Another significant limitation of XRF is the use of hazardous ionizing radiation. The area of the XRF analysis must be restricted to avoid the presence of non-authorized personnel (e.g. museum visitors). Warning signs of ionizing radiation must be put up and the authorized personnel must use a personal protective device.

For UV imaging, the area of the analysis must be dark to avoid the presence of other light sources. The dark environment is also preferable for the FORS analysis as the light of fluorescent lamps might affect the shape of the reflectance spectra.

## Potential costs

The cost of equipment used for pigment analysis mainly depends on the method of analysis (FORS, XRF, Raman, FTIR) and the set-up (handheld, portable, scanner). For example, FORS and imaging techniques are relatively cheap, with equipment costs not exceeding a few thousand euros. Other spectroscopic methods require more sophisticated configurations resulting in higher prices. The handheld machines for FTIR, Raman and XRF may cost from 30,000 to 50,000 EUR. The good quality portable, but non-handheld spectrometers could reach up to 100,000 EUR. Finally, machines equipped with scanner options may cost up to 300,000 EUR. However, the operational costs are low as no consumables are needed for non-invasive analysis.

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# CHAPTER 16

# Portable XRF as a guiding tool for sampling in archaeometallurgy

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### Introduction

The study of ancient metals with the application of scientific analytical techniques, often referred to as Archaeometallurgy, aims at reconstructing how metals were produced, worked, used, and circulated in antiquity (Rehren and Pernicka 2008). Additionally, analytical examination of metal artefacts can provide insight into their weathering and corrosion, aiding conservation science. Beyond the metal artefacts themselves, archaeometallurgy encompasses a range of other finds, utensils, by-products and other traces of metal production and working, spanning mine galleries and associated spoil heaps, slags, furnace and crucible fragments, metal spills, litharge and many others. The multitude of metallurgical remains is an important asset for the study of ancient metallurgy, allowing direct insight into the full operational sequence of metal artefact production in its cultural and natural environments. Comprehensive understanding of these materials, however, necessitates the use of analytical examination, using a range of techniques to gather macroscopic, microscopic, elemental and isotopic data.

Sampling should be guided by research questions, to ensure that conclusions are relevant, valid and statistically significant. In addition to visual observations and contextual information, sampling decisions can be aided by analytical data collected non-destructively in the field or the museum using a portable X-Ray Fluorescence spectrometer (pXRF). XRF is a technique for elemental analysis; nowadays instruments can be portable or handheld allowing fast analyses of material surfaces, with or without sample preparation (Shugar and Mass 2012). With adequate planning and sampling strategies, a pXRF can help address significant archaeological questions. This chapter provides an outline of research questions and approaches in archaeometallurgy, before focusing on the factors that influence the selection of samples for further analysis, with particular emphasis on the potentials and limitations of using pXRF.

## Research scope

Archaeometallurgy is concerned with all aspects surrounding ancient metals, including ore mining and primary production (smelting), secondary metalworking activities (refining, alloying, manufacture of artefacts from raw metal or through recycling/re-working etc), metal usage and metal circulation. This section compiles some relevant examples.

An extensive program of archaeomining investigations was undertaken in the 1970s aiming to identify Aegean sources of Archaic and Classical gold and silver. Work on the islands of Thasos (Wagner and Weisgerber 1988) and Siphnos (Wagner and Weisgerber 1985) included prospection of ancient mining galleries and identification of ancient metal production sites. Samples of ores from the mines were analysed for their elemental composition to assess what metals were being sought in each case, and in terms of their lead isotope composition to address questions of metal provenance.

At its earliest stages, production of metals took place primarily within settlements and being on a small scale left relatively few remains such as slags and metallurgical ceramics. Analyses of these remains, however, is crucial to establish what process was taking place and the particular technological parameters involved. One of the earliest known copper production sites is found at Belovode in Eastern Serbia dating from c.

