Quantitative X-ray mapping, scatter diagrams and the generation of correction maps to obtain more information about your material

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Abstract. Quantitative X-ray mapping with silicon drift detectors and multi-EDS detector systems have become an invaluable analysis technique and one of the most useful methods of X-ray microanalysis today. The time to perform an X-ray map has reduced considerably with the ability to map minor and trace elements very accurately due to the larger detector area and higher count rate detectors. Live X-ray imaging can now be performed with a significant amount of data collected in a matter of minutes.

A great deal of information can be obtained from X-ray maps. This includes; elemental relationship or scatter diagram creation, elemental ratio mapping, chemical phase mapping (CPM) and quantitative X-ray maps. In obtaining quantitative x-ray maps, we are able to easily generate atomic number ($Z$), absorption ($A$), fluorescence ($F$), theoretical back scatter coefficient ($\eta$), and quantitative total maps from each pixel in the image. This allows us to generate an image corresponding to each factor (for each element present). These images allow the user to predict and verify where they are likely to have problems in our images, and are especially helpful to look at possible interface artefacts.

The post-processing techniques to improve the quantitation of X-ray map data and the development of post processing techniques for improved characterisation are covered in this paper.

1. Introduction

X-ray mapping (XRM) was first developed by Duncumb and Coslett in 1956 [1-2] and is the collection of characteristic X-rays as a function of the position of the scanning electron beam on the specimen [3]. This analytical technique provides an image related to the distribution and relative abundance of elements within a given specimen. This capability makes XRM particularly useful for; (i) identifying the location of individual elements, and (ii) mapping the spatial distribution of specific elements and chemical phases within a sample [4]. Figure 1 shows the backscattered electron (BSE) image and regions of interest X-ray maps (ROIM) from a hard-facing white cast iron with niobium carbide (NbC) particles incorporated. X-ray mapping has become one of the most popular and useful methods of X-ray microanalysis today used extensively in areas of materials science, chemistry, physics, geology, environmental sciences and biology.
Figure 1. Regions of interest X-ray maps (ROIM) of a white cast iron hard-facing material with NbC particles. Map collected using a Be-window SDD at 20 keV, 512x512 pixels, 120 msec. X-ray maps for carbon, argon, cobalt, titanium and bismuth are artefacts. The detector cannot see carbon due to the Be-window, but does see Nb-Ln escape peak within the carbon ROI. Horizontal width of field (HWOF) = 300 µm.

X-ray mapping, in the past, was a slow process often being performed overnight. With the development of silicon drift detectors (SDD), it is possible to obtain live X-ray images. Currently there are very large area SDD’s as well as multiple SDD detector systems capable of handling millions of counts per second. This has made XRM a more popular technique for characterising a material’s microstructural properties by determining elemental distributions and phases in materials with subsequent chemical phase mapping (CPM) [3-5].

Silicon drift detectors allow the electron microprobes to operate at higher beam currents, which are more suited to wavelength-dispersive X-ray spectroscopy (WDS). Higher spatial resolution mapping is possible due to larger detection areas, improvements in the field emission guns (FEG) and lower keV mapping.

High pixel resolution X-ray maps of 512x512 pixels, with excellent counting statistics, can be acquired in a couple of hours. However, simple elemental X-ray maps can be misleading, so further post-processing (data manipulation) techniques may be required to obtain more information about a material’s unique properties.

