TRACE ELEMENT ANALYSIS USING ICP-MS TO IDENTIFY METALWORKING AT THE RIBCHESTER ROMAN FORT, LANCASHIRE

By

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ABSTRACT

ICP-MS was used to discern the functionality of a clay hearth in the remains of *Brementenacum Veteranorum*. Once a Roman fort built in 72 – 73 AD and stood for over three centuries, the archaeologically rich site offered a glimpse into the past and shows evidence of 'post-Roman' metalworking activities. By evolving an ICP-MS protocol to accommodate the study, the soil evidence was analysed. With the presence of trace amounts of lead, copper and zinc, a temporary smithy was identified instead of a domestic hearth. The pattern of lead suggested metalworking with this element, especially due to the lack of the metal from the samples of the hearth, but high concentrations around its immediate vicinity and tapering away from the forge remains. This was indicative of lead working. Precious metals such as gold and silver were investigated and yielded negative results, suggesting jewellery was not made in this location.

This find contributes to the current chronology as evidence suggesting 'post-Roman' activities in Ribchester. Soil samples were collected from an ongoing excavation at the site led by a team of archaeologists from the University of Central Lancashire. ICP-MS provides increased sensitivity and improved detection limits over other analytical techniques previously employed. This work offers an alternative method to those in need of stringent examinations of archaeological soil samples in the hopes of identifying potential anthropogenic traces of heavy metals.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS – Atomic Absorption Spectroscopy

AD – *Anno Domini*

BC – Before Christ

ICP – Inductively Coupled Plasma

ICP-MS – Inductively Coupled Plasma – Mass Spectrometry

ICP-OES – Inductively Coupled Plasma – Optical Emission Spectrometry

XRF – X-ray Fluorescence

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1 INTRODUCTION

1.1 Ancient Rome

Roman civilisation is perhaps the most well-known ancient civilisation in human history, with surviving written accounts by Roman historians during the rise and peak of the nation; and scholars who studied the enduring civilisation hundreds of years after its decline and eventual collapse. Much of our knowledge of Rome comes from historical texts by Roman historians such as Suetonius in *The Twelve Caesars* and Tacitus in works such as *Histories* [1-3]. On the other hand, history is far more than texts of historians, empirical evidence also coincides with these texts to form a more complete picture of what the past was like, these often come from the field of archaeology. The material culture of past humans is recovered and analysed, proving significantly more important when used to shed light in areas that are less well-documented. There are studies into famous archaeological sites within the city of Rome, as well as those into the remains of remote fortlets scattered across the Roman Empire [4-5].

1.2 Roman occupation of Britain

The conquest of Britain by the Roman Empire following the Gaelic Wars was unique when compared to its mainland European counterparts such as those in the Mediterranean regions. Referred to as an empire of cities by Esmonde Cleary [5,6], Britain did not fit in with the rest of Rome's provinces. In Britain, occupation of regions by the military was often a long-term affair. An example of this is the famed *Vindolanda* auxiliary fort, a small fort garrisoned and occupied for roughly 300 years and near the current village of Bardon Mill, Northumberland [7]. Compared to the transition of the Ptolemy dynasty of Egypt to a Roman province, which occurred around the same time as Rome's first emperor came to be in 30 BC. From 23 AD onwards, only two garrisons were needed to pacify the province, stationed at the capital of Alexandria [8]. A significant difference in the nature of encampments are observed, in Britain, even small marching camps and winter forts could become a permanent settlement. This phenomenon occurs due to the lack of pre-existing towns in Britain, as urbanism did not exist as it did in lands such as Egypt. Civilisations such as the Egyptians had well established urban centres from previous colonisations, namely by the Greeks, and when Rome annexed these regions, they only needed to leave a small number of troops to pacify entire provinces. There are some exceptions, large fortresses such as Tarraco in Hispania were in place and eventually formed major city settlements (modern day Tarragona), in order to suppress ongoing sentiment of rebellion [9]. Small forts for garrison are usually much shorter lived, especially summer camps which, as the name suggests, last a summer. The authority would then hand over the area to civil administrations based on a town system, which would take over the governing of its people for Rome, led by governors of different provinces [9].

This is not the case in Britain, as most of its population resided in the countryside, with no clear government or authority, instead having many dominant tribes and various kingdoms, meaning no well-formed structures for taxation or allegiance. In order to establish and protect settlements, different groups of military personnel had to reside in forts and outposts around them for significantly longer periods, and garrisons needed refilling when forces were to advance northwards [9,10].