5,000 BC (Radivojević et al. 2010). Analyses of small samples of ores, slags, minerals and artefacts showed that copper minerals were both smelted (heat-treated) to metal and cold-worked to make beads, while lead isotope analyses demonstrated the exploitation of different sources for these minerals. On the contrary, laboratory examination of an allegedly earlier copper slag from the site of Çatalhöyük in southcentral Anatolia disproved that this was a metallurgical by-product (Radivojević et al. 2017).

Production on a larger scale or sustained over long periods of time can lead to substantial accumulations of slags and other metallurgical remains, usually identified as slag heaps on dedicated metal production sites. Using stratigraphic sampling of slag heaps for analysis, coupled with direct dating of slag layers, it is possible to trace the evolution of technologies over time, as recently demonstrated in the copper-producing areas of Timna and Faynan in the Wadi Arabah (Ben-Yosef et al. 2019). Elemental analyses of numerous artefacts and debris from a single site can also provide insight into the selection and management of different alloys, as shown in a medieval workshop in Paris (Bourgarit and Thomas 2012).

The material and visual properties of a metal artefact and its suitability for a particular function are dependent both on its chemical composition and the way it was cast or worked. Macroscopic examination, particularly when aided by low power magnification, can reveal relevant information, but metallography, the examination of a polished metal surface under high magnification, is the ideal approach to understanding how a metal was worked to produce an artefact. For example, analysis of copper-base objects from Prepalatial Crete revealed great variability in production methods and skill (Tselios 2009); in Pre-Columbian Colombia, metallography helped understand gilding and other techniques applied to modify the surface appearance of gold artefacts (Sáenz-Samper and Martinón-Torres 2017).

Use-wear analysis addresses the question of what the metal artefact was used for. Low-power magnification is usually employed and observations on the working edges of tools or weapons are compared to experimentally produced patterns, as exemplified by a study of Chalcolithic metalwork from Italy (Dolfini 2011).

The question of metal provenance is always of prime interest, as it can reveal patterns of material circulation or trade. Lead isotope analysis, often combined with trace element analysis, remains the most common approach to this complex question for copper, lead, and silver-based artefacts. Extensive programs of metal provenance have been undertaken with this methodology, for example in the Bronze Age Mediterranean (Stos-Gale 2000), Shang China (Zhangsun et al 2021), and, increasingly, pre-colonial Africa (Stephens et al. 2020). The use of other isotope systems for metal provenancing is being explored (Stephens and Killick 2021).

## Sampling considerations

The majority of analytical approaches discussed above require the removal of a small sample, usually only a few milligrams. In studies where large assemblages are involved, judicious sample selection is necessary to obtain valid conclusions while avoiding wasting time and resources. The parameters guiding sampling depend on the particular questions being addressed. Generally, all relevant contexts, chronological and spatial, need to be represented, as well as different types of materials (e.g. slags, minerals, artefacts) or different types of metal artefacts. Sampling strategies in archaeology have been treated extensively elsewhere (Orton 2000); the focus of this section is to consider how portable XRF can be used to guide subsequent sampling; or, in some situations, be employed as the sole analytical method permitted.

The simplest way to use a pXRF is to gather qualitative data, that is, results on what elements are present, rather than how much of each (Figures 1-2). The approach can be particularly useful for large metal artefact assemblages. The identification of certain elements qualitatively can distinguish between the main copper alloys for example, through the presence of arsenic (arsenical copper), tin (bronze), zinc (brass) or lead (leaded copper) etc. The entire assemblage of 106 copper-based artefacts from the Early to Middle Bronze age settlement of Palamari was analysed with pXRF (Georgakopoulou et al. in press). Comparison with the results from a selection of samples sectioned for SEM-EDS analysis, showed that grouping on the basis of all elements detected by pXRF (As, Sn, Pb, Ni, Ag, Au) did not hold, due to the limitations of the analysed surfaces (see below). The distinction between arsenical copper and bronze was, however, validated in all cases, allowing broader inferences on the relative abundance of the two alloys across the four periods of habitation.

Figure 1: Use of a pXRF in handheld mode for the analysis of a metal artefact.

Figure 2: Placing a gold coin in a secure chamber for benchtop pXRF.

