The Curse of the pXRF: the Negative Consequences of the Popularity of Handheld XRF Analysis of Copper-Based Metal Artefacts

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Keywords

Portable X-ray fluorescence spectrometer (pXRF), copper-based metalwork, lead, silver, tin

Abstract

In this paper I shall explore some of the negative consequences of the current popularity of portable X-ray fluorescence (pXRF) analysis. There is no doubt that this portable device, which can be taken to museums and sites, has revolutionised the study of the compositions of many classes of archaeological material, but the apparent simplicity of its operation and the generation of analytical results has also created problems, particularly as regards the analysis of metals.

Many archaeologists and museum curators do not seem to understand that pXRF data generally does not reflect bulk composition of copper-based metalwork. PXRF analyses the surface of an artefact, which is of course subject to weathering and alteration, and, moreover, some elements segregate or enrich on the surface of objects during metallurgical processes. A further problem is that it is becoming more and more common for museum curators to refuse to authorize destructive methods of analysis since pXRF analysis can be effected without damage to ancient artefacts.

The misunderstanding by many archaeologists and curators of the nature and significance of pXRF is illustrative of the misunderstandings that exist between materials scientists and archaeologists.

Introduction

In this brief paper I shall discuss the application of portable X-ray fluorescence (pXRF) devices to the analysis of prehistoric copper-based metalwork, and the pitfalls that may not be immediately obvious to archaeologists who attempt to use the data that are generated by such studies, or even more so use such a device without a complete understanding of the principles and practice of its operation. The technique has been at the centre of debate for some time, and there is no doubt that correctly used it can be an excellent tool for the analysis of certain archaeological materials, such as obsidian (Speakman and Shackley, 2013). However the application of pXRF analysis to the study of ancient copper-based metalwork provides an excellent illustration of the pitfalls of communication between archaeologists and materials scientists.

A preliminary version of this paper was presented at the 23rd Annual Meeting of the European Association of Archaeologists in 2017; the abstract of another session organised at the conference, entitled 'Applications using hand-held portable X-Ray Fluorescence spectrometers', read: 'The production and use of hand-held X-ray fluorescence spectrometers has exploded over the last decade in its use on archaeological materials around the world due to its non-destructive nature, portability, and relatively modest cost for such analyses. … The portability of the instrument has allowed analyses to be conducted within museums and storage facilities, and in many cases where practicality, cost, or current laws prohibit taking destructive samples and/or transporting objects outside of the country' (Tykot and Vianello, 2017). Given these positives, we might ask, what is there not to like about archaeological applications of pXRF instrumentation?

There is a vast body of metal analyses for prehistoric Europe – for example, the Stuttgart optical emission spectroscopy analytical programme ('SAM') published some 22,000 determinations – and compositional data has been generated since at least the end of the eighteenth century, using many different analytical techniques (Pearce, 2016, p.47). The challenge is to integrate data from different analytical programmes using different analytical techniques, and to understand its archaeological significance.

It is a principle of good science that data is only valid if it can be reproduced experimentally and verified. However, analytical data is only significant if it can answer archaeological or other scientific questions. Although data can become important once its significance is understood, sometimes a long time after it was first generated, until such a time, data that does not document what it is claimed to document constitutes 'junk' data, with no value as it tells us nothing. A number reproduced in a data table is only valid if it meets the criteria of good science and has meaning.

Finally, if archaeologists are to understand analytical data then it is vital that they understand the limitations of the analytical techniques that produce the data they use.

XRF analysis

Textbook explanations of the principles and functioning of X-ray fluorescence (XRF) instruments emphasise a number of key points. XRF spectroscopy is a surface analysis whose accuracy may be affected by, e.g. 'the surface geometry, possible surface patinae and alterations, irregular shape of the probed sample volume, non-optimal geometry of detection, etc.' (Artioli, 2010, p.37). It has the great advantage of being non-invasive and non-destructive, which is of course of great interest to museum curators responsible for archaeological artefacts, but this of course conflicts with the observation that '[a]n ideal sample [for XRF analysis] is one which is polished flat …' in order to provide a consistent analytical geometry (Henderson, 2000, p.15-16).

The surface analysis of metal artefacts

It is widely understood that the surface of a metal artefact is subject to weathering and alteration, as well as conservation treatments (e.g. Vianello and Tykot, 2017; see Nørgaard, 2017, pp.107-111, for an example of the analytical detection of conservation treatments), but most XRF studies of ancient metal artefacts ignore the fact that many elements, for example silver, can be concentrated on the surface of an object through metallurgical processes, giving rise to phenomena of surface enrichment, which can also be the consequence of corrosion. This means that the surface composition of a metal artefact does not necessarily reflect its bulk composition. Moreover, such changes to the surface composition may not follow a linear pattern. This was well demonstrated by Beck, et al. (2004), who showed how the surface silver content of silver-copper coins reached the eutectic composition of 72% when the bulk silver composition was still around 18% and remained stable until 72% bulk silver was reached, which means that the surface silver content is not a simple reflection of the bulk composition. Thus the 'significant' silver contents found using pXRF analysis by Freund, et al. (2016a; 2016b) for three Copper-Age copper-alloy artefacts from Monte d'Accoddi (Sassari SS, Sardinia), of 3.30% (an axe), 3.90% (a pin) and 13.10% (a dagger) are highly unlikely to be an accurate reflection of their real bulk silver content (Pearce, 2018, p.97).

