

Danger! High Voltage! **The Application of Handheld X-ray Fluorescence (HH-XRF) to Experimental Glass: Pitfalls and Potentials**

R. Scott¹, D. Braekmans^{1,2,3}, D. Brems¹ and P. Degryse¹

1. Centre for Archaeological Sciences, Dept Earth and Environmental Sciences, KU Leuven, Celestijnenlaan 200E - bus 2408, B-3001, Belgium,
becki.scott@ees.kuleuven.be, dieter.brems@ees.kuleuven.be, Patrick.Degryse@ees.kuleuven.be
2. Materials in Art and Archaeology, Laboratory of Materials Science, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands, d.braekmans@tudelft.nl
3. Faculty of Archaeology, Leiden University, P.O. Box 9515, 2300 RA Leiden, The Netherlands

ABSTRACT

Handheld X-ray Fluorescence (HH-XRF) is growing in terms of its popularity for use in archaeological studies. It has been regularly used for studying soils, obsidians and metals, but the extent to which it can be applied to other, more heterogeneous archaeological materials, for example, glass and ceramics, is still under debate. Some of the concerns which need to be addressed include: how reliable are the studies that are undertaken using this technique? And, to what extent is a trained 'expert' needed to conduct and interpret the analysis? The influence of the size, shape and thickness of an object on the obtained analytical data can pose some significant problems. The appropriate instrumental parameters of the HH-XRF including analysis time, current and voltage settings vary between objects and material types. The attenuation properties and resultant critical depths also vary and require some knowledge of the system before analysis. These issues all have an impact on the qualitative, semi-quantitative and quantitative analyses that can be achieved with the use of this technique.

HH-XRF has huge potential for *in-situ* archaeometrical analyses, but the potential pitfalls for the unwary user can be many and great. This paper seeks to highlight some of the dangers associated with a 'point and shoot' technique by taking one material, an experimental glass, and determining the minimum basic parameters needed for a useful analysis.

KEYWORDS

compositional analysis, Glass, HH-XRF, Methodology, Provenance

Introduction

Portable XRF has received much attention in the archaeological literature in recent years. The development of the 'point and shoot' handheld devices are proving particularly attractive to archaeologists as they offer an *in-situ* method of non-destructive analyses. The appeal of this technique is due to both the practical and the economic advantages that it offers (Shackley 2011). The technique can detect multiple elements with ease, it is non-destructive, and it offers immediate information on the chemical composition

of the analysed sample (Potts 2008). In short, the technique is fast, efficient and relatively inexpensive (Scott *et al.* 2012). XRF and HH-XRF have regularly been utilised to study soils, obsidians and metals (Guerra 1998; Shugar and Mass 2012), and many studies have shown that HH-XRF is a very precise technique, especially for homogenous materials (Craig *et al.* 2007; Glasscock and Ferguson 2012; Shackley 2010). But, how reliable are the studies that have been undertaken? For example, to what extent has weathering affected the surface of the sample; or have the appropriate matrix matched standards been used in the study; have the samples been analysed for 30 seconds or 300 seconds? HH-XRF produces a spectrum, showing peaks for each element present in the sample, the interpretation of this spectrum requires a degree of knowledge on the principles of X-ray interactions in order to accurately define the relevant peaks. This in turn leads to questions over the attempted quantification of the elements, does one use the built-in manufacturer provided calibration files, or does one attempt an empirical calibration based on the use of standards. Ultimately, how are the results of the study affected by changing the operating parameters, does this affect the quantification process and how does this in turn impact on the interpretation of the nature of the sample?

This research is aimed at addressing some of the above issues. The main objective was to determine the minimum basic parameters needed for a useful analysis of an experimental archaeological glass.

