Superman Vision or Not: Examining the Use of Portable X-ray Fluorescence Spectrometry for the Study of Copper Alloys in Archaeology.

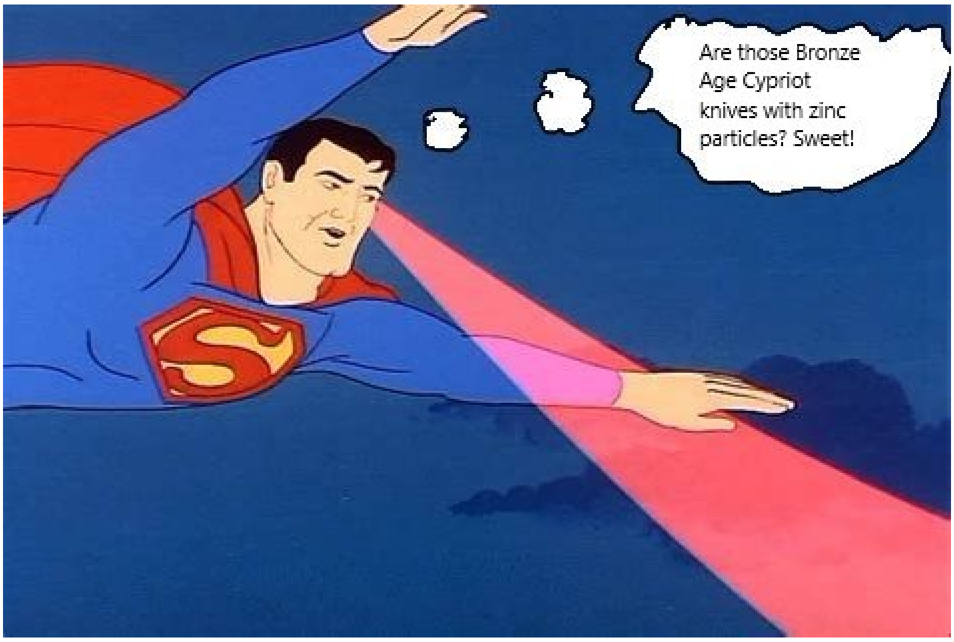
Verhage, Jan

Citation

Verhage, J. (2023). *Superman Vision or Not: Examining the Use of Portable X-ray Fluorescence Spectrometry for the Study of Copper Alloys in Archaeology.*

Superman Vision or Not: Examining the Use of Portable X-ray Fluorescence Spectrometry for the Study of Copper Alloys in Archaeology.

Wicher Verhage



Source for the front page figure: https://www.themarysue.com/wifi-xray-vision-at-mit/, accessed 01-05-2023

Superman Vision or Not: Examining the Use of Portable X-ray Fluorescence Spectrometry for the Study of Copper Alloys in Archaeology.

Bachelor Thesis

Wicher Verhage, s2656647

Thesis BA3, 1083VBTHEY

Dr. Braekmans

Leiden University, Faculty of Archaeology
Leiden, 14-06-2023, final version

Table of Contents

Figures

1: An Olympus Delta pXRF Instrument as an example of what a pXRF analyser looks like. https://www.portaspecs.com/product/olympus-pxrf-analyser/. Page 4.

2: The insides of a pXRF machine and a schematic depiction of x-ray fluorescence. https://www.thermofisher.com/blog/mining/technology-focus-x-ray-fluorescence-xrf-in-mining/. Page 10.

3: Publications using the search terms pxrf, handheld xrf, portable xrf and xrf in general. The graph is divided in 5 year periods, The top graph represents data from sciencedirect.com and the bottom graph data from AATA database. Credits go to A. Shugar, (2013). Page 13.

4: Map of Cyprus with a dot indicating the location of Enkomi. Credits go to Charalambous et al. (2021). Page 19.

5: Examples of objects from the assemblage. A) Unfinished dirks, b) ploughshare c) arrowhead d) miniature ingot e) broken fibula. Photographed by A. Charalambous. Page 23.

6: Pb versus Sn concentrations in the analysed assemblage of Charalambous et al. (2021). Credits go to Charalambous et al. (2021). Page 24.

7: The types of copper alloys in the habitation phases/Levels of Enkomi, analysed by pXRF. The numbers next to the bars correspond to the number of artefacts. Credits go to Charalambous et al. (2021). Page 25.

8: Histograms showing the Sn, As and Pb content of the copper-base artefacts from Enkomi. Credits go to Charalambous et al. (2021). Page 26.

9: Ternary diagrams a) Charm calibration; b) Classifications; c) Corrosion effects. Credits go to Roxburg et al. (2016). Page 29.

10: Compositional results organised chronologically and by type. Credits go to Roxburgh et al. (2016). Page 30.

11: Example of compositional results organised chronologically and by type. These diagrams belonging to the almgren 15 and almgren 19+20 typologies. Credits go to Roxburgh et al. (2016). Page 32.

Tables

Chapter 1: Introduction

Archaeology is by its nature an interdisciplinary field of study which draws upon different methodologies from various disciplines and formulates conclusions based on incomplete information. This is because regardless of what the written record (if present) or the material record may imply, it rarely provides exact data. Nevertheless, in the 20th century methods of obtaining more concrete and factual data have been discovered and invented, a well-known example is ancient DNA sampling. Yet, even though these methods have enriched the world with a lot of new information, a lot of these new methods are destructive to archaeological materials. Some methods, for example, require a researcher to take a sample in order to understand and characterize the materials at hand. These actions are often necessary to obtain the aforementioned concrete and detailed data. Sampling, however, can compromise the integrity of an object, it is a destructive technique. Relying on destructive techniques for archaeological data goes against what some view as the purpose of archaeology: to discover and preserve the past.

This conundrum has started to change with the advent of modern technology, as more and more non-invasive and non-destructive research methods have been developed. These methods are able to obtain the same information as destructive methods at times. In fact, sometimes even more information of a higher quality from objects or environments can be obtained, without causing damage. These methods are varied and range from both imaging to compositional techniques. Light Detection and Ranging (LIDAR) is an example of an imaging technique that is able to map large parts of a geological area whilst techniques like sonar multibeams can map aquatic landscapes.
Another one of these new methods is x-ray fluorescence spectroscopy (XRF). Devices using this method can supply high quality, detailed information about the composition of inorganic objects through their elemental make-up. Furthermore x-ray fluorescence analysers are not only lab-bound, there exist smaller, portable versions as well. This allows for researchers to maximise flexibility and to obtain information from excavated artefacts at the excavation itself.

Figure 1: An Olympus Delta pXRF Instrument as an example of a pXRF analyser. (https://www.portaspecs.com/product/olympus-pxrf-analyser/ accessed 14-3-2022).

This method has drawbacks and pitfalls that cannot be ignored however, as portable x-ray fluorescence spectroscopes (henceforth referred to as pXRF) can only penetrate a certain depth, which depends on the elements present. This means that most of the time, pXRF can only analyse the surface of materials. These surfaces sometimes have been subject to an incredibly wide range of changes and transformations. Common examples could be wear and tear from use or alteration from the environment. How accurate and precise pXRF measurements can be in regards to various altered, archaeological surfaces has not been properly examined. Nor has it been examined how researchers can best employ pXRF and whether the conclusions or assumptions they make based on pXRF data are valid.

Therefore this thesis will discuss and assess how such pXRF readings can be affected by various circumstances and what the disadvantages and merits of pXRF are. Furthermore, this thesis will discuss how to properly interpret that data whilst being aware of all these factors. This thesis will mainly focus on pXRF analyses on copper (Cu) alloys, as archaeological objects consisting of Cu-alloys are frequently studied with this methodology. Furthermore, the physical make-up of copper alloys supply a lot of information about cultures and environments, but I will expand on that topic further in the text. Ultimately, this thesis will attempt to provide a detailed overview and an interpretative framework for the non-destructive analysis of Cu-alloys through pXRF.

This thesis will attempt to answer the following research question as completely as possible:

To what extend are the readings provided by portable x-ray fluorescence spectrometry devices accurate and reliable for examining Cu-alloys?

To answer this main research question there are subquestions that need to be answered as well:

- Which elements are measured and/or affected in/under different circumstances?
- Are different approaches or risks present for certain archaeological or museological assemblages?
- Are there ways to minimize or solve the problems encountered.

This thesis will rely on reviewing various sources of academic literature in order to answer this question. In addition to technical considerations of the instrumentation itself, two case studies are put forward which will exemplify some of the uses of pXRF in archaeology. These case studies will also document weathering and surface interactions that might influence the final results of pXRF research. A comparison of methods and implications utilizing these case studies will be confronted with existing literature and discussed in the fourth chapter. These case-studies have been selected on the basis of their geographical circumstances, the similarity in their research questions and general methodological approach.

In the fifth chapter, this thesis will discuss and assess the shared and differential uses of pXRF and how to which practices ensure optimal use of pXRF, based on the gathered literature. Finally, this thesis will attempt to determine the conditions to validate of the use of pXRF in archaeology and conservation science. This will contribute to the development and use of pXRF in research in these fields, with a focus on copper alloy objects.

Chapter 2: copper alloys in archaeology

2.1 What are alloys?

According to the Oxford dictionary an alloy is "a metal that is formed by mixing two types of metal together, or by mixing metal with another substance."
(Oxford Learner's Dictionaries, n.d.)
Merriam-Webster defines it as "a substance composed of two or more metals or of a metal and a nonmetal intimately united usually by being fused together and dissolving in each other when molten."
(Merriam-Webster, n.d.)

Other accredited dictionaries provide similar definitions. Alloys have been used throughout history and our modern society could not function without them. Historical societies were reliant on them as well, if to different degrees. Perhaps the most famous alloy is the one created by combining tin and copper, namely bronze. This alloy heralds the start of the Bronze Age, a period that usually marks great societal changes when it occurs in an area. This era is dated to be as early as the third millennium BC (Webb & Frankel, 1999).

Alloyed materials often have one or more qualities that elevate them above their original materials. Bronze, for instance, is harder, more durable and has a lower melting point than copper. This makes it a material that had a lot more uses and was more accessible than copper in ancient times. Whether it was for tools, weapons or art, bronze was in many categories superior to copper. The act of alloying metals and finding the best ratio for the purpose you have in mind is one that humans have worked on for a long time.

2.2 The role of copper alloys in archaeology and how they are currently studied.

As mentioned above, bronze was used for a wide variety of things throughout history. Few metals get the moniker 'Age of' after all. But there are other copper alloys as well that are frequently encountered in archaeological contexts. Brass, another example of a copper alloy (copper (Cu) and zinc (Zn)), was widely used for creating musical instruments such as trumpets (Baines, 2015, pp.19-24; Hodson, 2003).

As archaeologists attempt to understand historical societies that made such intense use of copper alloys, archaeologists must ask questions such as: how did these societies obtain their copper? How did they use these alloys? Was there particular status attached to copper-alloy items? Researching copper alloys, then, is an important source of information for archaeologists. Thankfully copper alloy items are common, widely used and with modern techniques we can discover a lot about their object biography (Kopytoff, 1986). Archaeologists have realized this for a long time already and as such there exists a lot of different methods of researching copper alloys. Various ways to discover specific characteristics such as provenance, precise mixture, and others have been devised, such as inductively coupled plasma mass spectrometry (ICP-MS) and of course XRF. These techniques will probably continue to be further developed over time, likely getting more accurate as time passes.

Currently there are many methods to perform a compositional study of copper alloys. But the history of chemical analysis in archaeology dates back to the 18th century, when Martin Heinrich Klaproth performed the first known chemical analysis on ancient Greek and Roman coins (Glascock, 2014).

After the analysis of Klaproth and until the end of the 19th century most quantitative analyses of archaeological metal objects, including copper alloys, were performed using gravimetric methods. These methods involved weighing the solids an element produced after it had been treated (dissolution, precipitation, filtration and evaporation). Gravimetric methods were very precise and informative, but could only measure one element at a time (Glascock, 2014). This meant that performing analysis on a large scale was quite difficult and it is exactly the ability to measure many elements at once of a large group of objects that can give comprehensive datasets that are useful for archaeological research.

As technology kept improving across all branches of science, in the 1920s and 1930s instrumental methods of analysis were developed. These new methods were able to address the aforementioned issue, being able to determine multiple elements at a faster rate. An example of one of these methods is optical emission spectroscopy (OES) (Glascock, 2014). Instrumental methods did not stop at OES however and grew in number, quality and capabilities. Their applicability to other types of archaeological material also grew. OES, for example evolved into inductively coupled plasma atomic emission spectroscopy (ICP-OES), which we still use today to measure multiple elements in, especially liquid, materials (Elgalabs, 2021; Olesik, 1991). A major breakthrough worth mentioning is the employment of neutron activation analysis (NAA) by Sayre and Dodson in the mid 1950s to study pottery. Especially its ability to automate various procedures was of great use (Glascock, 2014).