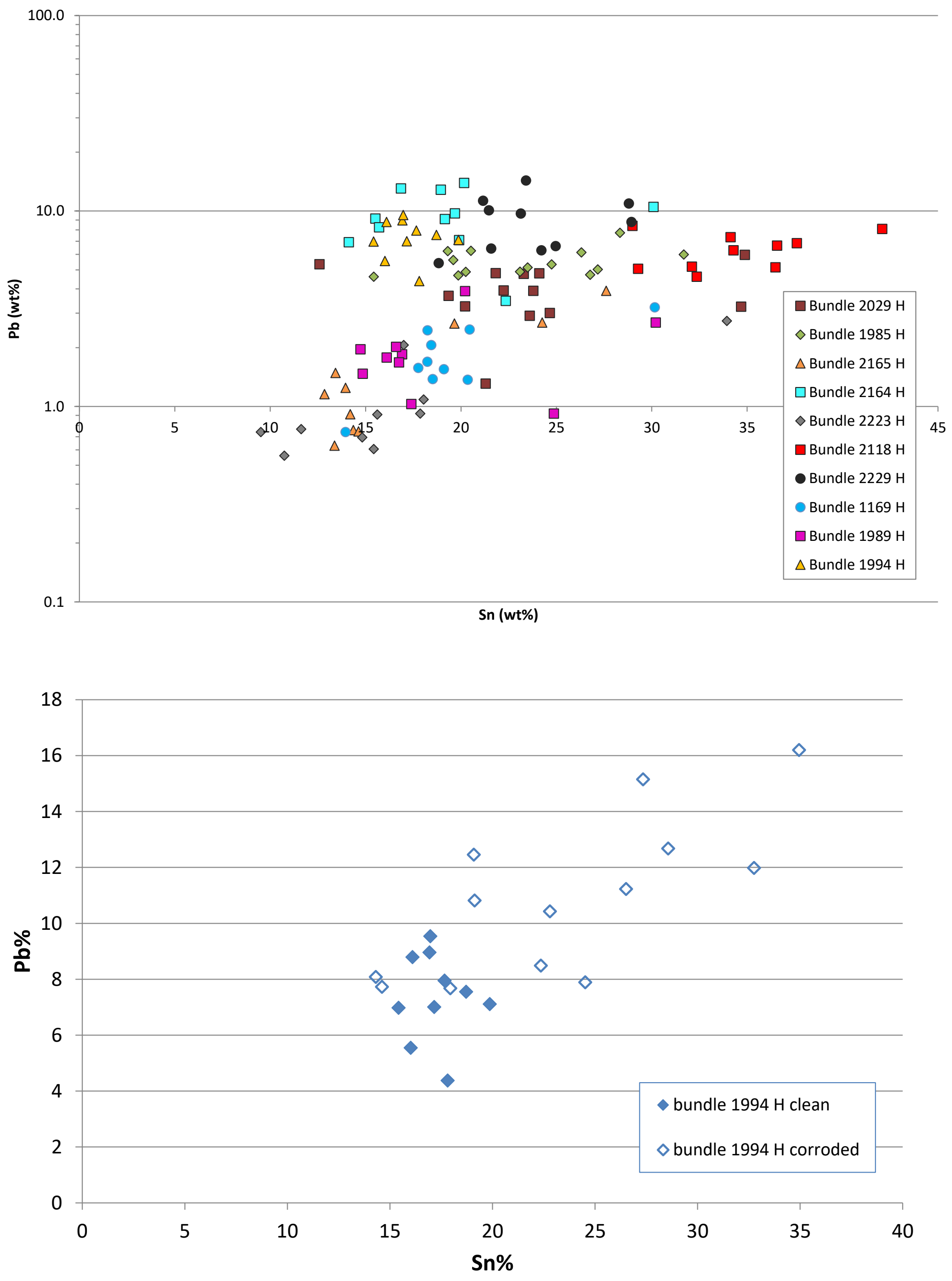
In a different example from Colombia, non-invasive XRF analyses of dozens of votive gold alloy figurines suggested that each offering was made of metal from a distinct metal source. Subsequent trace element analyses of a small subset using LA-ICP-MS validated this hypothesis (Martinón-Torres and Uribe-Villegas 2015).