However, it is not only silver enrichment that creates analytical problems: lead segregates during casting in copper alloys (this has been well known by archaeologists for a long time: Coghlan, 1953, p.99; cf. Caley, 1964, pp.6-7) and is enriched in the corrosion of copper alloys (Wadsak, et al., 2000). Furthermore, during corrosion processes, tin migrates into the patina in a process known as destanification or tin de-alloying (*ibid.*) and iron from the surrounding soil can be concentrated in the patina (Pernicka, 1995, pp.43-44; see Orfanou and Rehren, 2015, p.393 for a quantitative assessment of this phenomenon). As we shall see from the next two case studies, failure adequately to consider these phenomena can seriously impair the usefulness of pXRF analyses of copper-based metalwork, particularly those with significant percentages of lead. This means that not only is it highly unlikely that the data tables presented in the two publications discussed below accurately reflect the lead, tin, silver and iron content of these objects, but that as a result they do not reflect the true content of the other elements either, which are expressed as uncorrected percentages (and indeed nor can they do so, as the actual bulk compositions are unknown).

In another example from the archaeological literature, 223 metal objects were determined using a portable ED-XRF device from the huge (circa 14,800 objects) Early Iron Age San Francesco founder's hoard from Bologna (BO, Italy), which was probably deposited at the beginning of the seventh century BC (Bietti Sestieri, et al., 2002). Patina was removed from the artefacts at the point of analysis and we are told that where possible, the interior of breakages of damaged objects were analysed (*ibid.*, p.671), though unfortunately we are not told *which* of the published analyses were actually carried out on the interior of artefacts. Data are reported for copper, tin, lead, arsenic, antimony, iron and silver (*ibid.*, tables I-XIII). Lead was the most common element determined after copper and tin and the authors suggest that the copper/tin ratio is linked to the lead content in the case of razors, palettes and horse-bits (*ibid.*, p.672). 67 artefacts were analysed at least twice and Table 1 illustrates some of the analyses, illustrating the great variability in lead

Table 1. Selected portable ED-XRF analyses of artefacts from the Early Iron Age San Francesco hoard, Bologna (BO, Italy). Reported error: 30% for concentrations <1%, 20% for concentrations of 1-4%, 10% for concentrations of 4-10%, and <2% for concentrations >10%; detection limit for arsenic: 0.8%; n.d. = not detected. Source: Bietti Sestieri, et al., 2002, pp.671-672, tabs I and X.

Artefact	Inv. N.	Cu%	Sn%	Pb%	As%	Sb%	Fe%	Ag%
Type San Francesco axe	61344a	91.9	6.4	0.3	0.9	0.2	0.2	0.1
	61344b	90.5	7.3	0.6	0.9	0.2	0.4	0.1
Type San Francesco Axe	61441a	90	6.0	2.9	n.d.	0.4	0.5	0.2
	61441b	87.1	7.8	3.9	n.d.	0.5	0.4	0.3
Type San Francesco Axe	61449a	89.8	8.4	1.2	n.d.	0.1	0.3	0.2
	61449b	90	8.9	0.7	n.d.	0.1	0.1	0.2
Type San Francesco Axe	61453a	92.9	4.4	1.4	n.d.	0.5	0.5	0.3
	61453b	91.9	4.7	2.3	n.d.	0.6	0.2	0.3
Disk ingot	61286a	95.5	1.3	2.1	n.d.	0.2	0.8	0.1
	61286b	96.2	1.1	1.6	n.d.	0.2	0.7	0.2

content, which is in no small measure likely to be due to segregation and/or enrichment. We might ask what use this data has, other than to demonstrate that a tin bronze was used to make the artefacts and that lead was also present in relatively large proportions. Indeed, it could be commented that the use of tin bronze is hardly a surprise at this period! The tables record the results of the determinations, but are arguably of little archaeological significance as they are unlikely to reflect the artefacts' bulk composition.