Other major compositional analytical techniques for bulk material worth mentioning as they are commonly used in archaeology and conservation science are:
Particle-induced X-ray Emission (PIXE), electron probe microanalysis (EPMA), inductively coupled plasma-mass spectrometry (ICP-MS), and of course, X-ray fluorescence (XRF) (Calligaro, 2008; Ghazi, 1994; Wilson, 2017).

There is one problem with most modern compositional analysis techniques however. Many modern analysis methods requires a sample from the main object in order to work. This means that even though these methods offer incredible precision, reliability, speed of work and other advantages they do compromise the structural integrity of an object.
Methods such as pXRF, PIXE and EPMA are non-invasive and thus do not carry this risk. However, even if an object would be able to be analysed non-destructively, often the transport of goods to existing laboratories is a costly, risky and sub-optimal procedure. Utilising portable analytical equipment to go to the assemblages themselves can be the only option available at times.

2.3 Chronological overview of the production and use of copper

The act of mining copper and melting it, transforming it into objects that humans found useful or beautiful started what scholars used to call the Copper age, but now is often included in the Late Neolithic.

The first signs we can see of copper usage is at Catal Höyük, in Anatolia. This site was inhabited from roughly 7500 BC Till 6400 BC and its inhabitants seem to have acquired or produced beads and other jewels made of copper, mostly used as burial goods (Mellaart, 1962, pp. 41-65). But the Copper Age/Late Neolithic eventually transitioned into the Bronze age. In the Low Countries this happened roughly 2300-2000 BC. (Clerinx, 2017). This is an important development as copper, as mentioned before, is in most ways an inferior material to use for tools, weapons and art compared to bronze. As bronze has a lower melting point as well, it could be produced in simple hearths (Timberlake, 2007, p. 31). This low melting point also facilitated the easy recycling of bronze objects, if an axe got too dull or chipped, the owner might decide to recycle the bronze and create an entirely new thing. This practice makes it quite difficult to determine the exact provenance of the ores (Charalambous, 2021).
The combination of sedentism and the use of bronze changed the societal landscape in the Low Countries permanently. Bronze is not the only copper alloy with such a long history, brass has been dated back to 4700 BC in China, although it appeared much later in Europe.
Bronze, and therefore copper, remained one of the most important materials to society in the Low Countries until around 800 BC (Clerinx, 2017), at which point the Iron Age started.

Iron replaced bronze as the primary material used for weapons and tools, but bronze and copper did not entirely disappear. The metals were still used for art and the occasional tool or instrument. This situation did not change much during the medieval period. Jars and kettles in the 13th century of the Low Countries, for example, were widely made of copper (Scherpereel, 2012)

But bronze is not the only copper alloy worth discussing. In the 15th and 16th century brass was produced on a grand scale in the Low Countries, with large foundries dedicated specifically to the production of this copper alloy (Ruette, 1996, pp. 116-119). In fact, the word *dinanderie*, which is a catch-all term for copper and its alloys with a yellow or golden appearance, comes from the city Dinant. Brass has been used for art, was required for certain musical instruments and early cannons were also cast in brass. Using brass for creating instruments dates back to 1000 AD in Western Europe (Baines, 2015, pp.19-24; Hodson, 2003).

The usefulness of copper and its alloys for electrical engineering was discovered during the Industrial revolution. This changed the consumption and production of copper on a large scale comparable to the change to and from the Bronze Age. The insights about ways to use copper discovered in the 19th century have only been expanded upon in modern times.
Today, copper and its alloys are used for a wide variety of purposes. In fact, copper and copper alloys are the third major group of commercial metals regarding production and consumption. Modern scientific research and many devices could simply not function without copper alloys. High electrical and thermal conductivity, ease of production combined with good fatigue resistance and general lack of magnetism, makes them vital for all sorts of computers, for example. Pure copper itself is the 'go-to' metal for wiring, cables and other parts required for passing electrical currents.
Certain copper alloys have a high ability to resist corrosion making them suitable for constructing systems that carry or process aqueous fluids. Their high thermal conductivity and fatigue resistance also leads to them being extensively used for heating systems such as auto-mobile radiators (Davis, 2008, pp. 3-13).

Chapter 3: X-ray fluorescence and its uses in Archaeology

3.1 What is portable x-ray fluorescence?

X-rays have a rather short but interesting history. Although they are simply a form of radiation of a specific wavelength on the electromagnetic radiation spectrum, it took quite a while for scientists to discover them. It was not until Wilhelm Röntgen, a German physicist recognizing them and winning a Nobel prize for his discovery in 1901 that knowledge of x-rays spread (Shackley, 2010, pp. 7-8). Eight years later Charles Barkla discovered a relation between the atomic weight of a sample and the x-rays radiating from a sample, paving the way for elemental identification using x-rays. The following years Henry Moseley, another physicist, this time from England discovered many things about and through x-rays, from helping to number the elements using x-rays to laying the foundation for using x-ray spectrometry by discovering a relationship between the atomic number of an element and frequency. This discovery was used to catapult x-ray research upward and from 1914 till 1924 half of the Nobel prizes in physics were awarded to research pertaining to x-rays. (Shackley, 2010, p. 8)

The definition of pXRF that this thesis will work with is:

A highly portable, non-destructive, elemental technique that does not involve vacuum systems. Very useful for qualitatively measuring compositions of an object in a museum, etc. Excellent for the analysis of inorganic objects in the museum, especially metals, but also ceramics, glass, glaze and so on. A surface technique giving an average composition over 8x8mm. (D. Braekmans, personal communication, June 1, 2023)

This definition will be further expanded upon in this chapter.

X-ray fluorescence is the process of irradiating a material with x-rays, the material reacting to that and emitting another type of radiation. This works by the x-rays exciting the electrons of the element, causing them to detach. In order for the element to remain stable, another electron in the element moves to a shell that makes the atom stable again. This movement releases energy which is the other type of radiation emitted. As every element has a certain amount of energy, for the x-rays to dislodge an electron from its shell, the required energy of the x-rays must be higher than that of the element.

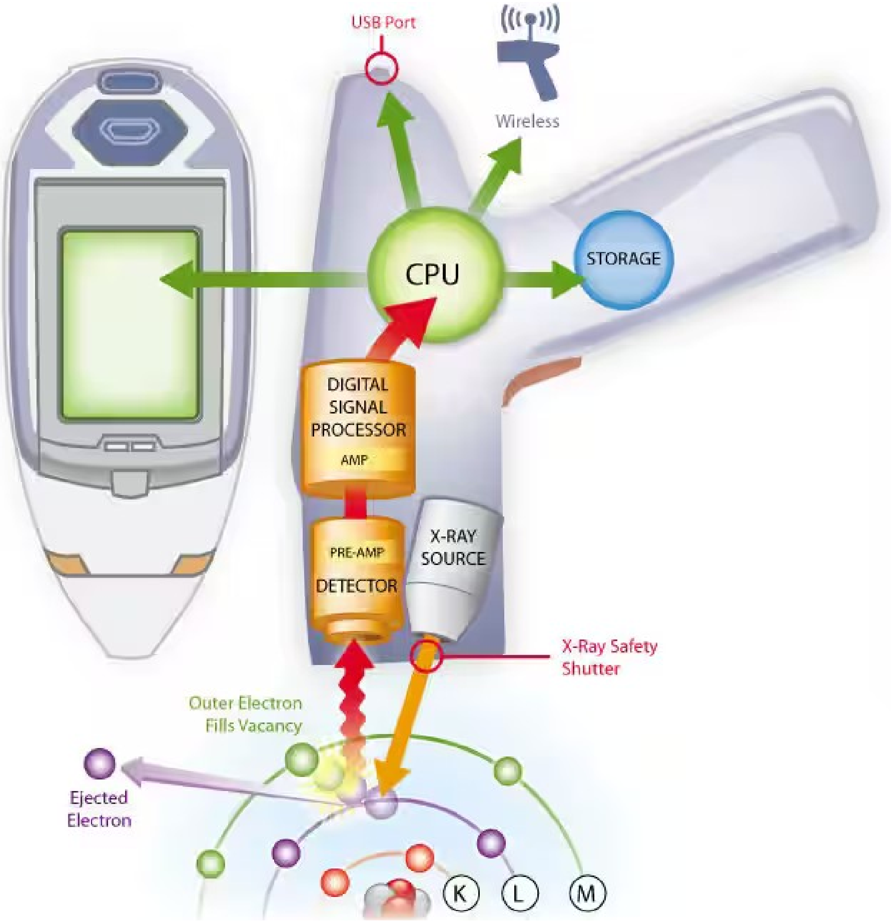


Figure 2: The insides of a pXRF machine and a schematic depiction of x-ray fluorescence. (https://www.thermofisher.com/blog/mining/technology-focus-x-ray-fluorescence-xrf-in-mining/).

Many XRF machines are laboratory based but portable machines have seen a significant rise in use over the past decades. Both so-called portable and handheld instruments have been used, although the term portable spans both pXRF devices that can be held in one hand (also called HHXRF or hXRF or even HHpXRF) others that can only be transported and otherwise stationary (Frahm & Doonan, 2013, pp. 1425-1434).

These portable versions of lab-based XRF have been in use since the 1960s, but the focus of this paper will be HHXRF devices as they transformed the possibilities of XRF in the archaeological field drastically. Whilst other pXRF devices offered many advantages over other methods, handheld pXRF ensured that someone can "point and shoot" to gain information. There is some controversy over this way of acquiring data, but it cannot be disputed that it is growing in popularity (Frahm & Doonan, 2013, pp. 1427; Shugar, 2013, p. 175).

Yet despite this controversy it is still a large improvement over the oldest XRF workstations that required a total identification time of up to 30 minutes (Frahm & Doonan, 2013, pp. 1425-1434). This was because a mainframe was required to translate measurements into elemental concentrations and data collection and processing happened separately (Nelson, 1975, pp. 91-95). The first improvement on this system was allowing immediate feedback by using online workstations, this meant that a researcher could instantaneously observe the status of the analytical process on the material. The analysis would produce results and the researcher could, with the obtained information, adjust the analytical process and obtain results that are more useful to their research.

As Frahm (2013) puts it: "*Measurement is no longer a passive process in which one has to acquire raw X-ray counts, hope for the best, and find out in the computer centre whether the analyses are good.*"

But handheld pXRF devices improved further beyond online workstations. Where those devices were limited to the specimens that were selected in the field, handheld pXRF can facilitate changing the sampling strategy devised by the researcher *in situ*. By allowing an expert that would in other scenarios be confined to a lab to operate in the field, the sampling and excavation strategy can be improved, avoiding problems such as collecting too much archaeological material (Frahm, 2013, pp. 1080-1092). Furthermore, a large amount of pXRF analysers that are currently on the market are actually superior in the resolution of their detectors compared to laboratory-based analysers produced in the last decade (Speakman & Shackley, 2013, pp. 1435-1443)

pXRF machines also contain filters to account for the background signal from primary radiation. There are filters for many different materials that allow for more precise measurements by reducing this background signal.
Once the pXRF device has obtained the raw data from the material, the data has to be calibrated through a combination of material standards and software programs.
Often the manufacturers of the pXRF device themselves pre-install some of this software, but there are also third-party options (Thermo, Bruker, or InnovX) that can help with specific materials or scenarios. This software is then combined with standards that are of a similar material as the material being analysed, this is required because the composition of the matrix influences how the secondary x-rays reach the detector of the pXRF device. This combination then allows for the calibration of the raw data (Speakman & Shackley, 2013, pp. 1435-1443).

3.2 Portable XRF in archaeology

As mentioned before XRF analysis offers important advantages over other methods in archaeological research. Archaeological materials are often highly susceptible to damage of any kind and methods that are more invasive can cause permanent damage to these materials. XRF is non-destructive, there are materials that can change or be damaged due to exposure to x-rays, but these are exceedingly rare. (Shackley, 2010, pp. 15-40)

Materials can be examined *in situ*. That means that not only archaeological artefacts, but also environmental factors can be examined (Mass & Shugar, 2012, pp. 17-35*).* This means that there are no (pre)treatments necessary in most cases, another huge advantage regarding time and financial costs.

Alternative techniques, such as ICP techniques, might require dissolution procedures, for example, whereas XRF analysis usually only requires a moderately clean surface, obtained by doing some simple washing of the object with (demineralized) water.

Also, XRF analysis is fast, results can be obtained in a few seconds to minutes depending on the mass of the object.
Lastly it is relatively easy to operate pXRF devices as most complicated processes have been automated. This allows for students to assist more senior archaeologists in obtaining important information despite their lack of experience (Shackley, 2010, p. 9). Quality control and data interpretation however remains in the domain of the expert.