Background

HH-XRF analyses rely on principles that are common to many techniques which involve the use of X-rays (Shackley 2011). High energy radiation, such as that generated by X-rays, is used to excite the atoms in a sample material. As an electron from the inner shell of an atom is excited, it leaves a vacant space, which in turn causes the atom to become unstable. An outer shell electron then drops down to fill the vacant place. As this occurs, energy is released because the inner shell electron is more strongly bonded than the outer shell electrons. This radiation is termed fluorescence and is of a lower energy than the primary incident X-rays. The emitted fluorescent radiation always has a characteristic

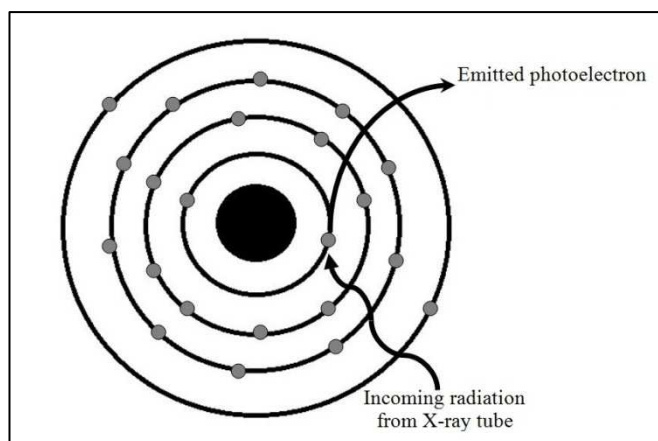


Fig. 1. Principle of X-ray fluorescence, as an outer shell electron drops down to fill the space left by the inner shell electron a characteristic fluorescence is released.

energy depending on the element (Shackley 2011). Figure 1 illustrates the principle of X-ray fluorescence.

Since HH-XRF is a surface technique, a flat, homogenous surface of the sample is recommended for analyses. The nature of the material being studied, i.e. the matrix, will affect the depth to which useful information can be obtained from a sample. For example, absorption of the fluorescence is greater in metallic lead, which has a high average atomic number than in a material such as glass with a much lower atomic number (Pollard and Heron 1996). It should be noted that not all materials of the same type, for example glass, have the same matrix, as is shown in Figure 2. In this instance, eight different glasses (Corning A, B, C and D; NIST 610; NIST 612; and two experimental 'Roman' glasses) were measured using the same parameters (40kV; 10 μ A; 60 seconds; vacuum and no filter). It can clearly be seen that one of the glasses has a completely different matrix to the other samples. This is due to the increased density of this sample caused by the higher levels of heavy elements such as Pb (36wt% PbO compared to <1wt% PbO).

The qualitative compositions of different samples can be quickly and easily identified using HH-XRF (Pollard and Heron 1996). Straightforward qualitative questions about the nature of a material, whether a particular element is present or not, or whether a sample is contaminated can be rapidly answered with this technology (Shugar and Mass 2012). Quantitative analyses are also possible, although care needs to be taken. "If you do not have good sample uniformity, which is afforded in a prepared sample, quantitative analysis of a non-uniform material, by any XRF system, [will result in] data [which] *must be wrong*" (Kaiser and Shugar 2012: 451). It is the purpose of this paper to highlight some of the areas where caution needs to be used when conducting a HH-XRF study.

Method

An experimental glass was created using a Roman 'natron' glass recipe. This glass was melted using calculated amounts of natural beach sand and synthetic sodium bicarbonate in order to replicate as close as possible an archaeological

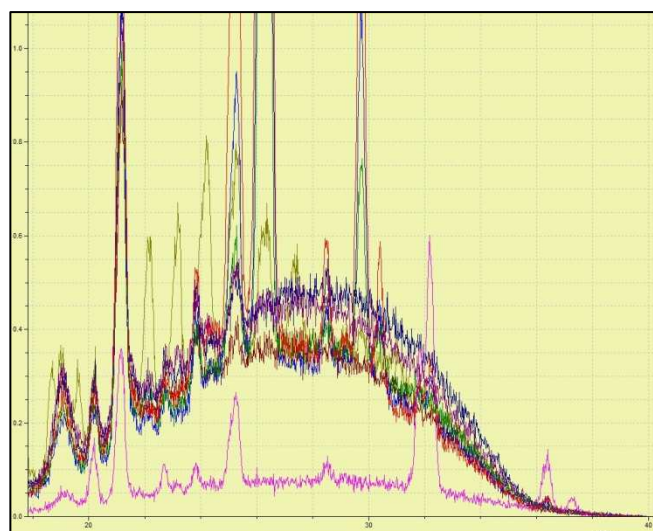


Fig. 2. Spectra of eight different glasses, clearly showing that one glass has a different matrix to the rest.