In some cases, however, in-situ analyses with pXRF may be the only analytical approach permitted due to restrictions in sampling and transporting artefacts. Quantitative

Figure 3:

A) Scatterplot of the tin and lead contents of a selection of bronze arrows from the Terracotta Army, as analysed non-invasively by surface pXRF. Although there are outliers and overlaps, and the actual figures have a significant analytical uncertainty, the large sample numbers support the proposition that each bundle of arrows represents a coherent metal batch.

B) Comparison of the results on clean vs corroded surfaces for a small selection within a particular bundle demonstrates that surface corrosion is largely responsible for the data scatter (Martinón-Torres et al. 2014).

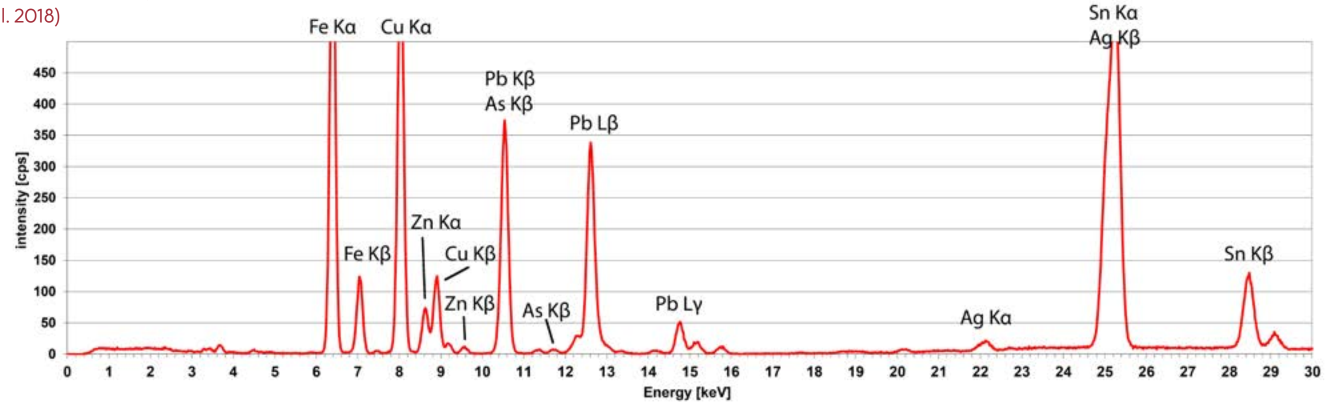


analyses are then favoured in order to collect as much information as possible, although sometimes it is possible to make useful inferences based on so-called 'semiquantitative' analyses, whereby we can at least differentiate 'high' from 'low' concentrations of a given element. As will be discussed in the following section, several parameters need to be taken into account to ensure good quality data, and limitations of surface analyses may reduce the quality of individual measurements. The power of the approach, however, lies on the ability to analyse easily large assemblages, looking at broad trends across different chronological periods or sites. Surface analyses with pXRF on approximately 1,000 copper alloy artefacts from Late Bronze Age and Early Iron Age contexts in Cyprus (Charalambous 2016; Charalambous et al. 2021) brought to light a number of patterns including differences between sites in the availability of tin, the use of high tin contents for certain categories of artefacts, deliberate addition of lead to improve castability, and the use of recycled metal. In China, pXRF analyses of hundreds of arrowheads from the Terracotta Army showed that each bundle of arrows, corresponding to the contents of a quiver, had been produced together and represented a single metal batch (Martinón-Torres et al. 2014, Figure 3).

pXRF also finds use in the analyses of metallurgical remains (Figure 4). Rademakers and Rehren (2016) analysed all 1042 fragments of crucibles at Pi-Ramesse in Egypt qualitatively with pXRF while a sample was removed from 49 of them for SEM-EDS analyses. The results show similar broad trends in terms of a higher presence of 'clean' versus iron-contaminated crucible slag. At the Aegean site of Palamari, simple qualitative assessments on the fragmentary ceramics, distinguished between materials associated with arsenical copper and bronze processing; some of the data were subsequently confirmed through sampling and SEM-EDS analyses (Georgakopoulou et al. in press).