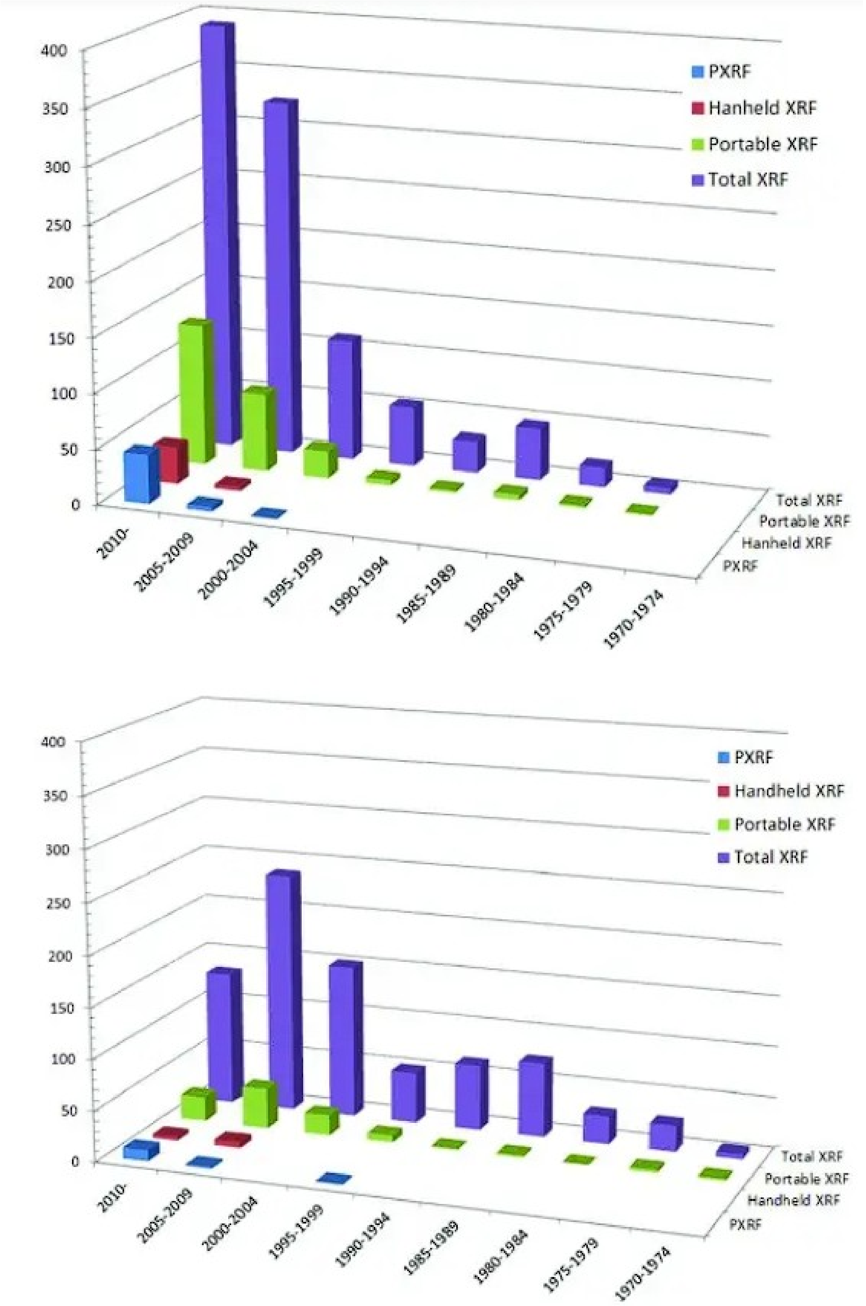


Figure 3: Publications using the search terms pxrf, handheld xrf, portable xrf and xrf in general. The graph is divided in 5 year periods, The top graph represents data from sciencedirect.com and the bottom graph data from AATA database. (A. Shugar, (2013)).

Commercial use for the elemental analysis using x-rays dates back to the 1950s and to this day the largest it is mostly used by the recycling industry (Shackley, 2010, p. 10; Shugar, 2013, pp. 173-

193). Its use in art, archaeology, forensics and other more ‘niche’ uses of XRF started rising in the early 2000s when portable XRF made its introduction (Shugar, 2013, pp. 173-193) As can be seen in figure 3, the amount of articles employing XRF had increased substantially, today performing research with XRF is a very popular method in archaeological research and it will likely increase in popularity as the technology is refined, specialized and made more affordable.

There are many uses for pXRF in archaeological research but there are some common research questions or goals associated with the use of pXRF. Shugar (2013) notes down three levels of inquiry regarding the use of pXRF (p. 176):

1. Determining what the material is. This usually does not require the use of XRF and in most cases researchers will go a level further when employing XRF devices.

2. What is the composition of the material? This question also holds a lot of variety as one can be researching bulk chemistry or trace chemistry or both.

3. Determining the concentration of trace elements in the material. This level of inquiry has a higher difficulty of obtaining the data required to answer questions related to this level of research.

These levels as proposed by Shugar are worth mentioning as, even though one might consider them arbitrary, they do represent different possibilities and different questions one can ask about archaeological material in a logical way. Furthermore these questions are very common in archaeological research and often lead to answering other important and common questions such as the provenance of a certain material. XRF analysis can also be used to discover changes in production technology, access to specific types of ore and practices of recycling (Tykot, 2016, pp. 42-56).

3.3 Portable XRF in conservation

Portable XRF devices and their stationary cousins are of importance to the field of the conservation of (archaeological) objects as well. There is a lot of overlap in how pXRF is used in a conservationist's lab and in an archaeologist's lab in regards to researching metal objects, such as the specific filters required for certain specific materials. There are also differences, such as portable XRF devices used in conservation contexts being mostly used for analysing a few objects or even just a single object. Whereas archaeological research more often employs XRF for bulk elemental composition analysis (Tykot, 2016, pp. 42-56).

The transportation of objects in a museum is something that most conservators wish to do the least amount possible. Transportation can be very risky for objects, from vibrations to burglary, and conservators try to minimize risks to an object wherever they can (Canadian Conservation Institute, 2017). This means that in-house analysis is preferred, but there plenty museums that do not own an XRF device or an other suitable analysis method for chemical compositional analysis. Thankfully a pXRF device can be transported to the museum, solving this issue.

Some museum objects that have not been researched in recent times, or where invasive studies were considered to harmful for the object can now also be studied using pXRF. This has led to various discoveries, such as Robert Tykot (2016) exposing 'fake' objects in the Orlando Museum (p. 50). Objects that were labelled gold actually consisted of tumbaga alloys, with surface treatments to make the objects look gold. Tykot also discovered that in the Tampa Museum there were objects labelled silver, such as some coins, but were in fact mostly nickel (Tykot, 2016, p. 50).

A frequent topic and issue in the conservation of metal artefacts is corrosion. XRF analysis can bolster conservation efforts by helping to identify metal corrosion products without compromising the artefact with invasive techniques. Most corrosion products create altered surfaces on objects through the enrichment or depletion of various alloys in this corrosive layer. What kind of corrosion forms depends heavily on what kind of material the artefact consists off, burial/environmental conditions of the archaeological site where the artefact was excavated, manner of storage once excavated and even conservation treatments (Karydas, 2007, pp. 419-432). Instant analysis both in the field but also in museum contexts can shed light on a lot of these questions even if this is only surface level, as pXRF devices have a limited depth resolution. Regardless, by referencing spectra from the same object but from surfaces clean of corrosion, or if need be 'clean' surfaces on similar objects (Karydas, 2007, pp. 419-432).

Whilst most of the pXRF devices used in the conservation context are handheld devices, there are also other "deconstructed" benchtop/desktop systems. Fram (2012) defines these as:
"*These instruments are primarily intended for museum use to assist in identifying materials for conservation, authentication, and art historical studies, as evidenced by trade names such as ArtAX. Here we refer to this as "museum-type" pXRF*."

3.4 Concerns about XRF

As shown, pXRF has been a useful invention in the field of archaeology and conservation. Yet it is not a perfect tool, researchers have mentioned various concerns about the technology and how people employ it in their studies.

The first issue is quite simple and relates to the analytical limitations of pXRF machines. The ability to be transported anywhere, means that the XRF device has been miniaturized, which limits the depth a pXRF can penetrate in and analyse a given material. Corrosion on metal objects can spread deep, even transforming the entire metal material to rust. Using pXRF to tell how deep *exactly*, is therefore not easy because of the aforementioned limited penetration depth (Karydas, 2007, pp. 419-432; Tykot, 2016, p. 43). How deep the x-rays can penetrate relies on the detected elements and the characteristic x-ray energy of those elements, with the depth increasing with higher elements (Karydas, 2007, pp. 419-432; Tykot, 2016, p. 43).

Related to this is a disadvantage that portable XRF devices have that their less-portable cousins have to a lesser extent, which is the accuracy of measurements of lower Z elements. The elements that pXRF is most suited to detect are in the mid-Z X-ray region (Shackley, 2010, pp. 12-14). Furthermore elements below Na on the periodic table are not detectable at all (Tykot, 2016, pp. 42-44). This is significant downside to pXRF analysis, as elements with low atomic numbers or hard-to-detect elements with low concentrations (or high detection limits) can help in narrowing down the source of the material. The lacking detection capabilities of pXRF devices are because of the lack of a vacuum, which is necessary for the detection of these elements. Without a vacuum, these elements are absorbed in the air. However, recent models (such as the Bruker Tracer 5g) use a helium pump to detect these lower Z elements.
Portable XRF devices also have a significantly higher 'background' signal causing some of the trace elements to almost not be detected (Pessanha et al., 2009, pp. 497-504; Shackley, 2010, pp. 12-14).

Because of this higher background and the lower detection limits of pXRF devices compared to, say, ED-XRF, pXRF results are not always as conclusive (Pessanha et al., 2009, pp. 497-504; Tykot, 2016, pp. 42-44). Metals are usually not rich in low Z elements, so the problem of their detection is not too important. However, the surface analysis that XRF performs not necessarily matching with the internal, bulk composition of the object *is* a significant issue (Speakman & Shackley, 2013, pp. 1435-1443).

But apart from these factors, the matrix composition of the sample and the type of excitation source play a critical role in determining the possible depth of pXRF machines. Analysis performed with pXRF on heterogenous materials/matrix compositions such as ceramic for example, tend not to be satisfactory.
The samples that pXRF can used are also limited in size. Samples must be larger than 10 millimetres and thicker than 2 millimetres for an analysis to have an acceptable degree of accuracy (the beam size of pXRF is usually 8x8mm) (Shackley, 2010, pp. 9-10).

As mentioned before, this detection issue is helped by creating a vacuum with helium pumps in new models and by using appropriate samples with a flat surface. This way a researcher can ensure there is little to no air space sabotaging their measurements between the sample and the instrument window (Tykot, 2016, pp. 42-56). The result is usually that pXRF devices can penetrate up to 2-3 millimetres deep (Shackley, 2010, pp. 7-40).

Aside from the penetration depth variation, it can be seen that this is still not a perfect solution as Bellegem et al. (2015) demonstrates. Here the researchers use XRF analysis on the surface of a silver bell (pp. 15-22). However, they treat the results from that XRF analysis as 'semi-quantitative' as the rough and curved surface of the bell prevents satisfactory analysis.

Other researchers mention how degradation, contamination of (metallic) surfaces and conservation treatments can all interfere with the reliability of pXRF analysis (Tykot, 2016, pp. 49-56). Bad storage conditions, damaging/less-advanced conservation practices or different conservation techniques for different artefacts in the same assemblage greatly affect the readings of pXRF devices (Charalambous et al., 2021). Conservation treatments done a long time ago can even permanently alter the composition of a metallic object, affecting the analysis as well (A.G. Kardyas 2007). Some of these issues can be treated by cleaning or different conservation practices, but that is not always the case.

After the initial development of pXRF, commercial units were developed for the mining and most prominently the recycling industry. These devices were simplified to make them easier to use, especially the software and user interface. However, this entailed limited analytical choices (Speakman & Shackley, 2013, pp. 1435-1443). In contrast, user customizable research units were developed has well for various materials.

It needs to be noted that research devices are also not ready to use straight out of the box. There might exist a 'point and shoot' mentality among some researchers, popularized by the manufacturers, that believe that pXRF devices are an easy and cheap solution to all their problems (Speakman & Shackley, 2013, pp. 1435-1443). This mentality is problematic and researchers need to be aware of the advantages, disadvantages, pitfalls and asterisks to using pXRF for material research (Kardyas 2007).