A recent paper by Vianello and Tykot (2017) provides another example of a pXRF study of prehistoric metallurgy, in this case presenting data for copper, tin, lead, arsenic, zinc and iron for 84 artefacts from Sicily (*ibid*., table 1; the contextual data is not always secure, but they assign four to the Copper Age, 40 to the Early Bronze Age, 34 to the Middle Bronze Age and 6 to the Late Bronze Age; in addition, qualitative data is presented for an unspecified Early Iron Age object). We are told that '…limited permission from the museums prevented scraping in most cases' (Vianello and Tykot, 2017, p.397), suggesting that their results are likely to be affected by corrosion-induced enrichment of tin and lead to the surface (Wadsak, et al., 2000). They claim that by taking measurements at multiple points they were able to 'assess variation in the measurements to estimate … [the artefacts'] original chemical composition'; no real proof is provided in support of this assertion, though they report that multiple analyses of an armring from Palermo Museum found 'no changes between the multi-point analyses of the surface and the analyses of the scraped surface' (Vianello and Tykot, 2017, p.397). Consequently, averages are reported for some objects (*ibid*., table 1), but unfortunately data are not given for the separate determinations. An added complication, which Vianello and Tykot (2017, p.398) acknowledge, is that in some cases 'peaks of zinc' were detected, most notably in two Early Bronze Age artefacts: 5.8% in an unspecified artefact from Castelluccio (Noto SR), 15.1% in a necklace element from Cava Secchiera (Melilli SR) (*ibid*., table 1). The presence of zinc is explained as due to 'the use of some preservative varnish … chemical preservatives' (*ibid*., p.398). This further weakens the argument that the chemical compositions reported, presented as simple percentages of the elements determined, reflect the bulk composition of the artefacts. Moreover, although they acknowledge that '[non]-destructive surface analysis is not suitable to provide exact quantities of the original bulk composition' (Vianello and Tykot, 2017, p.400), their data table could easily mislead archaeologists who do not understand the complex issues involved in its interpretation into believing it an accurate reflection of the composition of the artefacts analysed: after all, it is *prima facie* compositional data and not least because the aim of the research is described as 'to estimate their original chemical composition' (Vianello and Tykot, 2017, p.397) and we are told that '[t]he chemical composition of these artefacts is the only data that is available at present and offered in this publication' (second sentence, 'Results', Vianello and Tykot, 2017, p.399). Indeed, the data table (their table 1) is also described as showing 'compositional data' (*ibid*.)

The tables in Bietti Sestieri, et al., (2002) and Vianello and Tykot, (2017), like most reports of pXRF (and indeed XRF) determinations of prehistoric copper-based metalwork, simply report analytical results which do not reflect the precise bulk compositions of the artefacts analysed. We should therefore ask, what use are such data tables to the archaeologist? They are data in the sense that they report the results of determinations, or averaged determinations, but they are highly unlikely to provide an accurate reflection of the bulk chemical composition of the artefacts analysed. In this sense, they could be described, from an archaeological perspective, as being 'junk' data.

But, why a 'curse'?

The first commercial pXRF devices were designed to be used in mining and metals recycling to give rapid analytical information (Speakman and Shackley, 2013, p.1438). Chiari (2010, p.122) describes pXRF as '… a valuable way of getting valid information in a short time without having to move the object and without damaging it in any way'. As discussed above, we may question the use of the term 'valid' for the analysis of what may be a corroded or an enriched surface, but let us accept that information about surface composition may be useful, even if only in order to identify intentional alloys and detect the presence of, say, tin and arsenic, or to act as a preliminary tool for the selection of artefacts for further study (Prange, et al., 2016, p.247).

The problem is however precisely that the method causes no damage to the artefact analysed, as long as there is no sample preparation. Museum curators, and those responsible for artefacts, have learnt that pXRF analysis can be performed non-intrusively and non-destructively, not least because its proponents have actively promoted this technique on the basis of these advantages. Since curators are responsible for the preservation of the objects in their care, and many are on display and have been expensively conserved, they are loathe to authorise destructive analytical techniques when – as they see it – pXRF can be undertaken to ascertain artefact composition. Not understanding the drawbacks of a surface analysis, and not understanding that the data tables produced do not accurately reflect the actual bulk composition of the artefact analysed, they more and more insist on non-destructive methods of analysis like pXRF, rather than allowing invasive techniques to be applied that might provide more useful and reliable information. The effect of this is that it has become more and more difficult to obtain permission to undertake analyses that can inform us as to an artefact's actual bulk composition or to investigate raw material provenance, and so trade and exchange networks, through destructive techniques such as neutron activation or lead isotope analysis.

Conclusions

Portable XRF is a useful tool for the *preliminary* analysis of metal artefacts, but it does not in itself necessarily provide data that is useful to the archaeologist. Unfortunately, its prevalence is making it harder to get permission to carry out more informative programmes of analysis. While this is in part because archaeologists and curators do not understand the true nature and significance of pXRF, the promotion of the technique by its proponents is also to blame. This situation is illustrative of the misunderstandings that exist between materials scientists and archaeologists.

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