Our research aims at developing post processing techniques to improve the quantitation of X-ray map data and to develop further post-processing techniques for improved characterisation as an aid in assessing the practical properties of complex materials. These techniques include:
1. Atomic number, absorption and fluorescence (ZAF) corrected quantitative X-ray maps (QXRM), where the QXRM enables reliable quantitative results, that when grouped, can be an order of magnitude better than traditional analysis [6].
2. Scatter diagrams and rotational scatter diagrams for locating phases [7-8].
3. Pseudo colouring for locating phases. The colours of the elements can be rotated, which can often reveal further information (and other phases) in the material [4].
4. Elemental ratio maps. This is a powerful technique that helps to reveal subtle chemical variations in a sample. Ratio maps can also be created from different combinations of elements and from the different background regions near elements of the spectra [9].
5. Theoretical BSE maps. When generating quantitative X-ray maps, the computer can easily calculate the theoretical BSE coefficient for each point on the map. The comparison between the real and theoretical BSE map (image) gives us information about what is going on just below the surface of the sample [8].
6. ZAF maps, which give information on the correction that is required at specific points, or interfaces, of the different regions in the maps [9].
7. Totals mapping (wt%). The total at each point of the map can be calculated and mapped. These total maps give an idea of the quality of the analysis and also make it easy to determine problems such as missing elements and interaction volume effects [9-10].
8. Filtering to make phase selection easier, to produce cleaner images and aid in trace element location.
9. Identification of artefacts. Those effects in X-ray maps that should not be there.
10. X-ray map resolution determination through the use of Smart J package [11-12], can be used to do X-ray map resolutions for various elements compared to Monte Carlo simulations [13], aiding in determining interfacial boundary issues.

This paper will discuss several of the above mentioned techniques, all of which aid in obtaining a better understanding of a material’s chemical and microstructural properties.

2. Experimental method
Current research work involves the use of a number of different SEM/EDS and microprobes. These include a multi-detector EDS and WDS X-ray mapping system installed on a JEOL 733 microprobe with two SDD-EDS X-ray detectors and four WDS detectors, a JEOL 8600 microprobe with three WDS detectors and an Si(Li) EDS X-ray detector and a dedicated X-ray mapping system, which is a JEOL 840 SEM with an UTW Si(Li) EDS detector all operated with a Moran Scientific microanalysis system.

3. Results and discussion

3.1. ZAF corrected quantitative X-ray maps (XRM versus QXRM)
Electron beam induced X-ray mapping (XRM), whether using EDS or WDS, has become a very useful characterisation tool for determining the elemental distribution in materials. There are many types of X-ray maps, which include 1) dot mapping, 2) regions of interest (ROI) mapping, 3) background subtracted and overlap corrected mapping, 4) quantitative mapping, and 5) full spectrum mapping (or spectrum mapping) [4, 6].

Regions of interest mapping, is where you set up an energy range (or number of channels) where an elemental line exists to see the distribution of the element of interest. Regions of interest are assigned as a single channel analyser (SCA) and a different colour is assigned for different elements [1, 6, 14]. X-ray maps are usually collected using raw counts from the elemental peaks of interest, however traditional ROIM does not always provide a completely accurate description of the material phases or elemental distribution as the integrated peak counts are only partially related to the true composition of the material and in fact may not be related at all [6]. The ROIM is very problematic when looking at
moderate to low levels of elements and the accuracy of ROIM is dependent on what elements are present in the material. If the elements are present in reasonable amounts and have no overlaps with other elements then the ROIM may be near to correct. However, great care must be taken for the appearance of other artefacts [15], such as escape peaks and sum peaks that can occur on the EDS spectrum. Figure 1 shows several RIOM maps of the hard-facing white cast iron with NbC particles. However, some of the elements are not really present but represent a combination of density distributions, sum peaks, overlap errors and escape peaks. In this example; carbon is displaying the Nb-Ln escape peak generated in the carbon ROI; chromium, iron and niobium are substantially correct; manganese is predominantly the Cr-Kβ; silicon, argon, cobalt and titanium are predominantly a density distribution; bismuth is a Cr sum peak, and aluminium is a mix of real and density; titanium also contains the Nb-Lβ1 sum peak.

For a true spatial elemental distribution we require background subtraction, overlap correction and inter-element correction. Quantitative X-ray mapping (QXRM) is where an X-ray intensity map for an element is corrected through standards based ZAF or another matrix correction procedure revealing the quantitative composition at each pixel location. Thus, the quantitative maps shown in figure 2 reveal the correct spatial element distribution. Generating ZAF corrected quantitative X-ray maps enables reliable quantitative results that can be an order of magnitude better than traditional analysis and is also far superior to ROIM where low levels of an element or elemental overlaps are present [6]. There are also extreme examples where the actual composition shows reverse correlation to the intensity such as with carbon in NbC compared with M7C3 high-chrome carbide due to absorption by niobium.