Much like desktop analysis instruments, handheld portable XRF devices need to be empirically calibrated using international standards before they can even begin to be used in research (Shackley, 2010, pp. 7-40). Furthermore specific materials (i.e. matrix-matched) require specific calibrations for the most accurate results. Elemental references must be made in conjunction with a homogenous distribution of the elements in the analysis volume, standards libraries must be created as well as calibrations that can be adjusted quickly (A.G. Kardyas, 2007). Shackley (2010) describes a situation wherein two of his former students obtained two different pXRF instruments that were supposedly calibrated already, but as the students did not check, the actual results obtained were unreliable (p. 13). It is already a test of expertise to compare and reproduce pXRF data from other researchers when different analytical methods, models and different devices were used. Thankfully, procedures have been and are continuously being developed to make this easier.

This last factor must also be mentioned as among the major brands of pXRF devices used in archaeology/conservation there are differences that significantly affect research results (Speakman & Shackley, 2013, pp. 1435-1443). The most prominent brands are at the moment Niton, Thermo, InnovX and Bruker. An example of a difference is how Bruker devices usually have a single setting for a single analysis, whereas Niton devices often calculate a result by combining a two or three analyses together.

However, this issue does not mean that unsatisfactory results can be solely blamed on the manufacturer however, as software required to calibrate these devices is fully developed for big brands, sometimes by third parties (Speakman & Shackley, 2013, pp. 1435-1443). The manufacturers themselves do not often have these ready-set calibrations except for instructional purposes (Frahm & Doonan, 2013, pp. 1425-1434).
Instead, the users must make manual adjustments or use the aforementioned third-party software specifically developed for certain materials (Speakman & Shackley, 2013, pp. 1435-1443). Sometimes these third-party options are even required, as there have been cases documented were manufacturers do not allow users to make adjustments or cases where it was concluded that there were problems with the software the manufacturer provided (Dybowski, 2012, pp. 1-7). This was again not fully the fault of the manufacturer as the Niton XRF data was not calibrated for the right material, obsidian in this scenario (obsidian is a material that is also commonly examined using XRF). This example, showcases how expertise is required to operate these devices in a productive manner. The spectra obtained by pXRF devices are, in theory, never inaccurate, it is how experts operate the device that determines the quality of the quantification. Nevertheless, manufacturers must also be held accountable for the quality of their products and the claims they make regarding them.

There are also similarities of course, Niton and Bruker devices were, for example, for a time calibrated similarly. In this case that meant no calibration at all or calibration through a fundamental parameters routine (Shackley, 2010, p. 13). This is a rather basic calibration, that serves adequately for presence analyses but more complex analyses that require higher levels of accuracy cannot be done with this device (Shackley, 2010, p. 13).

Chapter 4: How is pXRF currently employed in the analysis of bronze objects?

4.1 The two case studies

The purpose of this chapter is to examine pXRF in archaeological research, specifically regarding analysis of bronze objects. Two case studies have been chosen, wherein pXRF was used in ways relevant to this topic, but with enough differences between the two studies to examine different issues in regards to using pXRF for archaeological research.

In Charalambous et al. (2021) the researchers used pXRF to determine the composition of 206 Late Bronze Age artefacts from Cyprus, specifically the copper alloys used to create them (p. 1). This data was then used to compare different chronological periods of the Cypriot settlement and how they used copper alloys.

Roxburgh et al. (2016) used pXRF to research 406 Roman copper-alloy brooches (p. 1). They too, studied the composition of the copper-alloys, but they used the obtained data to determine the provenance of the copper used to create the brooches.

These two papers are examples of archaeological research using pXRF devices. Determining the provenance, whether geographically or chronologically, is an important and common avenue of archaeological research. These papers illustrate how pXRF fits in to that avenue of research and will act as a main source to assess the validity of and common practices in copper alloy determination.

4.2 Enkomi (Cyprus): Using pXRF spectroscopy to identify LBA copper alloys

The first case study I will discuss is about the research done by Andreas Charalambous, George Papasavvas and Vasiliki Kassianidou on the assemblage of copper-based artefacts excavated at Enkomi (Charalambous et al., 2021).

To give context to the research I will discuss some background information first.
To start with Enkomi itself, it was a Late Bronze Age (LBA) town that was inhabited throughout this entire time period. In fact, it is considered one of the most important Cypriot bronze age sites and has been extensively excavated.

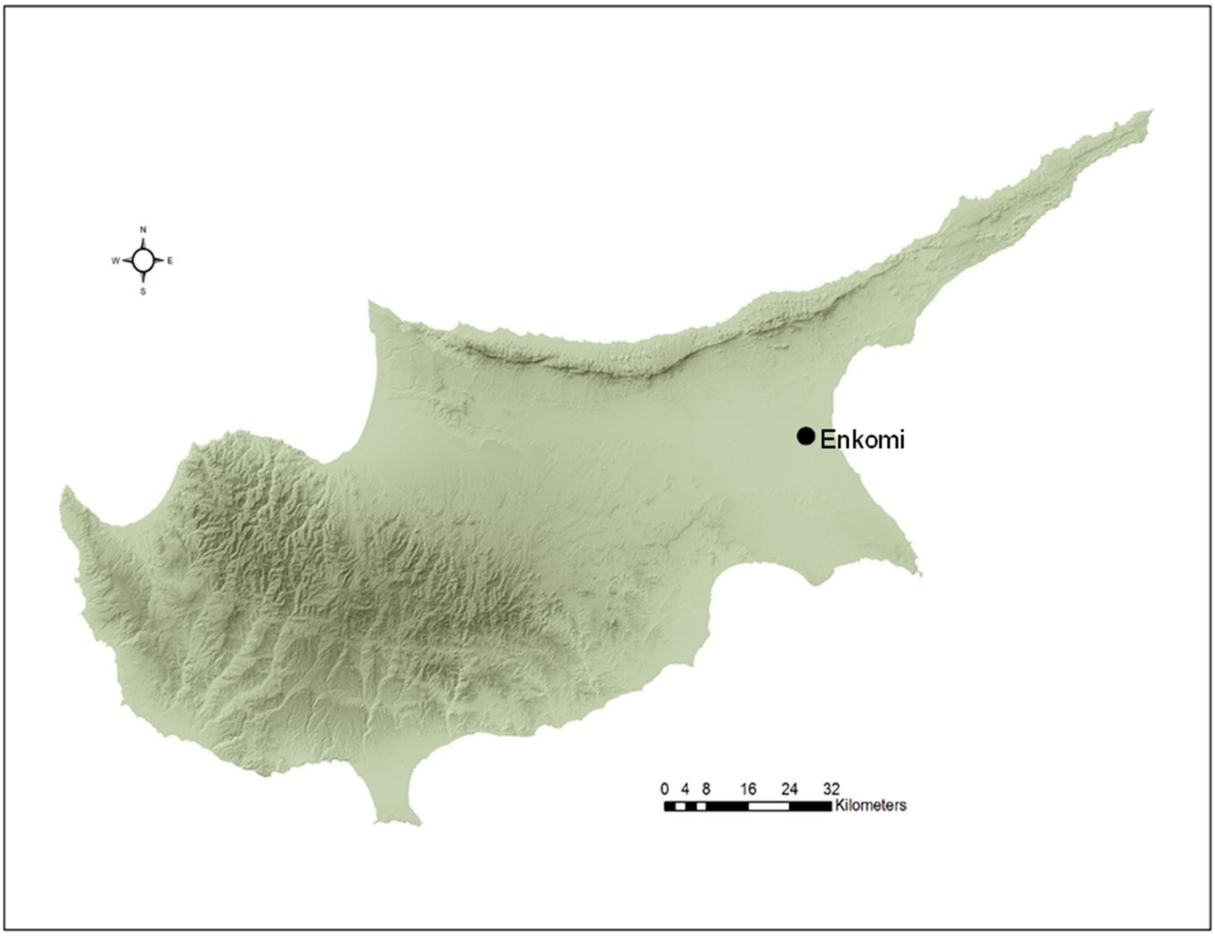
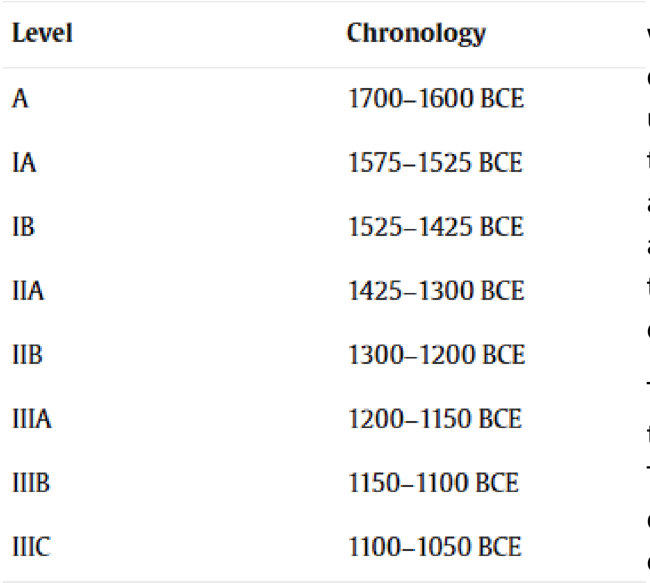


Figure 4: Map of Cyprus with a dot indicating the location of Enkomi. (Charalambous et al. (2021)).

The most important excavation of Enkomi was lead by Porphyrios Dikaios, an archaeological officer of the Department of Antiquities of Cyprus in the mid-twentieth century. He divided Enkomi into three areas, which where then subdivided into levels and then further subdivided into layers. The levels referred to the different strata and the layers were assigned to a chronological period (Porphyrios, 1969).

Table 1: Correlations of Dikaios' Levels and chronological phases of Enkomi's habitation. (Charalambous et al. (2021)).



Level	Chronology
A	1700–1600 BCE
IA	1575–1525 BCE
IB	1525–1425 BCE
IIA	1425–1300 BCE
IIB	1300–1200 BCE
IIIA	1200–1150 BCE
IIIB	1150–1100 BCE
IIIC	1100–1050 BCE

Areas 1 and 2 covered the centre of the town whilst area 3, on the northern side of Enkomi, contained metallurgical workshops that were in use in the majority of Enkomi's history. Thanks to this extensive excavation and others, archaeologists have obtained a wealth of metal artefacts and metallurgical materials. Some of these finds even indicate a state-level of organisation (Knapp, 2013).

This wealth of finds resulted in the assemblage that the researchers focused their research on. This assemblage of LBA copper-base objects consisted of weapons, tools, grooming items & ornaments and objects that were too damaged/fragmented to make out what they used to be. Table 2 contains the specifics.

Yet despite its large size and the rarity of the artefacts present in the assemblage, the assemblage has not been studied as a metallurgical entity, even after having been excavated over half a century ago. This motivated the researchers to be the first to do this and discover more about the metallurgical technology and culture of Enkomi in the LBA.
The researchers defined two major goals of their research, those being:
"1) the identification of the chemical composition and the type of alloy of as many individual artefacts as possible, and 2) the study of the distribution of the copper alloy types used in the different chronological phases (levels) of Enkomi's settlement."

Table 2: The studied assemblage. (Charalambous et al. (2021)).

Artefact group	Artefact type	Number of artefacts
Weapons and tool/weapons	Arrowhead	22
	Dirk	6
	knife/dagger/blade	6
	Spearhead	3
	Javelin	2
	axe/adze	2

	Sling-bullet	2
Tools	Fitting	10
	Needle	9
	Chisel	7
	Rod	6
	Nail	6
	Drill	6
	Sickle	5
	Hooks/fishing hook	4
	Ploughshare	2
	Others	7
Grooming items and ornaments	Pin	32
	Earring	14
	Ring	3
	Tweezers	5
	Bracelet	3
	Plaque	4
	Fibula	2
	Finger-ring	1
	Pendant	1
	Attachment	1
tableware/utensils/other use	Bowl	2

	Miniature ingot	3
	Handle	2
	Miniature object	5
	Others	2
fragments/scrap metal	Fragment	13
	Sheet	3
	Lump	3
	Ingot	1
	Tripod leg	1
Total		206

Not all copper-base artefacts excavated by Dikaios have been included by the researchers in the examined assemblage. This is because some artefacts could not be examined by pXRF devices as they were too corroded. Corrosion and/or patination layers have an effect on the detection of secondary metals by pXRF devices. Tin, arsenic and lead were often overestimated compared to their real concentrations (Charalambous et al., 2021). This left a total of 206 objects that have been examined by the researchers.

Figure 5: Examples of objects from the assemblage. A) Unfinished dirks, b) ploughshare c) arrowhead d) miniature ingot e) broken fibula. Photographed by A. Charalambous (Charalambous et al. (2021)).