These forts were built with offense in mind, as during the infancy of the campaign, aggression was favoured because Roman troops had better equipment and training, also none of the locals from Britain had sieging capabilities at the time. To begin with, forts would only have the necessities for garrisoning troops [9]. Since forts were erected at different geographic locations with various purposes, the designs often varied. A work called *De Munitionibus Castorum* (on the defences of camps), previously attributed to a writer named Hyginus, was meant to be somewhat of a manual for the laying of a fort. This work offers the most information regarding the thoughts that went into the building of the forts by Roman engineers across the empire. It also outlines elements that should be present in these fortifications: including dimensions – which introduced a shift in shapes of forts from square to rectangular – and buildings within, e.g. accommodation, granaries, defences and hospitals to name a few [11].

1.2.1 Ribchester Roman fort: *Bremetenacum Veteranorum*

This research centres on the small village of Ribchester in Lancashire, England, where one such Roman Fort existed – first established around 72 AD, called *Bremetenacum*. Built by the twentieth legion (*Legio XX Valeria Victrix*), and abandoned by the Romans some three centuries later. The Ribchester Roman fort was in a strategic location when the Empire marched over Northern Britain, it was 100 km from the Roman Fortress in modern day Chester: *Deva Victrix*, built before the Hadrian's Wall. The two were established around the same decade, and like many forts of this nature, the Ribchester fort was built first in wood. With minimal defences, especially in its location, on a flat floodplain, as opposed to atop a hill or surrounded by natural chokepoints, this fort embodied the reasoning of similar settlements: to expand in territory and not sit and wait for attackers to come [9,10,12,13]. When created, it served a similar function as many forts and fortlets in the North Western parts of Roman Britain. As a garrison for troops, though, it did not house the legion who built it, but mainly auxiliary forces including a cavalry unit of *ala II Asturum* from Spain. It served also as an outpost along one of the main North-South roads, securing a strategic trans-Pennines junction, which was part of the complex road systems set up by the Romans [14,15]. Fig. 1 shows the location of Ribchester and major Roman settlements in Britain according to the Antonine Itinerary [16].

Figure 1. Map of Roman Britain and its road systems according to the Antonine Itinerary by William Stukeley, published 1723. Highlighted is Ribchester Roman fort: *Bremetenacum*.

Forts such as the one in Ribchester would have to undergo certain evolutions to accommodate a long-term occupation, as seen in the upgrade of materials from timber to stone in its reconstruction in the early second century [17]. During this time, the fort had the usual characteristics of minor settlements in *Britannia*, such as the *vicus* or the civilian settlement, outside the fort to house and protect civilian populations who reside around the fort. Features of note were the double granary built around the same time as the fort's reconstruction, its remains survived to this day at the site of the excavations, as well as a bathhouse located also outside the walls in the *vicus* [10,17].

1.2.2 Previous excavations at Ribchester

Excavation around the Ribchester fort area first began back in the 16th century, according to some antiquarians the site was thought to be rich in extensive Roman remains. John Leland was believed to be the first antiquarian to have commented on the area, around 1540. It was of particular interest to those who were captured by the history of Roman Britain [10,17]. In 1796, the Ribchester hoard was discovered by Joseph Walton, of which the famous Ribchester helmet (Fig. 2) was a part of. The hoard and its associated finds came to light at a time when collecting antiquities for the sake of a private collection was more common than for their historical significance. It is not known if Charles Townley ever displayed the finds to the public at his house in London after he had made the purchase from Walton. The finds did however, encourage Townley to publish an account for the items in an irregular serial called *Vetusta Monumenta*. The cavalry parade helmet gained fame due to the rarity of items of this nature, only around sixty other similar objects are known from the Roman Empire, it also happens to be the most intact one from Britain. It is unfortunate that at least one piece from this early discovery was lost due to mishandling, and it is understandable as to why: those who made the discovery had no real reasons to give much care to the find, especially with smaller items such as the articulations of the harness of a cavalryman’s horse [10]. The helmet was subsequently acquired by the British Museum in 1814 and dated to the late 1st or early 2nd century. It is made of copper alloy and it resides in the museum to this day. Another discovery made not long after was the remnants of the bathhouse by labourers in 1837, which is opened to the public currently [17].