sample (Brems *et al.* 2012). The replicate sample removes the problems/issues that may be caused by the deterioration of a genuine archaeological sample. The replicate Roman glass was cut and polished until a flat surface was obtained in order to minimise any error that may be introduced by shape and surface effects. Based on the elements present in the sample and the nature of the sample matrix, the critical penetration depth of the heaviest element present was determined to be 5mm. Therefore, a minimum sample thickness of 6mm was used in this study. A NIST 610 glass standard was also used in the analysis to check for any machine drift.

A Bruker Tracer III-SD with Rh tube and silicon drift detector (SDD) was used in the analysis. The detector is covered by a 10mm² Be window. The spot size of the X-ray beam for analysis is 8mm. In order to reduce the number of potential variables in the experiment an energy of 40kV was used in combination with a vacuum. This enabled the detection of as many elements as possible within the sample, including light elements, without specifically focussing on any in particular. The current was varied between 5 μ A and 50 μ A in increments of 5 μ A. The time of each analysis was also varied, in the first instance between 10 and 60 seconds in 10 second intervals, secondly between 60 and 180 seconds in 30 second intervals and finally for 300 seconds and 900 seconds. The Bruker S1PXRF software was used for the analyses, but no attempts at auto-quantification were used.

The raw signal/background ratio for each current setting was determined and plotted against time for each element detected in the glass.

Results

A total of 13 elements (Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Rb, Sr, Zr) were analysed in the experimental glass and figures 3-6 illustrate the results of four of the elements. All of the spectra for all of the elements showed variation within the signal/background ratio, with the exception of Si (Figure 4). The ratio varied depending on the current chosen and the

duration of the analysis. Although in most cases (Figures 3, 4 and 6) the ratio appears to stabilise over time, this is a result of the experimental set-up. Measurements were made in 10 second intervals for the first 60 seconds, after this, measurements were made in 30 second intervals up to 180 seconds. The result of this is the potential masking of fluctuations in the resulting signal/background ratio for a given setting.

The results show that different elements appear to have preferential current settings, despite none of the elements having an ideal. For example, the highest and most stable ratio for Fe is with a current of 5 μ A (Figure 6). Some elements such as Sr do not appear to have a preferential current setting (Figure 5).

Discussion

In most cases, the worst signal/background ratio for glass, although often appearing the most stable, was at a current of 50 μ A. This is explained, because as the current is increased, the number of signal counts are increased, but so too are the background counts. The nature of the matrix determines the level of current needed. For example, this glass is a Si-rich matrix with a density of c.2.5. A more dense material, such as iron, would need a higher current in order to give the elements enough energy for the fluorescence to escape the sample matrix and reach the detector.

The lack of variation shown in Figure 4 is due to the nature of the sample. Glass is a Si-rich material, in this case SiO₂ is 67.18wt% (Brems 2012). It is also a light element, this means that Si will fluoresce from within a few μ m of the surface. The results show that at currents above c.15 μ A there is a decrease in the signal/background ratio. The lower sensitivity of Si combined with the Si-rich nature of the matrix means that at higher currents and a voltage of 40kV the signal is being 'saturated'. Likewise, the very irregular ratios seen in Figure 5 for Sr are probably due to the very low concentrations of Sr in the sample (175ppm; Brems 2012).