These corrosion or patination layers can be produced through various circumstances with an assemblage as old and excavated as long ago as this one. The artefacts excavated from Enkomi were treated in the Cyprus Museum, removing much of the surface encrustation. The museum did not treat the near-surface metal as thoroughly however, which means this material was still affected by corroded layers.

The main concern for the researchers was the corrosion affecting the Pb (lead) and Sn (tin) elements. To combat this concern at least three and up to five measurements were taken of each artefact, with each measurement being taken on a different exposed metallic surface of said artefact. The mean value of these measurements was taken as the final value, with outlier values ignored. The researchers discovered by comparing this data to data obtained from measurements intentionally taken from highly corroded surfaces, that the presence of secondary elements differed in corroded vs non-corroded areas.

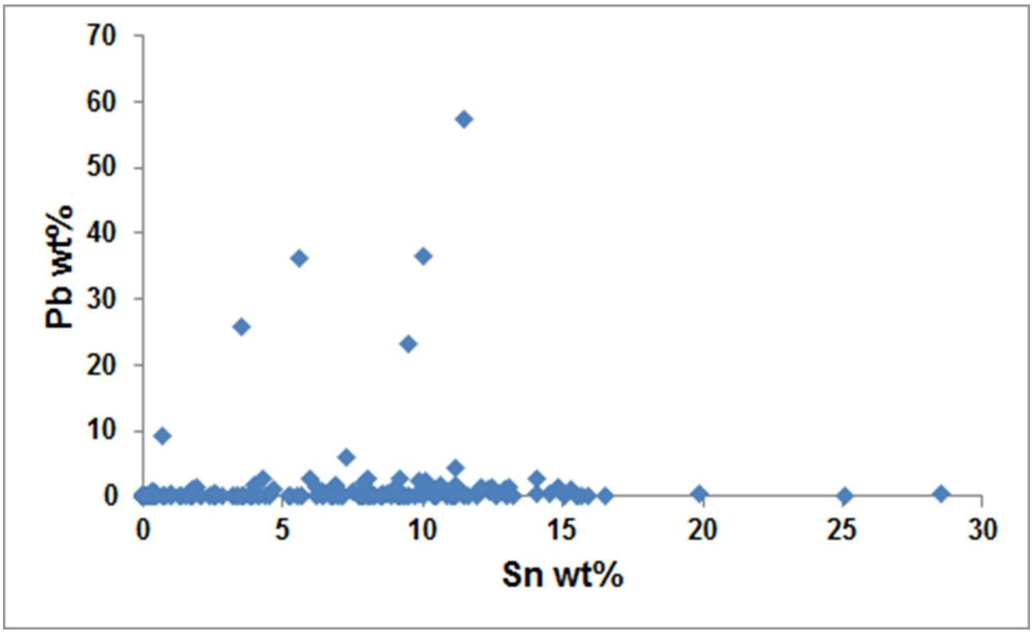


Figure 6: Pb versus Sn concentrations in the analysed assemblage of the case study. (Charalambous et al. (2021)).

Specifically, highly corroded surfaces had lower Sn, As and Pb values, but a higher Fe (iron) presence. Through this method the researchers intended to bolster the reliability of their methodology and its reliance on pXRF.

The researchers specified which pXRF device they used in detail, as can be seen in the following quote:
"*The HHpXRF (Innov-X Delta, now Olympus) used for the chemical analysis is equipped with a 4 W, 50 kV tantalum anode X-Ray tube and a high-performance Silicon Drift Detector (SDD) with a resolution of 155 eV (Mo-Kα). The diameter of the collimated X-Ray beam was 3 mm and the measurement time for each spot analysis was 70 s. The analytical mode of the instrument employed for the analyses was 'Alloy Plus'. Two certified reference materials (CRMs), BCR-691 and 32X SN7, were used for checking the accuracy of the applied analytical mode*."

This information allows other researchers to reproduce and check this data, creating a database that is accurate. The importance of this will be discussed in chapter 5.

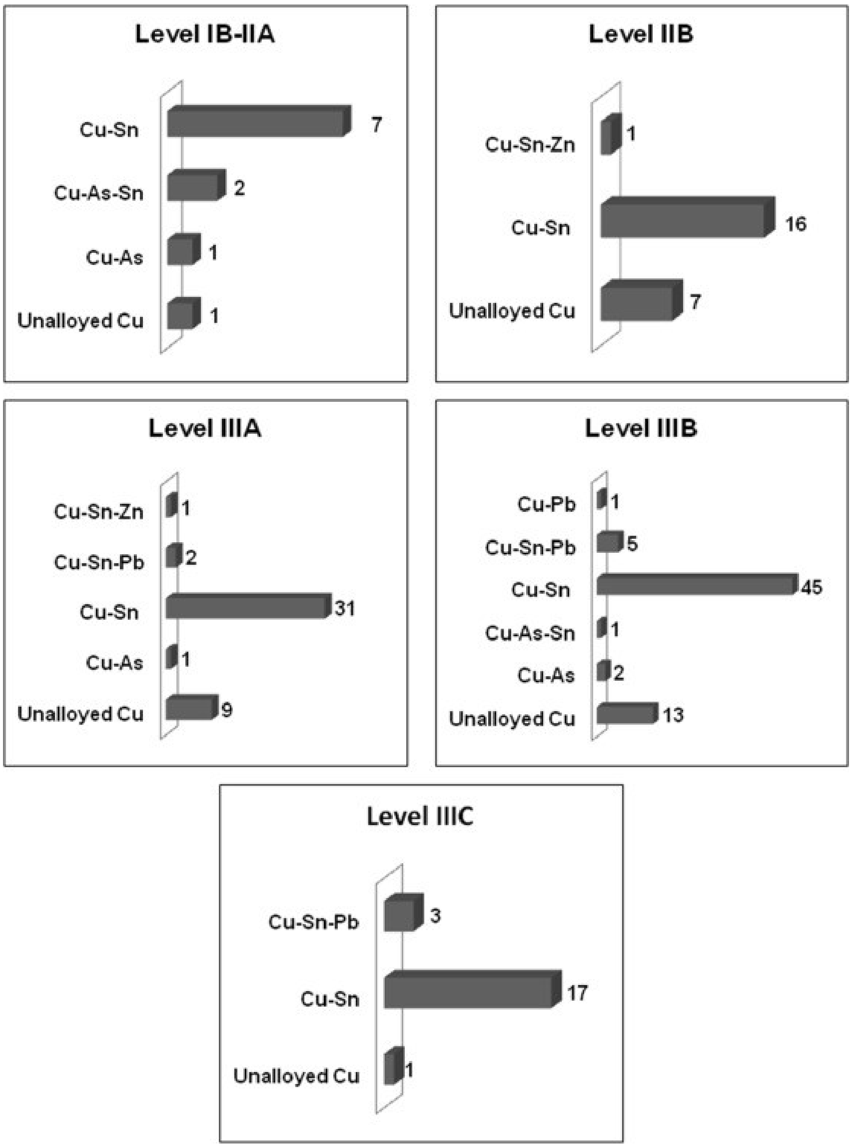


Figure 7: The types of copper alloys in the habitation phases/Levels of Enkomi, analysed by pXRF. The numbers next to the bars correspond to the number of artefacts. (Charalambous et al. (2021)).

The readings indicated that throughout Enkomi's history, bronze (Cu-Sn) was the dominant copper-alloy in all its levels. As can be seen in the figure above. But whilst tin was of course used for the production of bronze, it also served other purposes in Enkomi. The data indicates that tin is the main alloying element in most artefacts examined by the researchers. With the majority of artefacts having tin concentrations below 15 wt% although some had concentrations as high as 28.5 wt%.

This is an interesting point of data as Cypriot copper deposits contain no tin (Muhly, 1985, 275-291). This could imply many things, but the researchers of this paper think that the high presence of tin is most likely explained through recycling of both local and imported goods that originally had higher tin concentrations. The authors also do not deny that there is a possibility that near-surface corrosion affected the readings of tin presence.

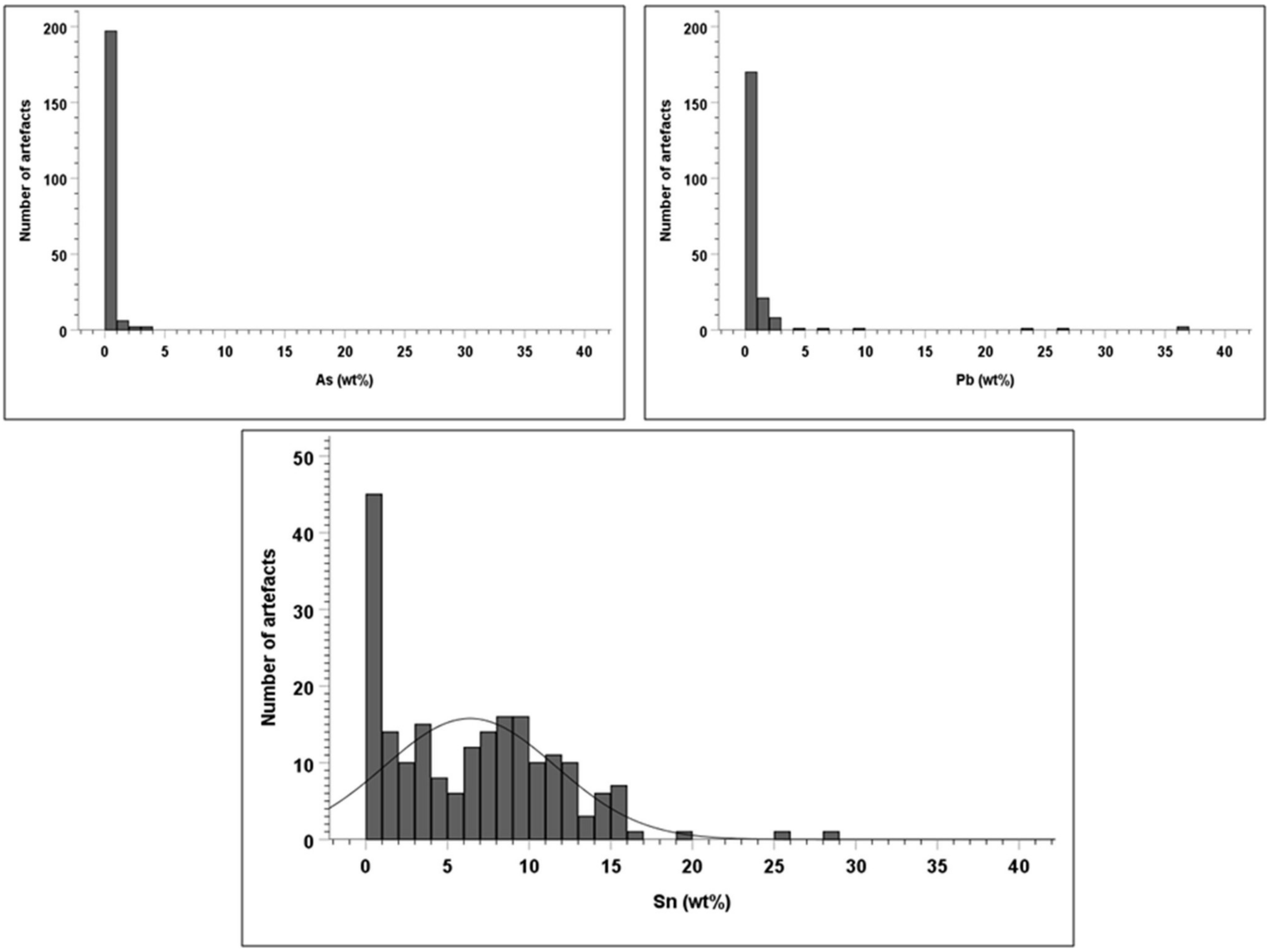


Figure 8: Histograms showing the Sn, As and Pb content of the copper-base artefacts from Enkomi. (Charalambous et al. (2021)).

Another point of interest in the data is the large amount of objects with a small presence of arsenic (As). A total of 123 artefacts contain arsenic according to the data, yet 113 of those have an As presence of 1 wt% or lower. This might not sound like much as the wt% is so low, but the fact that there is such a high number of artefacts with *any* arsenic presence is remarkable as, the environment of Cyprus or Enkomi does not particularly lend itself to the use of arsenic in objects as the only region on Cyprus that contains any notable amount of arsenic is the Limassol Forest (Gass et al., 1994). What throws a spanner in this explanation however is that there has been no convincing evidence uncovered for the exploitation of the forest during the Bronze Age (Stos-Gale et al., 1997, pp. 83-123). For this reason the researchers believe that a similar explanation of the tin presence can be used for the arsenic presence that relies on the inhabitants of Enkomi recycling objects that originally had a higher arsenic content.