Figure 2. Ribchester parade cavalry helmet, photo curtesy of the British Museum

Following the Ribchester hoard, more artefacts were unearthed, including coins dating to different Roman emperors. None of the coins found were issued after 367 – 383 AD (Emperor Gratian). Stone tablets were found and provided excellent evidence for the fort’s identity, including information of who built the fort, as well as which auxiliary unit it housed. Furthermore, accounts from the *Vindolanda* tablets confirm this fort’s existence in that period [17]. Whilst a great deal of work has been done, not all finds were documented equally, and it is fair to assume some information would have been lost. Those works which are documented, include numerous excavations within the stone fort, as well as around the town of Ribchester. Much of the work done in the early to mid-twentieth century was with regards to the western gate and defences of the later stone fort. Most accounts from that time suggest Agricolan characteristics especially regarding a timber rampart along with a set of ditches, which has been evolved and cut several times over the fort's life [9,17].

In 1980, prior to some extension work of the church, an excavation took place to determine the archaeological value of the proposed graveyard extension area. This trial dig unearthed evidence suggesting the fort was built pre-Agricolan, and its function was formulated from epigraphic evidence found in previous studies. This discovery eventually led to future works in 1989 – 1990, around the town of Ribchester, specifically at the periphery of the fort prior to modern redevelopment of the area [17]. Much of the remains of the stone fort were excavated by that time and most dated artefacts of the later periods of the fort's life are thought to be from the late 4th century [10,17]. The latest date of specific recorded activities within the fort's vicinity is undetermined, since much of the area had be settled over in later ages, and currently, St Wilfred's Church resides on top of much of the stone fort's remains, making excavations limited [10].

The Romans are thought to have occupied the fort well into the fourth century, though most of the garrison likely left the civilian settlement behind long before the end of Roman rule, due to various commanders requiring military to seize power when the empire descended into unrest. This meant Rome relinquished many of the territories to local populations, including concubines of the soldiers who lived amongst the auxiliaries as well as the veterans, who may have resided in Ribchester as their homes. This fort's unusually large *vicus* could suggest a large population of civilians resided here throughout the fort's life. There is much debate over identities of those who reside in Roman settlements in Britain including both military (be they auxiliaries or veterans) and non-combat civilians, with a large population of the latter the entire population's identity could be more blurred than most other settlements [9,18].

This fort, like many others had to fend for themselves against raids from tribes in the local region since its conception. Though there are many interpretations of whether Rome abandoned Britain, or Britain abandoned Rome during 409-410 AD [19], Roman officials were nonetheless expelled from Britain after they failed to secure support from the empire. With the withdrawal of garrisoned troops, local residents would find themselves at a severe disadvantage. Most importantly raw materials and resources flow had also stopped. With no doubt the remaining inhabitants in a Roman settlement would be seen as 'Roman' by locals, therefore residents in Ribchester may have needed to procure their own [9].

As the so called ‘Post-Roman’ period began, the debate for answers to the big questions of what life was like in these circumstances, as well as how the local population coped with mass immigration of Anglo-Saxons as the medieval times were dawning has been fierce [20]. There are two major case studies in Romano-British settlements offering some insight to this period, excavations at Wroexter – which housed the fourth largest Roman city in Roman Britain – and the excavation of Birdoswald Roman fort, which was situated along the Hadrian’s wall.

1.2.3 Similar excavations for evidence of Post-Roman activities

Currently a small village in Shropshire, England, Wroexter’s excavations in the 20th century provided evidence suggesting continuous urban activity post 400 AD as well as building activities [21]. The most influential of these evidences were the works done around the baths basilica, where the excavation techniques as well as archaeology science conducted from 1966 – 1990 were pioneering at the time. The finds included evidence suggesting repair works to large masonry buildings such as re-roofing as well as the reformation of a new town centre in timber across the fifth and sixth century [21]. Though there are since reviews of Barker’s work, notably Fulford’s review in 2002 as well as Lane’s in 2014, which demonstrate how many obstacles Barker had to overcome to make these claims. As a result, doubts were cast over the proposed chronology of occupation by the Romano-British for over 200 years after Rome’s departure, however the evidence of low-level urban activity cannot be completely refuted [6,22]. Even with the remains of the town left relatively intact and preserved, as well as excavated and studied, there is still no consensus as to what life was like. Interpretations of ‘scenarios’ observed vary so much and are often disproven, the most notable of which is by Thomas Wright, who discovered a skeleton with a coin hoard in the underfloor heating system of the baths. The interpretation was this person was hiding from raids of the town, though this has been since proven wrong by future examinations [23].