Similarly to crucibles, slags are heterogeneous materials and the interpretation of non-destructive surface analyses needs to be done with caution. In the case of the Early Bronze Age Cycladic site of Dhaskalio Kavos, qualitative pXRF analyses of a large number of slags without preparation helped attribute them into two previously identified distinct groups associated with the production of unalloyed and leaded arsenical copper, respectively, based on the presence or absence of arsenic and lead, demonstrating the significantly higher abundance of the unalloyed copper slags and guiding further sampling (Georgakopoulou 2018, 503). More robust semi-quantitative data were needed to classify Roman iron slags from the site of Sagalassos and its surroundings into two previously identified groups in the field, as sample export was no longer permitted (Scott et al. 2016). Sample pulverisation and preparation of pressed pellets was deemed necessary, as well as the development of a dedicated calibration for quantification.

Figure 4: Portable XRF spectrum obtained from the inner surface of an Iron Age crucible. The two main metallurgical peaks are for Cu and Sn, as the main elements in the alloy, but smaller peaks for Zn, As, Pb and Ag can be detected too. The large Fe peak comes predominantly from the ceramic fabric, and it is impossible to tell whether this element could have been present in the alloy (Adams et al. 2018)



## Potential biases/limitations

The advent and development of pXRF has opened up great possibilities for archaeometallurgy, generating important research data on its own merit, allowing fast analyses of large assemblages, replacing invasive methods, and guiding judicious sample selection when other analytical techniques are needed. The technology is particularly well-suited to the identification of the key elements typically encountered in archaeological metals. However, it is important to understand potential biases and limitations of the technique to avoid unfounded conclusions. Most of the examples of poor practice we have encountered can be explained by a lack of familiarity with these requirements and limitations.

The first important consideration is that pXRF is a surface technique, recording information from only a small fraction of a millimetre on the surface of the artefacts analysed (see review in Van Ham-Meert et al. 2020). The surface corrosion of most archaeological metal objects means that their non-invasive pXRF analysis will only give indicative values of

Figure 5: Using a rotary tool to remove the patina in a small spot of a metal object, to facilitate pXRF analysis.

the patina composition, and not of the underlying metal. In surface analyses of metallurgical ceramics, some elements such as lead, zinc or arsenic will always appear overrepresented at the expense of others (Kearns et al. 2010). For reliable compositional analyses of metal, it is necessary to expose sound metal by abrading a small area of the patina (from a few hundred micrometres to a few millimetres, depending on the instrument, Figure 3). Similar challenges apply, for example, on objects that were gilded or surface-treated in any other way – for example, in a previous conservation treatment. Furthermore, pXRF is optimised for flat, homogeneous surfaces – and this is often not the case for metal objects and, especially, for other metallurgical artefacts such as crucibles or slag.

Another set of challenges derives from the need to develop matrix-matched calibrations. The main elements in archaeological metals are generally easy to identify by pXRF, but we cannot assume that factory-built calibrations are suitable for archaeological metals. The peculiar nature of crucibles and slags, which often contain mixtures of metals and oxides, heavy and light elements, make them even more challenging for off-the-shelf pXRF analysis. Crucially, most pXRF instruments available commercially will assume that the samples are 'ideal', and proceed to turn the spectrum into numerical values, potentially creating a false sense of accuracy. It is the user's responsibility to assess the certainty of those values and adjust interpretations and further sampling accordingly.

Finally, users of pXRF, and archaeometallurgists more generally, should be wary of the risks of sampling bias, when only a subset of artefacts can be analysed: for example, if a study focuses only on broken artefacts, or on less corroded ones, there is a high likelihood that whole compositional categories may be excluded, e.g. objects that did not break, or corrode, precisely because of their particular composition.