The researchers conclude that: “*The results showed that the predominant alloy in Enkomi throughout its long habitation history is bronze, with an extensive use of tin, a metal that is not present in the geology of Cyprus.*”

Their methodology relied on surface XRF readings and by taking certain measures they concluded that their obtained data was reliable even though they do admit that the XRF data may not have fully accurate measurements of the tin and lead concentrations at all times.

4.3 Early Roman copper-alloy brooch production: a compositional analysis of 400 brooches from Germania Inferior

The second case study to be discussed is a compositional study of 406 Roman copper-alloy brooches taken from various locations in the Netherlands. The brooches date to the Late Iron Age until the 2nd century A.D (Roxburgh et al., 2016).

The researchers provide some background/context for their study, which I will briefly discuss as well. Research on Roman brooches has existed for a long time as they are quite common finds in the excavation of Roman sites. Also, because a lot of prior research on Roman-era brooches found in the Netherlands has focused on detailed descriptions of brooches from individual sites, brooches can be easily recognized and categorized, facilitating typological classifications (Buchem, 1941; Haalebos, 1986; Roest, 1988, pp. 142-202).
Despite this, much remains unknown about the production of these brooches in Germania Inferior, the Roman province that included the south of the modern-day Netherlands. This is because whilst the brooches are common, the workshops wherein they were produced are rare. Only two workshops had been excavated in this province by the time the researchers wrote this paper (Roxburgh et al., 2016, pp. 411-413).

Furthermore, this angle of research would benefit from compositional analysis, but doing that has long been limited by technology. Not only would one need a precise enough methodology to be able to distinguish between different compositional groups, but one would also need to analyse a large group of brooches as well.

That became possible with the invention of pXRF devices. They allowed the research to examine the brooches non-destructively. Furthermore, its low cost, ease of use and portability led the researchers to favour pXRF over laboratory equipment. The researchers do indicate the problems of pXRF devices such as the shallow depth that the X-rays can penetrate, especially on an altered surface, such as gilded or corroded metal objects.(Hall, 1961, pp. 62-66; Pollard & Heron, 2008, pp. 33-49; Roxburgh et al., 2016, pp. 411-421).
To mediate these faults the researchers rely on:
"*appropriate research questions and qualitative or semi-quantitative approaches*"
(Roxburgh et al., 2016, p. 412)

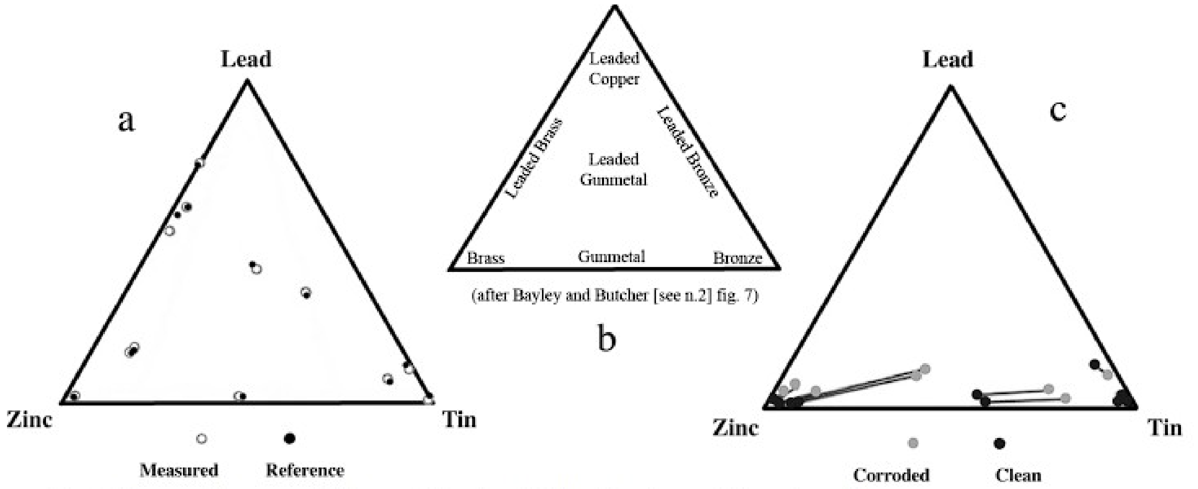
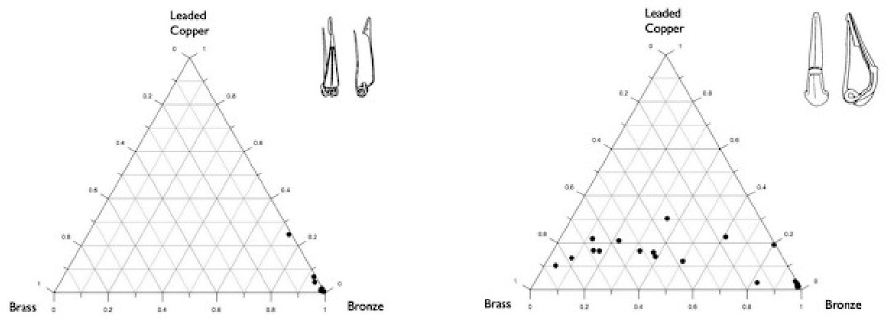


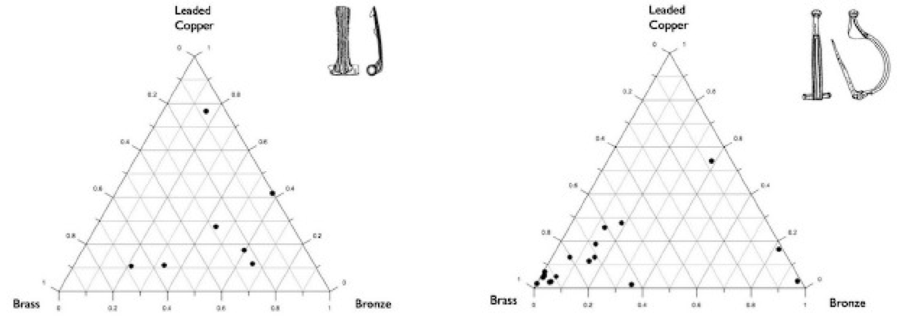
Figure 9: Ternary diagrams depicting the composition of the material. a) Charm calibration; b) Classifications; c) Corrosion effects. (Roxburg et al. (2016)).

The researchers go into further depth about corroded metals and how pXRF readings are affected by corrosion. Figure 9 shows the difference between corroded and non-corroded readings. This figure implies that decuprification and dezincifiation are the most common corrosion processes at work. The amount of Cu decreasing was observed to be the most active change, but zinc depletion from brass objects was common as well. Despite the issue of corrosion, the researchers managed to categorize these measurements into broad compositional groups, as can be seen in figure 10.

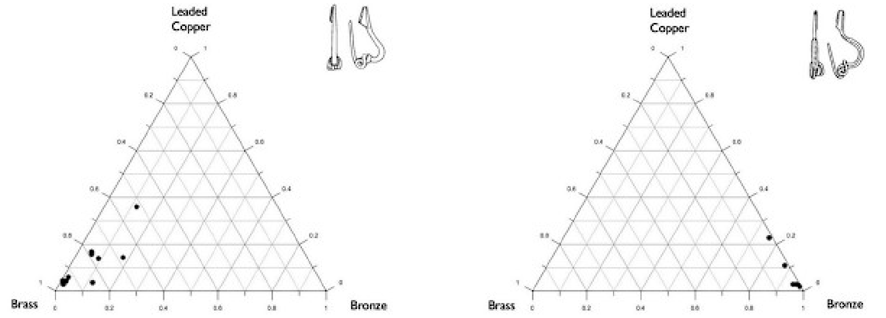
Yet despite the limitations of pXRF and the effects of corrosion there do exist theories on the organisation of brooch production, as there are similarities between brooch types and certain military gear. This, combined with the high amount of brooches found in military camps indicates that many brooches were produced in military workshops, according to the researchers. The production of brass artefacts also plays a role in these theories as it appears that the Roman state mostly used brass in the production of coins and military gear (Dungworth, 1997, pp. 901-910). Brass was used on an industrial scale by the Romans starting around the 1st century B.C. by using a technique known as the 'cementation process' (Craddock, 1998).
Around the end of the 1st century A.D. this changes, however and the increased amount of bronze present in brooches indicates that the use of brass declined (Bayley & Butcher, 1995).



Nauheim 150 - 70 B.C. n. 7 Spoonbow 30 B.C. - A.D. 40 n. 20



Bow on Spring-tube (Gallic) 20 B.C. - A.D. 40 n. 8 Aucissa Series 20 B.C. - A.D. 80 n. 19



Almgren15 Related 15 B.C. - A.D. 70 n. 11 Almgren15 Related 15 B.C. - A.D. 70 n. 6

Figure 10: Compositional results organised chronologically and by type. (Roxburgh et al. (2016)).

To investigate these theories on brooch production, researchers have focused mostly on investigating the brooches themselves. This focus on the production led to examining the specific elements present in the copper-alloys of the brooches, which indicated a complex relationship between composition and typology (Dungworth, 1997, p. 902). The methods used for most of this research were quite destructive however, holding back the research.

Furthermore, the researchers proposed various conditions on their research and their selection of brooches. The brooches all came from various locations in the Netherlands, but there also needed to be enough of them for each type. The researchers decided on a minimum of six brooches per type and for certain, more defined types such as the Nauheim series the researchers wanted even higher amounts.
To get a complete picture of the organisation of the brooch production they needed to be able to compare the composition of Iron Age pre-Roman conquest brooches and Roman-era brooches. If this comparison indicated a considerable difference in the alloys that were used and the Roman-

era alloys were homogeneous over large areas, they can be dubbed ‘real Roman’ brooch alloys according to the researchers.

Luckily, this was indeed the case for some of the brooch types the researchers investigated. Alloys used for Roman military brooches such as the Aucissa series were different than Late Iron Age alloys and also homogeneous over large areas.

This meant that the Aucissa series was a ‘real Roman’ alloy and therefore as a ‘real Roman alloys’ needed to be compared once more to local typologies. As mentioned before, at least six of a type needed to be present for the research to include them. These brooches also needed to be datable and easily recognized/identified to bolster this typology.
This allowed the researchers to make conclusions or hypotheses about the: “*level of compositional control in different brooch types*.”
(Roxburgh et al., 2016, p. 421)

Comparing these Dutch results further to results from other regions, more can be said about the organization of production and distribution of Roman brooches and possibly other items.

To make sure the results can be checked and are empirically valid the researchers specified the exact pXRF they used and its calibrations:

- The specific type was a Niton XL3t GOLDD XRF analyser.
- The device was calibrated for metals and alloys, with a silicon drift detector with optimised geometry. This calibration was checked for it suitability regarding copper-alloy research against the CHARM reference set (Heginbotham et al., 2014, pp. 856-68)
- The electronic metals mode was used throughout the data-gathering phase.
- The device was mounted on a lead-covered portable test bench.
- After testing, a reading time of 30 seconds was determined to keep the signal stable.
- After the analyses, the spectra were checked for inconsistencies.
- The data was reproduced on an Excel database

The researchers decided that building on an existing methodology when it came to Roman brooches was suitable. This methodology being that of visualising the pXRF results in ternary diagrams with tin, zinc and lead on their various axes (Bayley & Butcher, 2004).

The researchers did not include the presence of copper in their diagrams as they knew it was present in copper-alloy brooches and their interest was in the other additions in the alloys. Furthermore by ignoring copper presence like this, they claimed that their readings were more reliable even when the objects were corroded (Roxburgh et al., 2016, pp. 411-421).

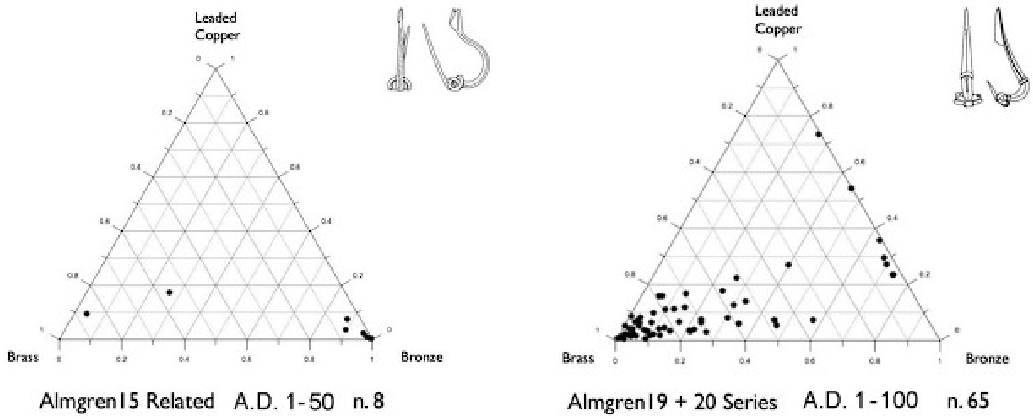


Figure 11: Example of compositional results organised chronologically and by type. These diagrams belonging to the almgren 15 and almgren 19+20 typologies. (Roxburgh et al. (2016)).