Birdoswald was a more similar case study to Ribchester, both were in the Northwestern parts of Britain, and were substantially smaller settlements than Wroexter. They also both served similar functions, as military garrisons, and contained a *vicus* according to disposal evidence. In fact, patterns of rubbish pits and refuse from the fort, as well as positive identifications of remains of various structures provide most of the evidence for life in Birdoswald in the late fourth century and further. The excavations during 1987 – 1992 provides the most significant finds, and provides a chronology detailing activities throughout the ‘Post-Roman’ period [24].

The project utilised many types of archaeology science to help make sense of the finds, including macrobotanical sample analysis [25], pollen analysis, soil analysis [26] and stonemasonry survey, all of which were combined into the monograph report of Birdoswald by Wilmott in 1997.

As encompassing as the Birdoswald excavation was, there are a few lacklustre aspects. According to McDonnell, there is little evidence for metalworking in the fort throughout its life, there are minuscule amounts of metal objects even in the small finds recovered, yet a guard chamber towards the north of the fort was identified to be repurposed as a temporary smithy, along with other theoretical, small-scale *fabricae* located amongst the guard chamber. These were identified with the presence of metal flakes and ‘micro-slags’. These were not examined in detail, nor were the soil samples from the areas of these workshops. Only five samples were sieved and recovered from the guard chamber, the reasoning behind this is the lack of apparent industrial waste, as they were thought to have been disposed of via a nearby cliff and little evidence remained [27].

Though there is sound logic behind not examining these further, it could provide insight as to the sort of metalworking done during this time. Since it was a guard chamber that was repurposed, it is likely in the later part of the fort’s life that the short period of metalworking took place, and possibly after the garrison had largely departed. It is suggested that the population went on as a self-perpetuating settlement, with a symbiotic relationship between what remained of the garrison and civilians in the *vicus* [24], and this model could describe what life could be like in Ribchester around the same period.

1.2.4 Ribchester Revisited project

A project led by the University of Central Lancashire in conjunction with project partners Ribchester Roman Museum, the Australian National University, as well as the Institute for Field Research, Ribchester Revisited is a contemporary archaeological excavation project aimed to unearth more of the history of this location [28].

An excavation trench was marked out towards what is believed to be the northern gate of the stone fort (see fig. 3), and the rationale for this choice directly forms from two previous points. Firstly, much of the previous fort areas are currently resided in, and accessibility for a long period without concerning the locals in the village restricts the amount of potential dig site.

This site is near the church yard and is free of commercial use on a regular basis, furthermore, due to its inaccessibility, contamination from modern history is thought to be low. Secondly, the trench is located near the north gate of the stone fort, this is approximately the same area where temporary workshops and smithies were set up in Birdoswald, this project hopes to find evidence of activities post Roman occupation, thus the choice of its locale.