Figure 2. Quantitative X-ray maps of a white cast iron alloy, where the elemental maps have been corrected through standards based ZAF matrix correction procedures revealing the quantitative composition at each pixel location. Map collected using combined SDD-EDS (Be-window) and WDS at 20 keV, 512x512 pixels, 120 msec. Carbon, manganese and molybdenum were mapped using WDS. HWOF = 65 µm.
X-ray mapping and QXRM uses chemistry through use of either EDS and/or WDS analysis. For accurate QXRM, all elements need to be mapped, as some chemical phases are determined from very minor elemental variation and even elements that are difficult to analyse. Full spectrum X-ray mapping (FSXRM) which saves a spectrum for each pixel of an image makes the process of looking for other elements much easier at a later stage. The elements of interest do not need to be identified before starting the map, allowing the user to acquire data and recall all information at a later time away from the microscope. This form of mapping allows the user to produce new maps, construct spectra from any region of the image and quantitatively analyse these regions [16].

3.2. Scatter diagrams

The X-ray maps that are generated quite often have so much quantitative information that it is extremely complex to visually interpret them. Other techniques are required to correlate elements and phases in materials. One technique involves the use of scatter diagrams, which are pixel frequency versus element concentration profiles plotted against each other in two dimensions for selected elements within the sample [7]. Other terms used for scatter diagrams are concentration-concentration histograms (CHI) [17] or correlation diagrams. The scatter diagrams may be derived from ROIM or QXRM.

Scatter diagram generation is best understood by considering the information given in the linear intensity distribution histogram from each individual element X-ray (figure 3). An intensity histogram shows the frequency with which each value of the image intensity occurs against the full range of intensity values. From this information, a two-dimensional scatter diagram is produced, which is a plot of the frequency of occurrence of intensity values for one element against another for each pixel in the X-ray map (figures 3 and 4).

![Figure 3](image-url). Scatter diagram generated from the chromium distribution plotted against the iron distribution. The vertical scale of the intensity histograms, represent the number of pixels and the horizontal scale represents the intensity of the pixel. The arrows indicate corresponding phases as clusters of points.
Figure 4. A set of scatter diagrams showing the different clusters for the X-ray maps shown in figure 1. a) Iron versus chromium, b) niobium versus iron, and c) niobium versus chromium, d) scatter diagram cluster selection and the points then displayed and redrawn on the electron image with the quantification results from the selection of the areas. These clusters have a two sigma variation of ± 5 % relative. The quantification was calculated using combined EDS and WDS data.

These scatter diagrams provide a visual means of determining how elements are associated with one another in the specimen and make it easier to understand X-ray maps. There are many features observed when scatter diagrams are created. From these scatter diagrams we observe clusters, also referred to as nodes, which correspond to different chemical phases. The type of clustering observed in the scatter diagram, whether spherical, oval or linear, can give more information about the major and trace element distributions within phases as well as qualitative and quantitative phase information [7] through looking at the different node types, size and shape.
For any point on the scatter diagram of figure 3, the vertical axis of the scatter diagram shows the iron X-ray intensity at a pixel, whereas the horizontal axis shows the chromium X-ray intensity at the same pixel. The intense group of pixels at the bottom (co-ordinates 0, 0) corresponds to the low-Fe and low-Cr pixels, that is, the niobium carbides. Referring to figure 4, the reconstructed trace back (redrawn) image of these pixels shows the NbC (left image). This image shows the selected analysis points superimposed on the electron image which was collected while mapping, giving perfect correlation. The redrawn image from the high-Fe region of the scatter diagram reveals the matrix and the redrawn image from the high-Cr region of the scatter diagram reveals the M7C3 carbides.

Selecting areas on the scatter diagrams and observing where the points lie on the image is a very important part of the phase identification process. These selected analysis points may then be summed for a more accurate analysis in total or by selecting strategic areas on the image. Selecting areas on the electron or X-ray image, and showing where these points plot (retrace) on the scatter diagrams, is also important in locating “missing” clusters.

We can also observe linking (connection) between clusters indicating the boundaries between phases within a material as well as branching from clusters (some links may contain branches). Branching is defined as a link with a node at one end only, and is often referring to solid solutions (compositional variations) of the same phase or separate phases of similar chemistry [7]. Figure 4d shows that by selecting the links between the clusters, this linking is actually the boundary between the NbC particles and the matrix white cast iron and is most likely an artefact.