Chapter 5: Discussion: The advantages and pitfalls of portable XRF for the study of copper alloys.

5.1 Assessment of errors and pitfalls

In chapter 3 I discussed what concerns there were about portable XRF devices. In chapter 4 I examined two case studies to see how those concerns are dealt with in reality.
There are a major concerns regarding the use of pXRF in archaeological research and some common errors that researchers could make. Some of these problems can be solved, other problems can only be reduced in their effects, or even only be accounted for. To create a clear oversight table 3 was created. This table can also be considered a main outcome of the research carried out here, to facilitate a proper procedure when starting similar studies.

The most impactful problems as mentioned by the case studies and prior appear to be the limited depth that x-rays can penetrate and corrosion affecting what the pXRF machine detects. These problems cannot be truly solved until technology advances, as right now the only way to increase penetration depth seems to be higher-powered devices, but that entails more safety issues in regards to radiation.
If researchers are aware of the limitations however and avoid the 'point and shoot' mentality, making sure that they have prepared their research and device properly, pXRF machines are great research tools. Including appropriate calibrations in your preparation can also mitigate the effect of background signal. Thankfully, most researchers are aware of these issues. Karydas (2007) for example, developed in-house software specifically for their research to make their research more accurate (pp. 419-432). One group of researchers also developed the Copper CHARM set in 2015, a set of certified reference materials for researchers working with XRF analysis on copper pre-modern copper alloys (Heginbotham et al., 2014). Including measures like this can help researchers construct an empirical calibration.

Charalambous et al. (2021) goes into depth about corrosion and attempted to reduce the inaccuracy that corrosion introduced in the results by taking multiple measurements of a single sample, each measurement being taken on a different surfaces (p. 3). Comparing the mean value of these measurements, with outliers being ignored, to data obtained from highly corroded surfaces they were able to examine the differences. In their case the difference was lower values of Sn, Pb, As and higher Fe values.

Roxburgh et al. (2016) in comparison focused more on visualising their results (pp. 415-419). Figure 9 was created to show the difference between corroded and non-corroded measurements. By visualising the difference between the two, the effects of the corrosion processes become clear. In this scenario decuprification and dezincification were the most common. The researchers also acknowledged the problems that pXRF has with corrosion.

Both studies used different measures to combat the issue of corrosion, but the important point is that both studies did attempt to combat it. Furthermore, by being open and transparent about their methods and results, other researchers can verify their research.

The inaccurate measurements of lower-Z elements is an issue that does not seem to have a concrete solution. The problem was not mentioned in either case study as well, but this is because these elements almost never show up in metals. These elements are, however, common in glass and ceramic materials.

Table 3: Concerns, solutions about pXRF and how they are reflected in the discussed literature. Created by W. Verhage.

Concern	Reflected in the literature	Solutions
Limited x-ray penetration depth, being unable to tell how deep corrosion is with pXRF because of this.	Charalambous et al. (2021) does not mention it directly, but in a way discusses it when it discusses corrosion (p. 3). Roxburgh et al. (2016) mentions the concern directly (p. 415).	Working with suitable samples (matrix composition + shape/size) and types of excitation sources. Appropriate research questions and qualitative or semi-quantitative approaches.
Corrosion affecting pXRF readings.	Both papers address this issue directly and offer ways of mitigating the effect corrosion has on readings. Charalambous et al. (2021) does admit that their measurements are probably not 100% accurate because of this issue (p. 3).	Not including artefacts that are too corroded in your research. Taking multiple measurements with the pXRF device of the same sample. Appropriate research questions and qualitative or semi-quantitative approaches. Comparing corroded vs non-corroded readings of the same sample. Excluding certain elements, Roxburg et al. (2016) excluded Cu in their research for example (p. 417).
Inaccurate measurements of lower-Z elements. Elements below Na being undetectable for pXRF.	No.	No solutions have been mentioned, but lower-z elements are not common in metallic materials, which reduces the problem.
Risk of high background signal from primary radiation.	Neither text referred to the use of actual filters, but both calibrated their devices for their specific materials (copper alloys).	Specific filters for matching materials that reduce the background signal.

The 'Point and shoot' mentality.	No, but it does not seem to be present in either text as both texts, especially Roxburgh et al. (2016) goes into depth about what device they used and how it was calibrated (p. 415).	Educating and informing researchers. Not fully relying on pre-installed software to calibrate a pXRF device, but also using third-party options. Following international standards when calibrating a pXRF device. Using appropriate material standards.

5.2 Assessment of advantages and potential

The most major advantages of pXRF devices are the portability of said devices and the instantaneous feedback of the analysis performed. These two advantages are combined in pXRF devices, multiplying their potency.
Instead of having to wait for up to 30 minutes or much longer, like stationary XRF workstations, researchers can observe and adjust their analytical process (Frahm, 2013, pp. 1080-1092). This not only allows for more useful results from the analysis, but also altering the sampling strategy *in situ* and potentially even the excavation strategy itself. Factors such as the amount of archaeological material, environmental factors can be more easily taken into account compared to an excavation that does not use pXRF (Mass & Shugar, 2012, pp. 17-35*)*.
The high resolution of pXRF devices compared to laboratory-based analysers also means that in most cases there is no (pre) treatment required for most objects (Speakman & Shackley, 2013, pp. 1435-1443). This not only saves on time and money, but again facilitates the use of pXRF *in situ* as objects do not need to be taken to a lab for these treatments, but usually only need to be washed. Not to mention how some treatments of objects can be harmful to the materials.

Avoiding these invasive methods allows pXRF devices to lend themselves to conservation efforts. Identifying corrosion products on metallic artefacts, for example, can be done with pXRF without risking the integrity of the artefact with invasive techniques (Karydas, 2007, pp. 419-432). Another example is museums preferring to take the analysis equipment over to their museum instead of transporting their objects to a lab, due to the fragility of said objects.

Portable XRF devices are also easy to use, in theory. With sufficient oversight, less experienced archaeologists like students can learn to use pXRF quickly. This allows more experienced archaeologists to focus their energy on other parts of a project (Shackley, 2010, pp. 7-40). This ease of use also motivates researchers to use pXRF in their projects, where without pXRF they might not have employed any type of comparable analysis.

5.3 Comparison of pXRF parameters

It was the goal and the ambition of this thesis to assess how XRF on copper alloys work and to move forward in constructing a suitable framework to compare this dataset. In order to do so I selected a few exemplary case-studies. From these case studies, I observed there are aside from material specific issues, such as surface condition and orientation, also instrument specific variables. I will therefore end the discussion by comparing the different information that a selection of authors give about the pXRF devices they used for their research and accompanying parameters. This will hopefully give an initial overview of what different researchers use for their pXRF-reliant research.

Table 4: A comparison of pXRF devices and relevant variables used in the two case studies and two additional studies. Created by W. Verhage.

Study	Brand	Detector	Time (in seconds)	kV	Analytical mode/ Filter	Certified Reference Materials (CRM's)/ Standard reference materials (SRM's)
Enkomi (Cyprus): Using pXRF spectroscopy to identify LBA copper alloys. Charalambous et al. (2021)	Innov-X Delta (Now Olympus)	Silicon Drift Detector (SDD)	70	50	Alloy Plus mode	BCR-691 and 32X SN7
Early Roman copper-alloy brooch production: a compositional analysis of 400 brooches from *Germania Inferior.* Roxburgh et al. (2016)	Niton XL3t GOLDD	SDD with optimised geometry	30	NA	Electronic metals mode	CHARM – heritage bronze reference set (Heginbotham et al. 2014)

Identifying American native and European smelted coppers with pXRF: a case study of artifacts from the Upper Great Lakes region. Dussubieux & Walder, 2015)	Innov-X Delta (Now Olympus) Alpha Series	Si PiN diode	60	35	Alloy mode	B10, B13 from Centre de Développement des Industries de Mise en Forme des Matériaux, France. 71.32–4 and 51.13–4 from the Bureau of Analysed Samples Ltd, England. 500, C1123 and 1275 from the National Institute for Standards and Technology, U.S.A.
"Community practices" and "communities of practice" in smelting technology by XRF analysis of Archaic bronze votive figurines in central Italy (6th – 5th centuries BC). Fulminante & Unavane, (2020).	Bruker Tracer III-SD	NA	180	40	Filter: 0.012" Al + 0.001" Ti	NA
Neutron diffraction analyses of Bronze Age swords from the Alpine region: Benchmarking neutron diffraction against laboratory methods.	Röntgenanalytik Systeme GmbH & Co. KG, model Eagle III XXL	Si (Li) detector	150	40	NA	Local reference materials.

As can be observed, there are various differences between what information different researchers provide. A number of other variables could have been added with only one author mentioning the variable in certain cases, such as the diameter of the x-ray beam only being mentioned by Charalambous (2021). Some variables that have been included are not mentioned by all the authors either, such CRM's/SRM's missing in Fulminante & Unavane (2020).

Based on this snapshot of articles, it can be observed there is a myriad of settings that are used by different scholars. While these can be partly instrument governed, there is no clear guidance on optimal settings. The advantages of pXRF, being fast, mobile and non-destructive are particularly suited to accumulate and analyse large datasets. Different settings of the machines as illustrated in table 4, make these datasets highly difficult to compare, certainly if no communal certified reference materials have been measured and reported. Therefore this thesis argues for the systematic analysis of a similar set of reference materials, such as the CHARM set (Heginbotham et al.(2014)), in order to start to compare different instruments with each other as a continuation of the bachelor paper.

Chapter 6: Conclusion

Portable XRF is a relatively new technology, but it has already had great impact on the fields of archaeology and conservation. It is easy to use, cheap, provides information instantaneously and is non-destructive. The technology is not perfect though. It has clear flaws, such as the limited depth that the x-rays can penetrate, results that are not as precise as other methods, or even the mentality of easy results that it spawned. These problems however, can be largely compensated for or even outright solved. This requires researchers to do their due diligence however and not just buy a pXRF machine and start using it out of the box.

Appropriate reference materials, software, filters and research questions are necessary for pXRF results to be reliable. Researchers must share the details of which pXRF device they used and all its specifications. An international standard of all the required information should be established for future research employing pXRF to be reliable and empirical. Inspiration should be drawn from the Copper Charm set developed by Heginbotham et al.(2014) and similar CRMs should be created for other materials to increase inter-laboratory reproducibility.

But, as we currently lack such a uniform standard for various materials, it would be a prerequisite to share the quality control data gathered in order to be verifiable. Furthermore, if researchers are aware that portable XRF is not an easy solution for all their research, but actually requires thought and preparation, the future of pXRF in research looks bright.

Reference List

Baines, A. (2015). Introduction. In *Brass Instruments: Their history and development* (pp. 19–24). Introduction, Dover Publications.

Bayley, J., & Butcher, S. (1995). Acta of the 12th International Congress on Ancient Bronzes, Nijmegen 1992. In *Pascal and Francis Bilbiographic Databases*. Rijksdienst voor het Oudheidkundig Bodemonderzoek. Retrieved April 13, 2023, from https://pascal-francis.inist.fr/vibad/index.php?action=getRecordDetail&idt=2463197.

Bayley, J., & Butcher, S. (2004). *Roman brooches in Britain: A Technological and Typological Study based on the Richborough Collection*. The Society of Antiquaries of London.

Bellegem, M., Thornton, D., Buck, P., & Niece, S. (2015). *Conservation treatment and technical observations on two objects from the Waddesdon Bequest with life castings*, 15-22. Academia.edu. Retrieved March 20, 2023, from https://tinyurl.com/yj8u2d5b

Buchem, H. van. (1941). *De fibulae Van Nijmegen*. Centrale Drukkerij Nijmegen.

Calligaro, T. (2008), PIXE in the study of archaeological and historical glass. X-*Ray Spectrometry 37(2),* 169-177. https://doi.org/10.1002/xrs.1063

Canadian Conservation Institute. (2017) *Agents of deterioration.* https://www.canada.ca/en/conservation-institute/services/agents-deterioration.html

Charalambous, A., Kassianidou, V., & Papasavvas, G. (2014). A compositional study of Cypriot bronzes dating to the early iron age using portable X-ray fluorescence spectrometry (pXRF). *Journal of Archaeological Science*, *46*, 205–216. https://doi.org/10.1016/j.jas.2014.03.006

Charalambous, A., Papasavvas, G., & Kassianidou, V. (2021). Enkomi (cyprus): Using PXRF spectroscopy to identify LBA copper alloys. *Journal of Archaeological Science: Reports*, *35*. https://doi.org/10.1016/j.jasrep.2020.102726

Clerinx, H. (2017). Einde van de eerste welvaartsmaatschappij. In *Een Paleis voor de Doden: Over Hunebedden, dolmens en menhirs.* Athenaeum-Polak & van Gennep.