The manufacturer's recommendations for the analysis of non-metallic samples, such as glass, is a voltage of 40kV with the highest possible current. The results show this to be untrue. The highest ratio available is not necessarily the best option either, the results indicate that the best signal/background ratio for a given element varies with duration of the analysis. Figure 3 clearly shows that between 20 and 40 seconds the optimum current for the fluorescence of Al switches between 5 μ A and 10 μ A. The ideal option would therefore be a current setting which results in the most stable signal/background ratio. This unfortunately varies between the elements. Figure 3 shows that a reasonable signal can be detected at relatively low current for light elements; Figure 6 indicates that the mid-range element Fe is fairly stable at 5 μ A and 15 μ A. The heavier element Sr, however, (Figure 5) does not appear to have an optimum stable setting. In all cases the signal/background ratio is lower at settings above 25 μ A, due to both an increased signal and increased background counts. But, at lower current settings, although a better ratio is seen, i.e. a lower background interference, the intensity of the signal is

also lower. This can impact on some subsequent methods used for quantification, especially those that rely on peak heights or counts per second (cps) to determine the concentration of an element.

This research shows that a prior knowledge of the elements of interest within a sample and therefore also the nature of the sample is essential. The optimum stability of the signal/background ratio for a specific element in a Si-rich glass matrix will not be the same for that element in an alternative matrix. The study shows that the length of time chosen for the study is also important. It is well known that a longer analysis time will give a 'smoother' appearance to the spectrum. Likewise, certain interference peaks can be reduced by changing the duration of an analysis. Other spectral interferences can be reduced/removed by changing the applied current (Shugar and Mass 2012). But, without an understanding of both the nature of the material and the interaction behaviour of X-rays, the optimum settings can be difficult to define.

One method of improving the stability of the ratios over time would be to adjust the voltage to an optimum value to fluoresce the elements of interest. For example, if the focus were on the lighter elements present, then a voltage of 15kV would be better than 40kV. This is because the lighter elements fluoresce from nearer to the surface of the sample than heavier elements, therefore, the fluorescence yield of the lighter elements is lower. For example, if the Si concentration and Fe concentration were the same in the sample, because Fe is a higher atomic number and fluoresces from a greater depth in the glass, it will have a higher fluorescence yield than the Si (Kaiser and Shugar 2012). It should also be noted that the probability of fluorescence decreases exponentially with higher energy (Ferguson 2012), therefore, a voltage of 40kV is not an optimum setting for the detailed analysis of light elements.

Conclusion

Although HH-XRF offers a fast and efficient method of analysing samples, both in the lab and the field, it does have limitations. Many of these do not necessarily prevent the use of the technique, but rather require a specific amount of prior knowledge.

Information on the nature of the sample is of paramount importance. The matrix itself and the elements therein will determine whether corrections need to be made for the thickness of the sample. Although the influence of the size and shape of the sample on the data obtained were not investigated in this study, it is known that these can have a great effect on the results of an analysis (Shackley 2010).

The nature of the sample will also affect the choice of current and voltage used. This research found that lower current settings were generally better because they resulted in a lower background, but this is again dependent on the nature of the material and the purpose of the analysis. The highest signal/background ratio is also not necessarily the best because the ratio may be unstable or the signal counts too low. The optimum time and current settings vary between elements within the same matrix, highlighting the