3.3. Colouring

Usually X-ray maps are displayed as grey scale images. The use of colour can enhance the visibility of intensity levels in a map because the human eye can distinguish many more shades of colour than grey levels [16].

Pseudo-colouring is often referred to as false colour and is used to display different elements. However, pseudo-colouring can be very helpful for locating phases, as shown in figure 5a. Pseudo-colouring is a simple method for determining elemental associations and is also called “primary colour imaging” [16]. This technique is where three elemental maps have been assigned the colours red, green and blue. Because the colours red, green and blue form specific colours when combined on a computer graphics monitor, elemental associations are clearly shown in a single pseudo-colour image. Figure 5 shows a pseudo-colour image of a polished section of a hard-facing white cast iron with NbC particles in which Fe has been assigned the colour red, Cr green, and Nb blue. From the combination of colours, it is clear that the orange/yellow region is a phase that contains both Fe and Cr, whereas if there were pink/purple regions this phase would contain both Fe and Nb.

The rotation of the colours between elements can often reveal further information (and other phases) in the material (elemental association), such as fine precipitates, trace elements, hairline cracks and small boundary interfaces that would be otherwise missed [7]. Indeed, the higher magnification pseudo-coloured X-ray map of the hard-facing white cast iron and rotating between different elements and colours reveals coring in some of the carbides in different areas of the hard-facing material (figure 5b).

3.4. Elemental ratio mapping

Elemental ratio mapping is a powerful technique that helps to reveal subtle chemical variations in a (figure 6). Ratio maps can also be created from different combinations of elements and from the different background regions near elements of the spectrum.
Figure 5. a) Pseudo-colour map for the elements (Fe-red, Nb-blue and Cr-green). Maps collected at 20 keV, 512x512 pixel, 120 msec/pixel. HWOF = 300 µm. b) Higher magnification pseudo-colour map of another white cast iron for the elements (Cr-red, Fe-blue and Mo-green). HWOF = 65 µm.

Figure 6. Elemental ratio mapping of the quantitative X-ray maps shown in figure 2. a) Ratio map of chromium to iron (Cr/Fe), b) ratio map of carbon to iron (C/Fe) showing changes around the eutectic carbides, c) ratio map of chromium to molybdenum (Cr/Mo), and d) ratio map of molybdenum to iron (Mo/Fe). Map collected at 20 keV, 512x512 pixels, 120 msec, HWOF = 65 µm.

3.5. Theoretical BSE maps
When generating elemental X-ray maps, the computer can easily calculate the theoretical BSE coefficient ($\eta$), by looking at the quantitative data, and use this to generate the BSE coefficient for each point on the map (figure 7). The theoretical BSE map (or image) gives us information on what is going on just below the surface of the sample. The ratio of real BSE to the generated BSE can be used to identify problems such as interaction problems and ZAF correction problems.
Figure 7. Quantitative (wt%) elemental X-ray maps produced from a hard facing bonded to a chrome steel. a) Cr 0 - 20 %, b) Fe 0 - 30 %, c) Ni 0 - 70 %, d) Cu 0 - 30 %, e) W 0 - 100 %, and BSE images using f) electrons, g) calculated BSE coefficient ($\eta$) using W-L$\alpha$, and h) calculated $\eta$ using W-M$\alpha$. Map collected using a UTW-window Si(Li) EDS detector at 20 keV, 512x512 pixels, and 12 hours. HWOF = 100 $\mu$m.

Figures 7a-e show the quantitative elemental x-ray maps produced from a hard facing bonded to a chrome steel. Figures 7f-h shows three different BSE images, first from electrons, second from calculated $\eta$ using W-L$\alpha$ and third from calculated $\eta$ using W-M$\alpha$ respectively. The three BSE images show the effect of the depth distribution of the different signals that make up the images. The BSE image from high energy electrons shows the surface detail and atomic number differences to a depth of about 0.02 $\mu$m. The calculated $\eta$-image (from summing C$Z_i$) using W-L$\alpha$ (8.396 keV), shows composition to a depth distribution of about 0.7 $\mu$m. The calculated $\eta$-map using W-M$\alpha$ (1.777 keV), shows composition to a depth distribution of about 1 $\mu$m.