Craddock, P. T. (1998). *2000 Years of zinc and brass*. British Museum.

Davis, J. R. (2008). Introduction and Overview. In *Copper and copper alloys* (pp. 3–9). ASM International.

Davis, J. R. (2008). The Copper Industry: Occurence, Recovery and Consumption. In *Copper and copper alloys* (pp. 10–13). ASM International.

Dungworth, D. (1997). Roman Copper Alloys: Analysis of Artefacts from Northern Britain. *Journal of Archaeological Science*, *24*(10), 901–910. https://doi.org/10.1006/jasc.1996.0169

Dussubieux, L., & Walder, H. (2015) Identifying American native and European smelted coppers with pXRF: a case study of artifacts from the Upper Great Lakes region. In *Journal of Archaeological Science, 59,* 169-178. https://doi.org/10.1016/j.jas.2015.04.011

Dybowski, D. G. (2012). PXRF/WDXRFS Inter-Unit Data Comparison of Arizona Obsidian Samples. *Journal of Arizona Archaeology 2012*, *2*, 1–7.

ELGA LabWater (2021) *Mass Spectrometry | Water Impact | Laboratory Applications |*. https://tinyurl.com/5etj8mxv

Frahm, E., & Doonan, R. C. P. (2013). The technological versus methodological revolution of portable XRF in archaeology. *Journal of Archaeological Science, 40(2),* 1425–1434. https://doi.org/10.1016/j.jas.2012.10.013

Frahm, E. (2013). Validity of “off-the-shelf” handheld portable XRF for sourcing Near Eastern obsidian chip debris. In *Journal of Archaeological Science, 40(2),* 1080-1092. https://doi.org/10.1016/j.jas.2012.06.038

Fulminante, F., & Unavane M. (2020). “Community practices” and “communities of practice” in smelting technology by XRF analysis of Archaic bronze votive figurines in central Italy (6th – 5th centuries BC). In *Journal of Archaeological Science: Reports, 31.* https://doi.org/10.1016/j.microc.2015.12.017

Gass, I. G., MacLeod, C. J., Murton, B. J., Panayiotou, A., Simonian, K. O., & Xenophontos, C. (1994). *The geological evolution of the Southern Troodos transform fault zone*. Republic of Cyprus, Geological Survey Departement.

Ghazi, A.M. (1994). Lead in archaeological samples: an isotopic study by ICP-MS, *Applied Geochemistry 9(6), 627-636.* https://doi.org/10.1016/0883-2927(94)90023-X.

Glascock, M. D. (2014). Compositional Analysis in Archaeology. In *The Oxford Handbook of Topics in Archaeology*. Oxford Academic. Retrieved March 28, 2022, from https://academic.oup.com/edited-volume/43506/chapter/364131553?login=false.

Haalebos, J.K. (1986). *Fibulae uit Maurik.* Rijksmuseum van Oudheden.

HALL, E. T. (1961). Surface-enrichment of buried metals. *Archaeometry*, *4*(1), 62–66. https://doi.org/10.1111/j.1475-4754.1961.tb00535.x

Heginbotham, A., Bassett, J., Bourgarit, D., Eveleigh, C., Glinsman, L., Hook, D., Smith, D., Speakman, R. J., Shugar, A., & Langh, R. (2014). The Copper Charm Set: A New Set of Certified Reference Materials for the Standardization of Quantitative X-ray Fluorescence Analysis of Heritage Copper Alloys. *Archaeometry*, *57*(5), 856–868. https://doi.org/10.1111/arcm.12117

Hodson, H. (2003). The Royal Arsenal at Woolwich - The Master Founders. *Steel Times International*, 76. *https://doi.org/info:doi/*

Karydas, A. G. (2007). Application of a Portable XRF Spectrometer for the non-Invasive analysis of Museum Metal Artefacts. *Annali Di Chimica*, *97*(7), 419–432. https://doi.org/10.1002/adic.200790028

Knapp, A. B. (2013). *The Archaeology of Cyprus: From Earliest Prehistory Through the Bronze Age*. Cambridge University Press.

Kopytoff, I. (1986). The cultural biography of things: commoditization as process. *The social life of things: Commodities in cultural perspective*, *68*, 70-73.

Mass, J. L., & Shugar, A. N. (2012). Chapter 1 Introduction. In *Handheld XRF for art and archaeology* (pp. 17–35). Leuven University press.

Mellaart, J. (1962). Excavations at çatal hüyük: First Preliminary Report, 1961. *Anatolian Studies*, *12*, 41–65. https://doi.org/10.2307/3642517

Merriam-Webster. (n.d.). Alloy. In Merriam-Webster.com dictionary. Retrieved March 22, 2022, from https://www.merriam-webster.com/dictionary/alloy

Mödlinger, M., Godfrey, E., & Kockelmann, W. (2018). Neutron diffraction analyses of Bronze Age swords from the Alpine region: Benchmarking neutron diffraction against laboratory methods. *Journal of Archaeological Science: Reports, 20,* 423-433. https://doi.org/10.1016/j.jasrep.2018.05.017

Muhly, J. D. (1985). Sources of Tin and the Beginnings of Bronze Metallurgy. *American Journal of Archaeology*, *89*(2), 275–291. https://doi.org/10.2307/504330

Nelson, E., 1975. Uses of X-ray fluorescence analysis in archaeology. Syesis 8, 91-95

Olesik, J. W. (1991). Elemental analysis using ICP-OES and ICP/MS. *Analytical Chemistry*, *63*(1), 12A-21A. https://doi.org/10.1021/ac00001a001

Oxford Learner's Dictionaries. (n.d.). *Alloy*. alloy_1 noun - Definition, pictures, pronunciation and usage notes | Oxford Advanced Learner's Dictionary at OxfordLearnersDictionaries.com. Retrieved March 22, 2022, from https://www.oxfordlearnersdictionaries.com/definition/english/alloy_1?q=alloy

Pessanha, S., Guilherme, A., & Carvalho, M. L. (2009). Comparison of matrix effects on portable and stationary XRF spectrometers for cultural heritage samples. *Applied Physics A*, *97*(2), 497–504. https://doi.org/10.1007/s00339-009-5251-x

Pollard, A. M., Heron, C. (2008). 2.4 Techniques Using X-rays. In *Archaeological chemistry* (2nd ed., pp. 33–49). The Royal Society of Chemistry.

Porphyrios, D. (1969). *Enkomi: Excavations 1948-1958*. Philipp von Zabern.

Roest, J. van der. (1988). *Die römischen Fibeln von "De Horden"* 142-202. Rijksdienst voor het Oudheidkundig Bodemonderzoek.

Roxburgh, M., Heeren, S., Huisman, H., & Os, B. (2016). Early Roman copper-alloy brooch production: a compositional analysis of 400 brooches from germania inferior. *Journal of Roman Archaeology*, *29*, 411–421. https://doi.org/10.1017/s1047759400072202

Ruette, M. (1996). Brass foundry workshops of the Southern Low Countries and the Principality of Liege. A Technical Approach. *The Journal of the Historical Metallurgy Society*, *30*(2), 116–119. Retrieved April 4, 2022, from https://www.hmsjournal.org/index.php/home/article/view/421/403.

Scherpereel, K. (2013). *Drinkgerei en brouwovens uit de Middeleeuwen en Vroegmoderne Tijd in de Lage Landen*. Academia. Retrieved April 4, 2022, from https://tinyurl.com/ynjnhh66

Shackley, M. S. (2010). An Introduction to X-Ray Fluorescence (XRF) Analysis in Archaeology. In *X-ray fluorescence spectrometry (XRF) in Geoarchaeology* (pp. 7–40). Springer. Retrieved March 25, 2023, from https://link.springer.com/book/10.1007/978-1-4419-6886-9.

Shugar, A. N. (2013). Portable X-ray fluorescence and archaeology: Limitations of the instrument and suggested methods to achieve desired results. *Archaeological Chemisty VIII,* 173–193. https://doi.org/10.1021/bk-2013-1147.ch010

Speakman, R. J., & Shackley, S. M. (2013). Silo science and portable XRF in archaeology: A response to Frahm. In *Journal of Archaeological Science, 40(2),* 1435–1443. https://doi.org/10.1016/j.jas.2012.09.033

Stos, Z. A., Maliotis, G., Gale, N. H., & Annetts, N. (1997). Lead Isotope Characteristics of the Cyprus Copper Ore Deposits Applied to Provenance Studies of Copper Oxhide Ingots. *Archaeometry*, *39*(1), 83–123. https://doi.org/10.1111/j.1475-4754.1997.tb00792.x

Timberlake, S. (2007). The use of experimental archaeology/archaeometallurgy for the understanding and reconstruction of Early Bronze Age mining and smelting technologies. *Metals and mines: Studies in archaeometallurgy*, 27-36.

Tykot, R. H. (2016). Using Nondestructive Portable X-ray Fluorescence Spectrometers on Stone, Ceramics, Metals, and Other Materials in Museums: Advantages and Limitations. *Applied Spectroscopy*, *70*(1), 42–56. https://doi.org/10.1177/0003702815616745

Webb, J. M., & Frankel, D. (1999). Characterizing the Philia Facies: Material Culture, Chronology, and the Origin of the Bronze Age in Cyprus. *American Journal of Archaeology*, *103*(1), 3–43. https://doi.org/10.2307/506576

Wilson, C.A. (2017). Electron Probe X-ray Microanalysis (SEM-EPMA). *Techniques. In Archaeological Soil and Sediment Micromorphology*. https://doi.org/10.1002/9781118941065.ch43

Figures

https://www.portaspecs.com/product/olympus-pxrf-analyser/ accessed 14-03-2022

https://www.thermofisher.com/blog/mining/technology-focus-x-ray-fluorescence-xrf-in-mining/, accessed 21-03-2022

Charalambous, A., Kassianidou, V., & Papasavvas, G. (2014). A compositional study of Cypriot bronzes dating to the Early Iron Age using portable X-ray fluorescence spectrometry (pXRF). *Journal of Archaeological Science*, *46*, 205–216. https://doi.org/10.1016/j.jas.2014.03.006

Charalambous, A., Papasavvas, G., & Kassianidou, V. (2021). Enkomi (cyprus): Using PXRF spectroscopy to identify LBA copper alloys. *Journal of Archaeological Science: Reports*, *35*. https://doi.org/10.1016/j.jasrep.2020.102726

Charalambous, A., Papasavvas, G., & Kassianidou, V. (2021). Enkomi (cyprus): Using PXRF spectroscopy to identify LBA copper alloys. *Journal of Archaeological Science: Reports*, *35*. https://doi.org/10.1016/j.jasrep.2020.102726

Charalambous, A., Papasavvas, G., & Kassianidou, V. (2021). Enkomi (cyprus): Using PXRF spectroscopy to identify LBA copper alloys. *Journal of Archaeological Science: Reports*, *35*. https://doi.org/10.1016/j.jasrep.2020.102726

Charalambous, A., Papasavvas, G., & Kassianidou, V. (2021). Enkomi (cyprus): Using PXRF spectroscopy to identify LBA copper alloys. *Journal of Archaeological Science: Reports*, *35*. https://doi.org/10.1016/j.jasrep.2020.102726

Charalambous, A., Papasavvas, G., & Kassianidou, V. (2021). Enkomi (cyprus): Using PXRF spectroscopy to identify LBA copper alloys. *Journal of Archaeological Science: Reports*, *35*. https://doi.org/10.1016/j.jasrep.2020.102726

Roxburgh, M., Heeren, S., Huisman, H., & Os, B. (2016). Early Roman copper-alloy brooch production: a compositional analysis of 400 brooches from germania inferior. *Journal of Roman Archaeology*, *29*, 411–421. https://doi.org/10.1017/s1047759400072202

Roxburgh, M., Heeren, S., Huisman, H., & Os, B. (2016). Early Roman copper-alloy brooch production: a compositional analysis of 400 brooches from germania inferior. *Journal of Roman Archaeology*, *29*, 411–421. https://doi.org/10.1017/s1047759400072202

Roxburgh, M., Heeren, S., Huisman, H., & Os, B. (2016). Early Roman copper-alloy brooch production: a compositional analysis of 400 brooches from germania inferior. *Journal of Roman Archaeology*, *29*, 411–421. https://doi.org/10.1017/s1047759400072202