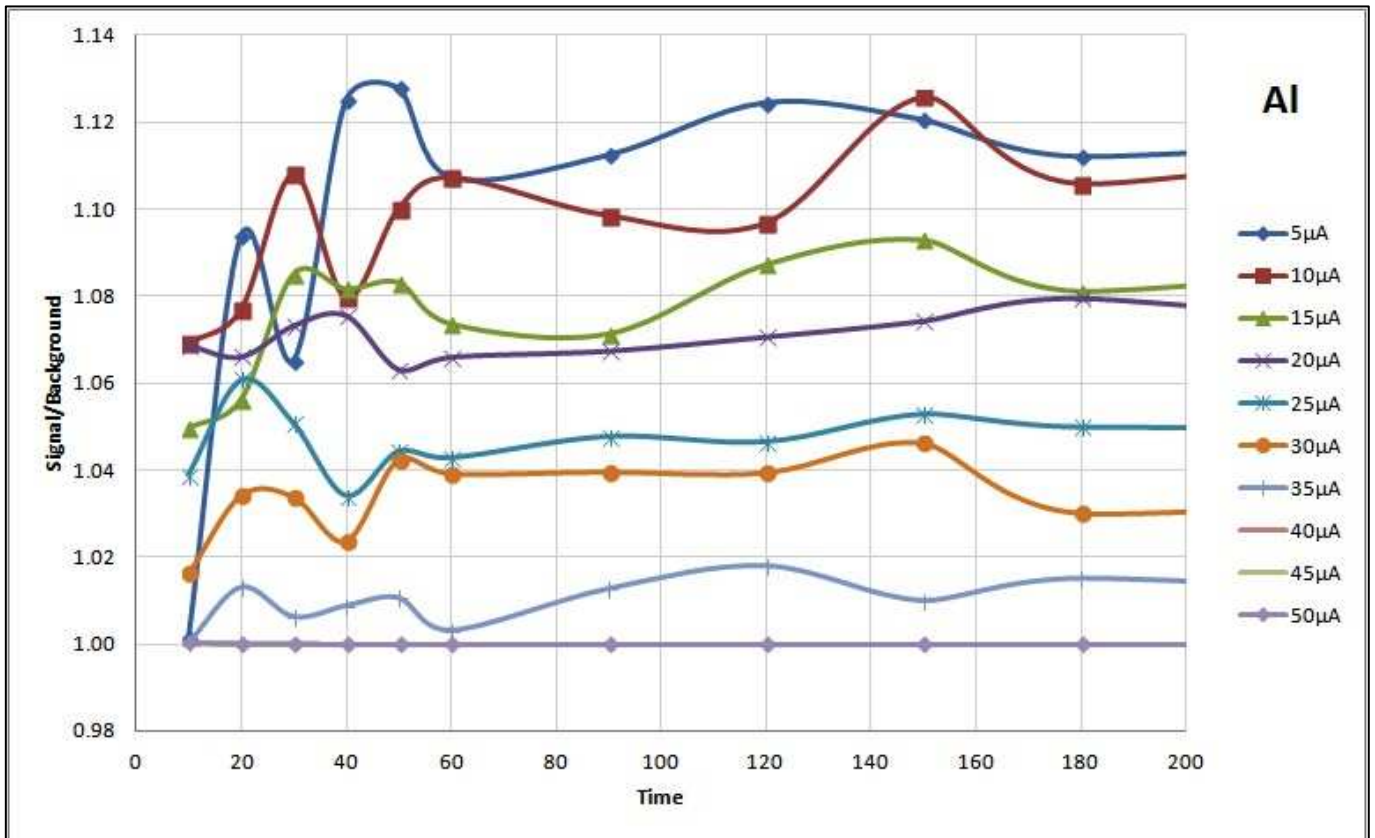


Fig. 3. Variability of current settings as a function of time and signal/background for aluminium.