## Necessary infrastructure/instrumentation

Depending on the hardware, accessories and factory calibrations selected, a pXRF instrument costs around €25-50,000. The instrument itself is relatively small, weighing around 2 Kg, and it can be operated easily in hand-held mode, with results displayed on a small screen. Additionally, various stands are available that can be connected to the instrument, creating analytical chambers where small objects can be analysed in a safer and more stable environment. The whole kit, including a hard case for transport, weighs between 8 and 15 Kg. Most instruments can also be operated from a laptop and have facilities for wireless data back-up. Although relatively sensitive, they are designed to be moved and used in the field. Reference materials of known compositions ('standards') should also be purchased with the equipment, for method development and data quality control. These will assess the performance of the instrument under perfect conditions, where flat and clean surfaces are tested; users should take into account the inherent limitations of archaeological materials discussed above in their interpretation.

Each analysis takes from less than 10 to around 200 seconds, depending on the material and set up, though it is preferable to obtain several repeat analysis per artefact. Most of the research time is spent preparing the materials for analysis (particularly when patina abrasion is required) and processing the data.

Overall, pXRF instruments are very versatile, easy to operate and comparatively inexpensive. However, it is essential that instruments are calibrated for the types of materials being studied. Normally several 'methods' or set ups can be available for the same instrument depending on the material analysed, but they typically require specific customisation for archaeological materials (e.g. gold alloys, copper alloys, ores, and crucibles, each having their own requirements). For this reason, it is essential that an analyst with an understanding of the fundamental physics of XRF is involved in the set up and data analysis. In addition, operators should be trained in health and safety requirements.

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# CHAPTER 17

## Urban micro-metallurgy: from the field to the lab

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### Introduction

For the past 5,000 years or more, metallurgy has played a very important role in most societies. The archaeological traces of this are varied, ranging from high-end well-preserved elite gold objects, to mundane metal items of everyday use, as tools, utensils, weapons or jewellery, to workshop remains where artefacts were cast, hammered and finished, and the often very substantial left-overs from the primary production of the metal: ancient mines, spoil heaps, and slags and furnace remains.

This chapter focusses on micro-remains related to metallurgical activity as preserved in archaeological contexts, typically urban or village workshops, and how they can be discovered, documented and analysed *in situ* during the excavation, and through sampling and laboratory analysis. It does not cover the recovery and analysis of metal objects or metallurgical remains such as furnaces and crucibles, nor the study and recording of major features such as slag heaps. However, these micro-remains have an important contribution to make to our understanding of a site, while they often go un-detected due to their low visibility in the field. This chapter aims to raise awareness of some of their key features, and how to document and sample them.

There are two main types of metallurgical micro-remains related to workshop activities that often go unnoticed, due to the inconspicuous nature of the remains. Firstly, traces of non-ferrous metal working such as tiny copper or copper alloy droplets spilled during casting can indicate the former presence of a foundry, large or small. Secondly, there is the scatter of hammer scale as a material diagnostic for black smithing, in addition to the more commonly recognised smithing slags. These smithing slags, however, are often cleared out and discarded elsewhere, and therefore cannot pinpoint the exact workshop area in the same way as the micro-remains that are trampled into the workshop floor.

Beyond these 'standard cases', several types of traces can indicate mining, smelting or other metallurgical activities, even if no furnace remains or slag fragments or droplets are preserved. Finely crushed mineral-rich ore remains can indicate the crushing and grinding of ores to separate the metal-rich mineral component from the sterile gangue. Tracing these micro-remains in the archaeological surfaces can identify activity zones otherwise invisible.

The initial discovery of these archaeologically significant activity traces is often haphazard since none of them are particularly conspicuous, and the faint visual traces may easily go unnoticed, particularly in rescue excavations where time is of the essence, or in inclement weather conditions.

## Research scope

### Foundry floors

Foundries or casting workshops regularly handle significant quantities of copper or copper alloys, melting them in crucibles before pouring them into moulds as the first and major forming step. The actual melting of the metal in their crucibles can take place in a variety of hearths and furnaces, which often leave only non-diagnostic burnt spots in the soil. Crucible fragments may offer a first line of approach to recognize a non-ferrous workshop, and their study can give important insights into the processes and technologies