)
      'If the if the X or Y value is in the strip's range then sum it and count it (in order to calculate the average Z for it)
         If XPos! >= Min! And XPos! < Max! Then
            n& = n& + 1
            ReDim Preserve temp(1 To n&) As Single
            temp!(n&) = ZVal!
            Sum# = Sum# + temp!(n&)
         End If
   Loop
```

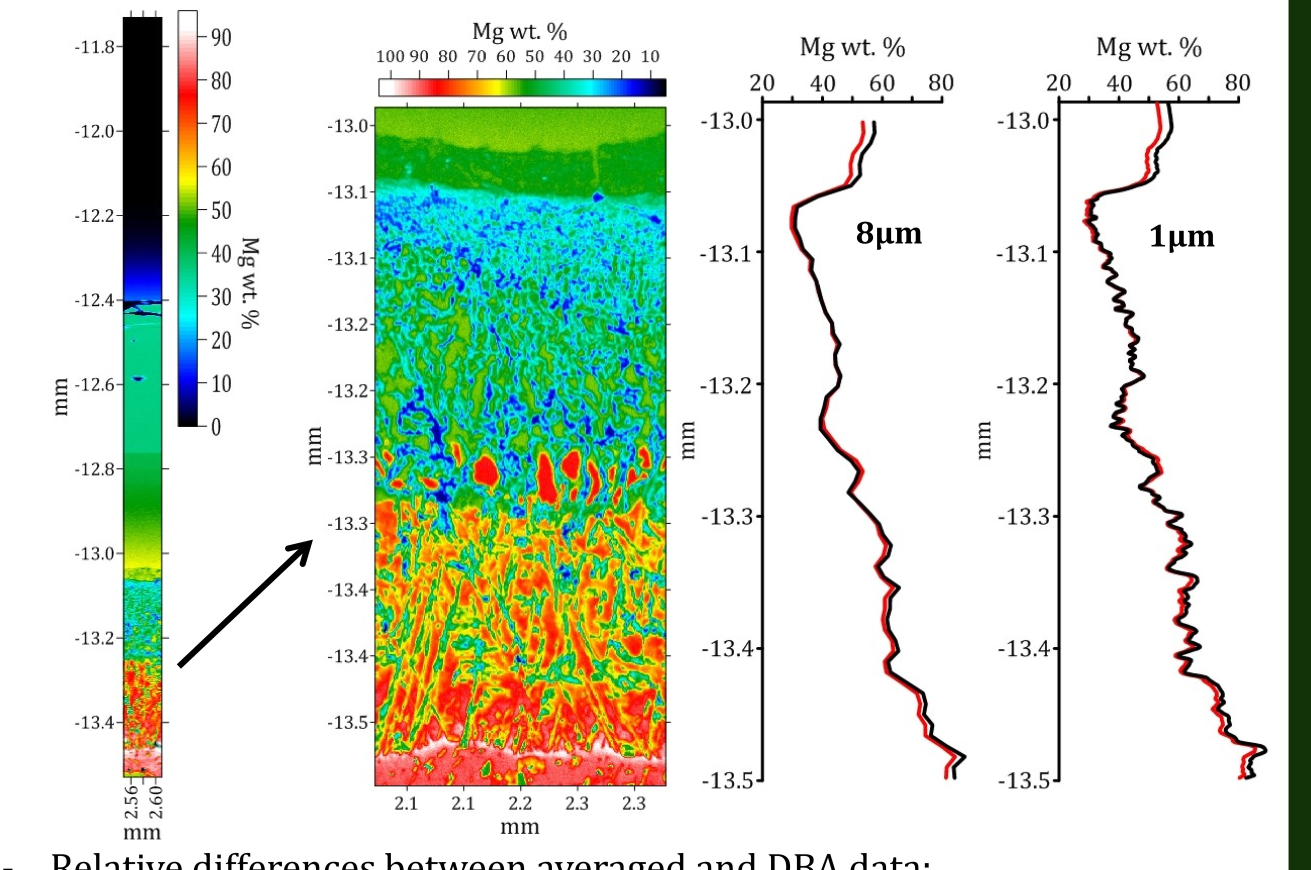
    - Problem with the program remembering the appropriate directory → ultimately language doesn't have a way to set this as was desired

- **Duplicate Data Removal Script**
  - Removes every second data point, which were duplicates. In order to quantify the DBA simulated data (average intensity for each strip), the averages had to be converted into grid file which require at least 2 data points in each dimension.