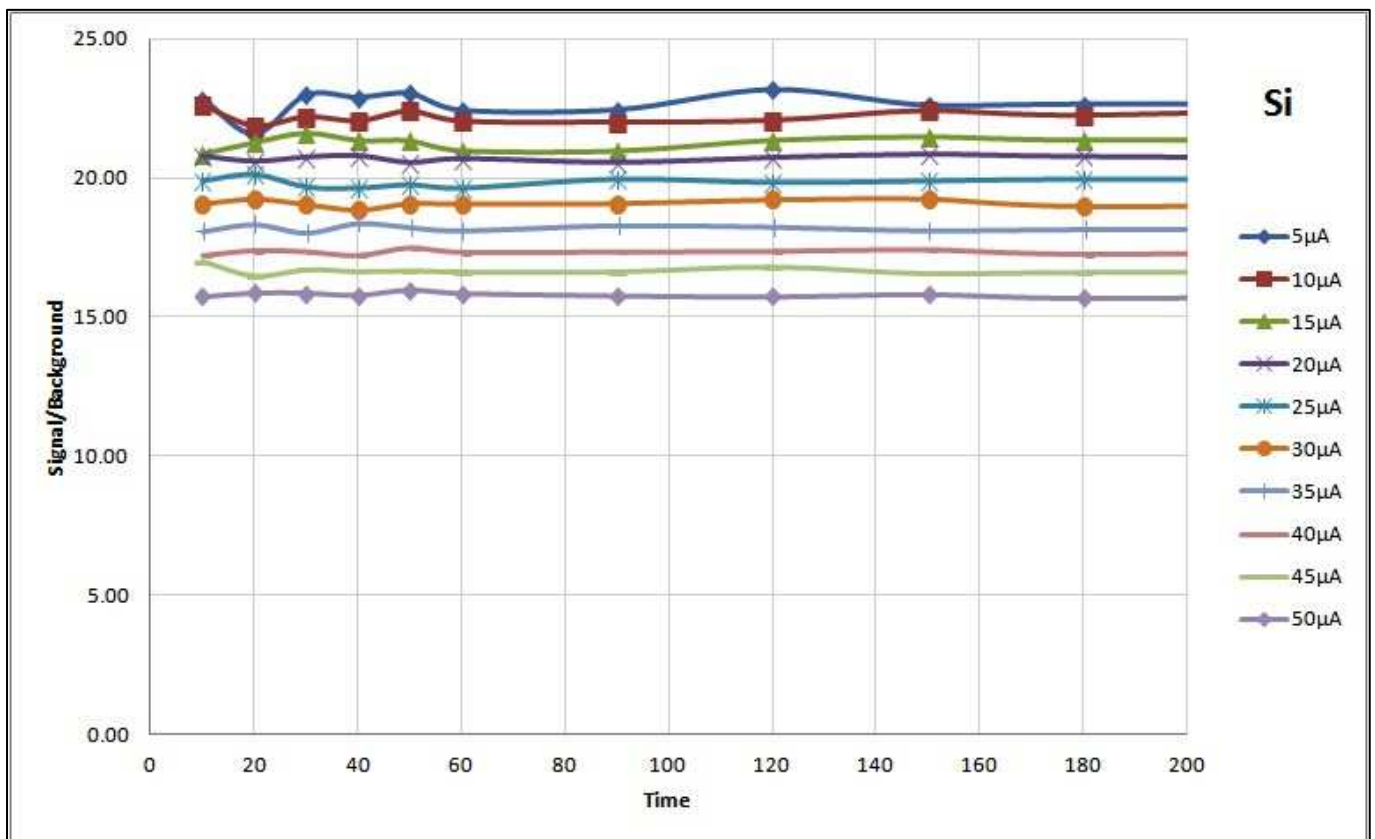


Fig. 4. Variability of current settings as a function of time and signal/background ratio for silicon.