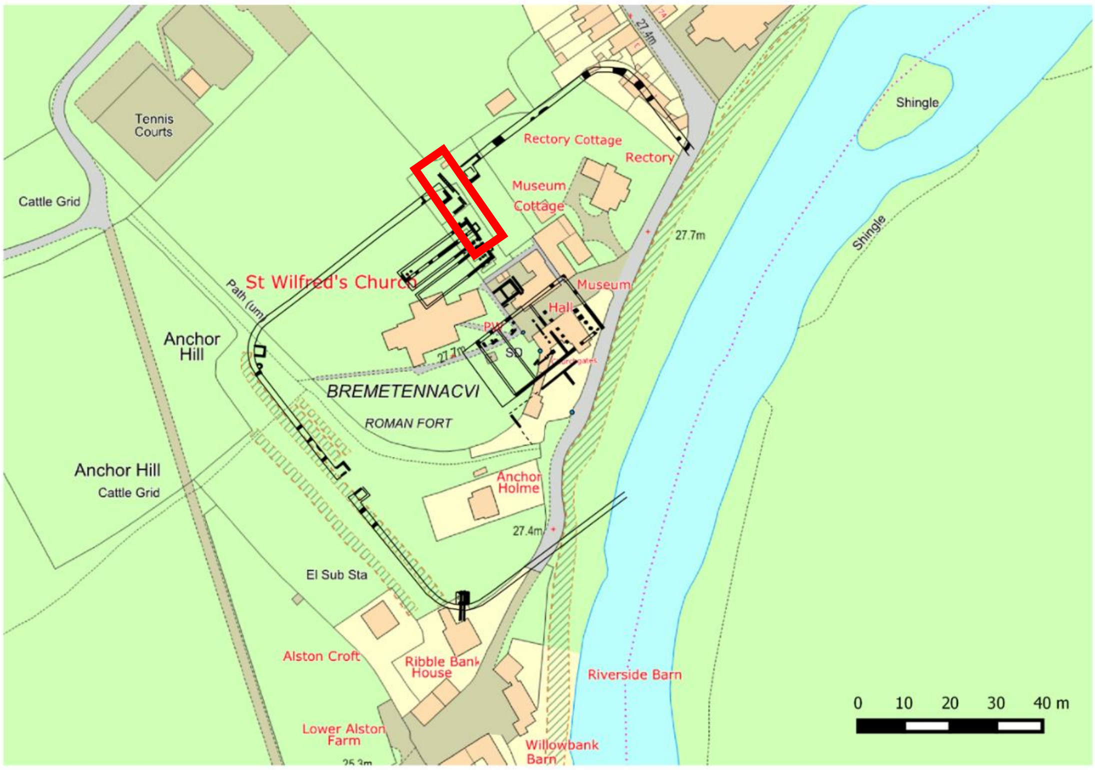


Figure 3. Plan of Ribchester Roman fort with its stone wall perimeter, highlighted (in red) is the excavation area for the Ribchester Revisited Project

This idea of inhabitants of the fort having to defend themselves or reuse and repurpose existing metals tied in with a discovery made by the team on the Ribchester Revisited project, where signs of a metal working forge were found in the heart of the trench, with scorching of the soil being visible as well as remnants of slag. The finds can be compared to those in Birdoswald, and from the current chronology, the finds are dated after the late fourth century, specifically, the hearth was unearthed with pottery dating to around 380 AD underneath, thus cementing the chronology of a late Roman, if not "post-Roman" hearth.

These soil samples were initially analysed for using X-ray Fluorescence (XRF) in a previous mini project involving students from UCLan in 2016, where a handheld XRF was brought on site to examine the soil *in-situ*. According to Cook *et al.*[29], an elemental analysis can differentiate metalworking hearths and domestic hearths, as some metals would not be worked on domestic hearths e.g. lead or copper or zinc. Since XRF was employed in Cook's study, it was also the choice of analysis in this initial study. However, this elemental analysis technique was found to not be suited to the site: soil from the excavation contaminated the XRF gun and samples were collected to be examined *ex-situ*. Once the samples were brought back, a variety of analytical techniques were employed, including X-ray diffraction (XRD), scanning electron microscopy (SEM) and further XRF [30,31]. Following this, a further investigation was carried out using inductively coupled plasma spectroscopy by a different group of students in 2017, as a method with improved sensitivity and detection limits compared to the preceding study [31].

With the initial survey results of the ICP-OES coming back with mercury and gold, this piqued the interest of those involved with the investigation to come up with a follow-up analysis using appropriate standards to accurately quantify concentrations of metals of interest in the soil samples excavated by the archaeologists.

The presence of precious metals such as gold and metals such as mercury at an ancient forge could indicate works to make jewellery via fire-gilding [32,33].

If jewellery was made in the Post-Roman period, this could mean those who resided within the remains of the fort had extended their powers matching those of leaders of local tribes. It is important to realise if this could affect our understanding of life in these settlements in the years following the empire's retreat, as well as behaviours and interactions between those who lived in Ribchester and those around them. Since there are only a few conclusive Roman settlements displaying post-Roman inhabitation such as Worxeter or Birdoswald, any insight to life in this period has great archaeological value.

1.3 Current methods of elemental analysis in archaeological science: their strengths and drawbacks

Currently, multi-elemental analyses of archaeological soil samples are done in a few different ways [34]. X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES) were used in the predecessor study, this is expanded upon with the use of inductively coupled plasma mass spectrometry (ICP-MS) in this study.

1.3.1 X-Ray Fluorescence

First, the technique used in the preceding study of the soil samples from this excavation site was XRF. This is a widely used multi-elemental analysis technique in various medias, including soil samples. XRF is known for being non-destructive, aside from this, it can also perform analysis *in-situ*, which often saves time from collecting and transporting samples. In addition, this also decreases the chance of contamination. The system utilises X-rays to excite and eject electrons from inner shells of an atom in the sample, an electron from a higher energy shell fills the vacancy by releasing radiation that are indicative of the element due to its specific energy. The overall process takes little time, with virtually no sample preparations required, and in theory no samples need to leave the excavation trench [35]. The handheld XRF used was the Bruker Tracer III-SD and fig. 4 shows how XRF works [36].