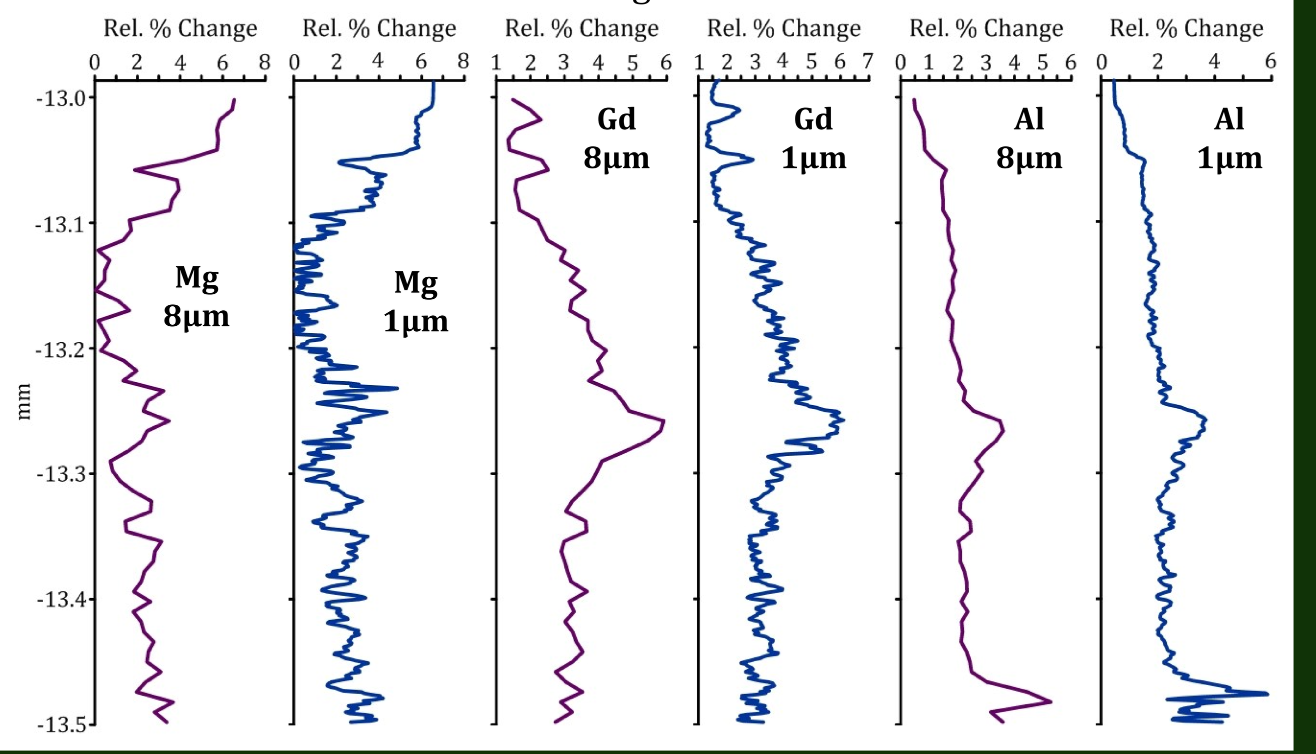
```
'Create a new document window
Dim DataFile As Variant
DataFile = GetFilePath(" ","DAT;TXT;CSV;XLS",Directory$, "Select Data File", 0)
Dim Wks As Object
Set Wks = Grapher.Documents.Open(DataFile)

'Delete douplicate data rows
Dim i As Integer
Dim TotalRows As Integer
Dim TotalRange As Object
Set TotalRange = Wks.Columns(1, 1)
TotalRows% = TotalRange.RowCount
TotalRows% = (TotalRows% / 2) + 2

For i% = 2 To TotalRows%
   Wks.Range("A" & i%).Delete(wksDeleteRows)
   Debug.Print i%
Next i%
```

RESULTS

- Largest variations between data treatments were in Mg values
- Unpredictable variances between the averaged quantitative and DBA data



- Relative differences between averaged and DBA data:



CONCLUSIONS

- **DBA:**
  - Using currently available matrix corrections, acquiring intensity data across a heterogeneous area will yield flawed results
  - With quantitative mapping the composition of each pixel, of a user determined size, can be obtained; the limiting factor of the resolution being the size of the electron beam
  - Despite beam size restraints and a reduction in precision from lower counting times, averaging sections of quantitative maps seems to be a more accurate method than DBA for establishing the average areal composition of a heterogeneous material
- **Code Utility:**
  - Greater flexibility → can just change parameters and rerun script, don't have to completely reanalyze data
  - Significantly speeds up analysis and reanalysis of data
  - Provides others with analytical tools they can use