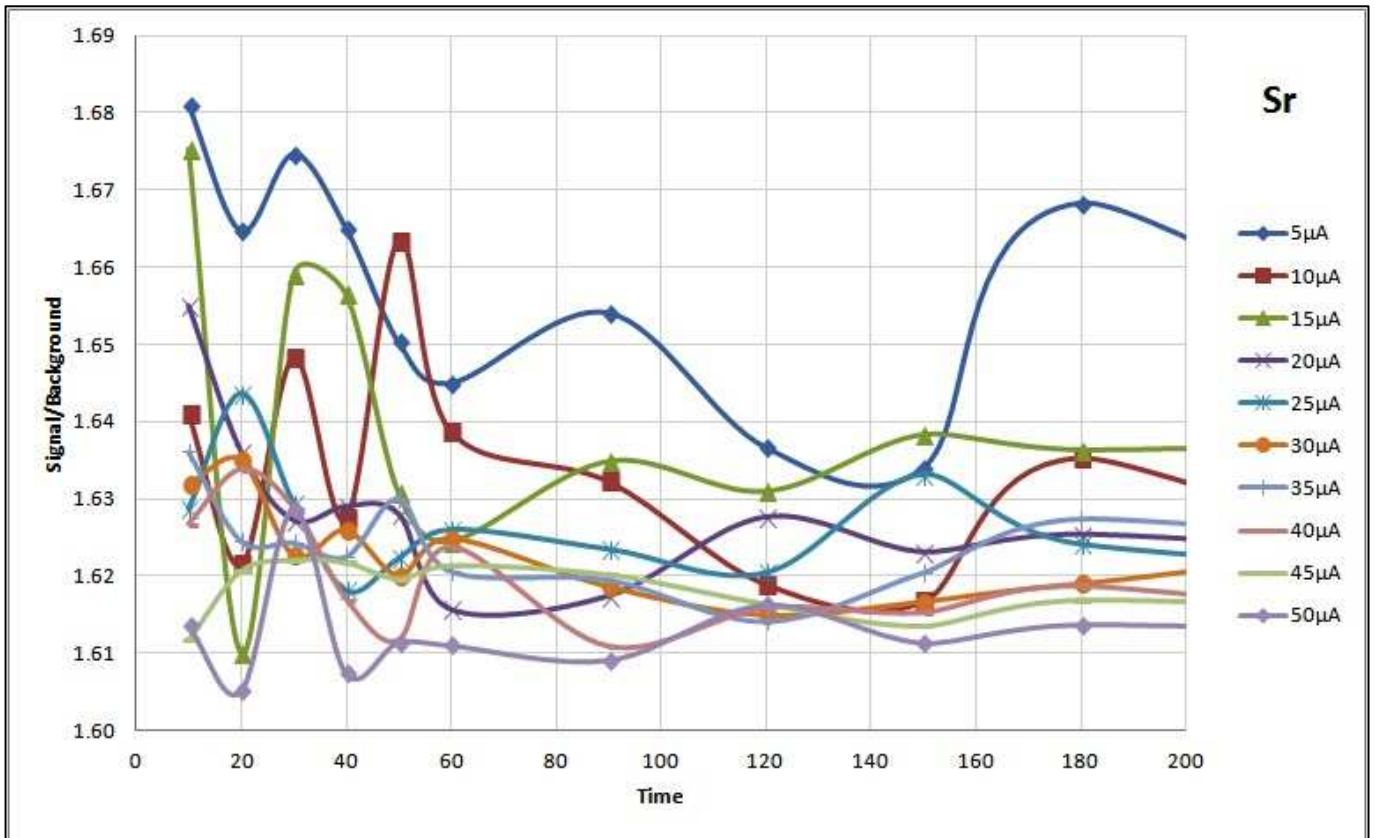


Fig. 5. Variability of current settings as a function of time and signal/background for strontium.