The electron image is sharp and shows surface scratches, whereas the theoretical image is diffuse from the subsurface effect of the excitation volume. The differences in the images can be quite dramatic. The calculated $\eta$- images are also affected by statistical variations, especially with the W-L$\alpha$ line. This line is a low intensity line compared with the W-M$\alpha$ line. There is almost a 3D effect (W-M$\alpha$ line) in the calculated $\eta$-image, which can be seen when looking around the dendritic growths. The change in spatial resolution is also obvious between the three images.

Another technique to obtain a better understanding of the effect of low energy and high energy theoretical BSE mapping is to look at the ratio of the theoretical BSE to the K$\alpha$-line BSE (BSE/K BSE ratio map). Figure 8 shows the BSE image and figure 8b shows the BSE/K BSE ratio map indicating a reasonably flat grey level image with an even range, which means the correlation between the actual BSE with theoretical K BSE is very good. The grooves that are seen in these images are polishing grooves in the sample. The BSE/L BSE ratio map shows greater changes due to the L X-rays emanating from deeper within the sample.
Figure 8. Hard facing bonded to a chrome steel. a) BSE image collected with electrons, b) BSE/K BSE ratio map showing a reasonably flat grey level, and c) BSE/L BSE ratio map showing major changes (greater change in grey scale compared to BSE/K BSE). Map collected using a UTW-window Si(Li) EDS detector at 20 keV, 512x512 pixels over 12 hours. HWOF = 100 µm.

3.6. Atomic number, absorption and fluorescence (ZAF) maps
ZAF maps give information on the correction that is required at specific points, or interfaces, of the different regions in the maps. Figures 9a-c shows the $Z$, $A$- and $F$-correction factor maps for chromium, respectively. Because of the elements present in this sample, there are large variations in the $Z$, $A$- and $F$-correction factors. Chromium is a good example to show the fluorescence effect from iron, and atomic number effect from tungsten, with each element present having its own set of ZAF images.

Figure 9. Hard facing bonded to a chrome steel. These images are of the hard facing section only. a) Fluorescence factor image for chromium where the fluorescence factor varies considerably; in this case from 1 (black) to 1.1 (white), b) atomic number factor image for chromium where the atomic number factor varies considerably; in this case from 1 (black) to 1.37 (white), and c) absorption factor image for chromium where the absorption factor varies in this case from 0.9 (black) to 1 (white). Map collected using a Be-window Si(Li) EDS detector at 20 keV, 512x512 pixels and 12 hours. HWOF = 100 µm.
3.7. Totals mapping
When standards based analysis gives totals in the range 99 - 101 there is confidence in the accuracy of the results. This also applies to X-ray mapping. With X-ray mapping, the total at each pixel can be calculated and mapped (figure 10). Totals map then give us an idea of the quality of the analysis at each pixel and also makes it easy to determine problem areas within the map. As seen in figure 10, totals maps and total scatter diagrams can be generated. The total for each pixel is plotted against the concentration of an element for the same pixel. The totals image (figure 10c) shows the image for the range of 94 wt% to 103 wt% and reveals bright and dark edges which correspond to low and high absorption for carbon.

![Figure 10. a) Total (wt%) scatter diagram of Cr plotted (vertical) against Totals (Horizontal axis); b) Total scatter diagram of Fe plotted (vertical) against Totals (Horizontal axis); c) Totals image where the bright and dark edges correspond to low and high absorption for carbon. Arrows indicate the same phase for each element. The black vertical lines in figures 10a and b represent 100 wt%.](image)

4. Conclusion
So much more information about a material can be obtained by further processing the X-ray maps through data manipulation. The collection of full spectrum X-ray maps (FSXRM) and the subsequent post processing of the data to obtain quantitative X-ray maps, elemental ratio maps, scatter diagrams, pseudo-coloured maps, theoretical BSE maps, totals maps as well as ZAF maps allows the user to 1) determine more information about their material through identifying the location of individual elements and phases, 2) map the spatial distribution of specific elements and chemical phases within a sample, 3) predict and verify where there is likely to be problems in the maps (images), and 4) help look at possible interface artefacts.

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