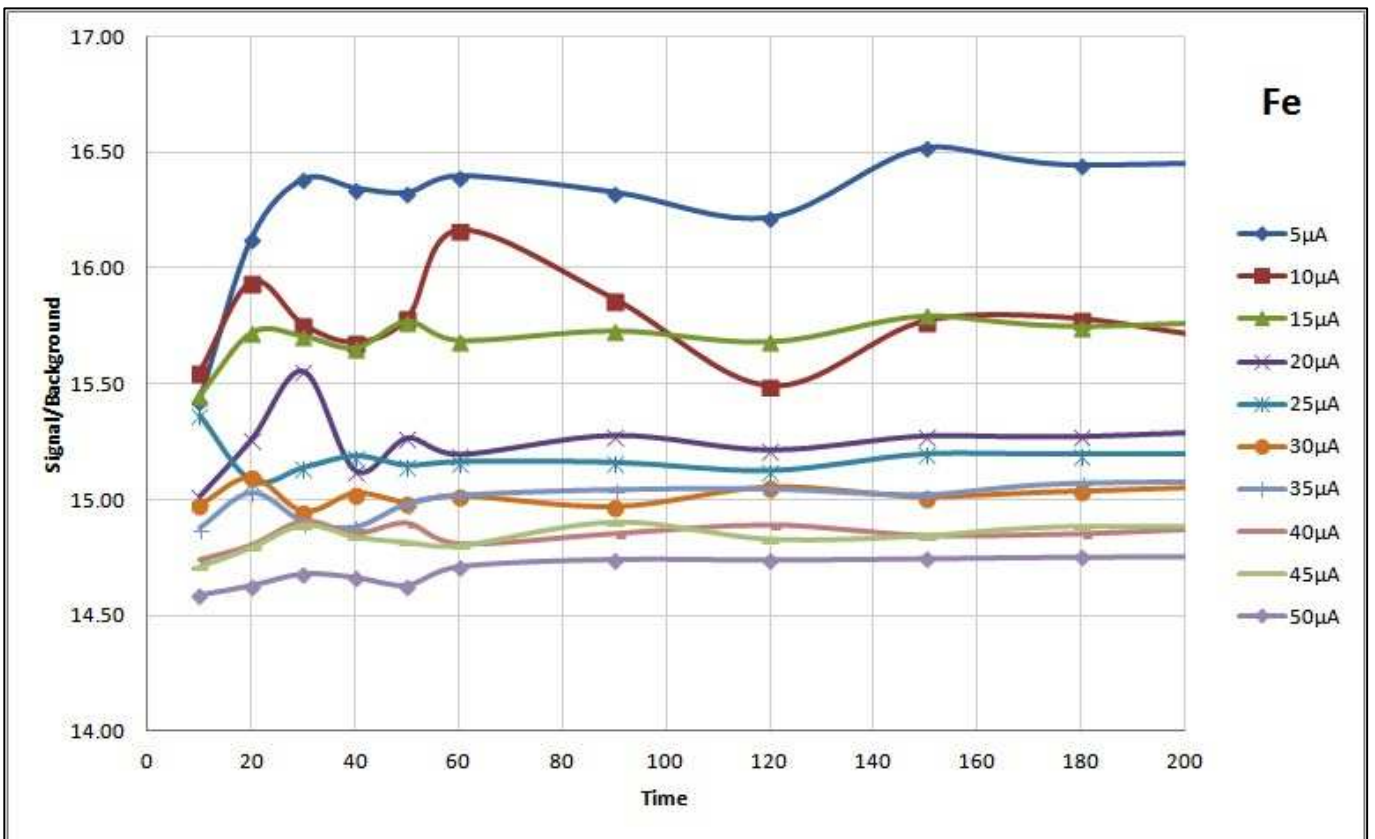


Fig. 6. Variability of current settings as a function of time and signal/background for iron.

importance of knowing in advance which elements are being sought. It is most likely that any study involving a complex material will require a number of analyses at a selection of settings, i.e. a low voltage setting focussing on light elements and higher voltage settings to look for heavy elements. Major elements will give a more stable signal/background ratio than trace elements, but the detection of both are strongly influenced by the atomic weight of the element and the matrix of the sample.

In terms of qualitative analyses, a 'point and shoot' approach will allow the identification of major and minor elements within a sample. Caution would need to be used to ensure that any trace elements identified are in fact elemental peaks and not interference peaks (Bearden 1967), this in itself would require a certain knowledge of X-ray interactions. Likewise, if a meaningful qualitative study of the nature of the material were to be undertaken, not only would the analyst need to be familiar with the technique of XRF, they would also need to understand the nature of the sample. In all probability, more than one type of analysis would be needed per sample, thereby further reducing the 'point and shoot' nature. All of this would need to be carefully planned so as not to waste valuable field time. For quantification purposes, the stability of the signal/background ratios would need to be considered. If changing the duration of the analysis has a such a marked effect on the ratios, then this will surely affect any quantification attempted. Care would also need to be taken to ensure that the right matrix matched standards were used for calibration.

HH-XRF has a lot of potential for archaeometrical studies, but this research has shown that caution needs to be taken. The technique is far from being a simple 'point and shoot' method, and a lot of preparation is required for a thorough analysis. Samples themselves need to be optimised, so too does the HH-XRF. Ideally, an analyst trained in the interpretation of X-ray spectra is also required on the project.

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