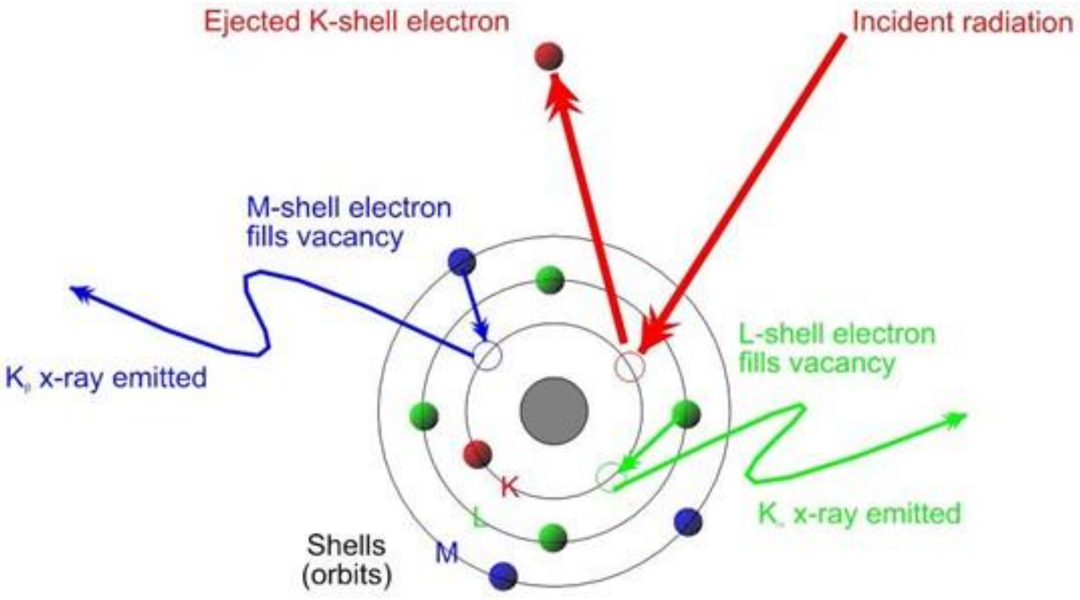


Figure 4 image showing incident radiation ejecting electron from inner K shell and its vacancy filled by L and M shell electrons, emitting K$_\alpha$ and K$_\beta$ emissions.

However, this technique was proven unsuccessful in determining what metals were present due to several factors, one of which was the sensitivity – compared to the other techniques, the handheld XRF had a worse detection limit in ideal conditions, and this was no ideal condition. When the analysis took place, the trench was wet due to poor weather conditions, (fig. 5 shows *in situ* analysis using the handheld XRF), compared to studies such as the one carried out by Šmejda *et al*, which was in Israel, and remained arid throughout the study [37]. Another potential downfall of this technique is information is obtained from surface layers, which are often contaminated when exposed by the excavation process. *Ex situ* analysis with the XRF was also conducted, however the finds were inconclusive, as the abundance of iron affected the sensitivity and its ability to determine if lead was present [30].

Figure 5 Handheld XRF was used unsuccessfully to analyse the hearth area *in situ*. (From left to right: Dr. Duncan Sayer, Dr. Jennifer Readman, Dr. James Morris)

1.3.2 Inductively Coupled Plasma Spectroscopy

The technique used in this research: ICP-MS. Like ICP-OES, this technique uses an inductively coupled plasma, to ionise samples in the form of an aerosol mixed with the inert carrier gas that forms the plasma, in this case argon. This is done via a pneumatic nebuliser. The ICP begins within three concentric glass tubes of a plasma torch (see fig. 6), the sample tube, the intermediate tube and the external coolant tube. When power input is directed to the copper coil it acts as an electromagnetic coil around the outer glass tube, creating an oscillating magnetic field. With the carrier gas flowing through the intermediate tube temporarily paused, a spark is added from a Tesla coil attached to the outside of the torch, initiating the plasma by introducing free electrons. They ionise the argon gas and this becomes a self-sustaining process, with argon, its ions and electrons co-existing in the confines of the torch, forming the plasma. It protrudes at the top in bright white fashion, and when the carrier gas flow is back on, punches a hole in the centre of the plasma to allow the introduction of the sample aerosol. The difference between the ICP-MS and the OES lies in their detection methods. In ICP-OES, the sample undergoes atomic absorption and emission, like atomic absorption spectroscopy (AAS), where the changes in energies are specific to each element, the emission is in the same form: a photon of radiation. The use of an optical spectrometer separates this light into its component wavelength, which is then detected by either photomultiplier tubes or more recently charge-transfer devices [38].

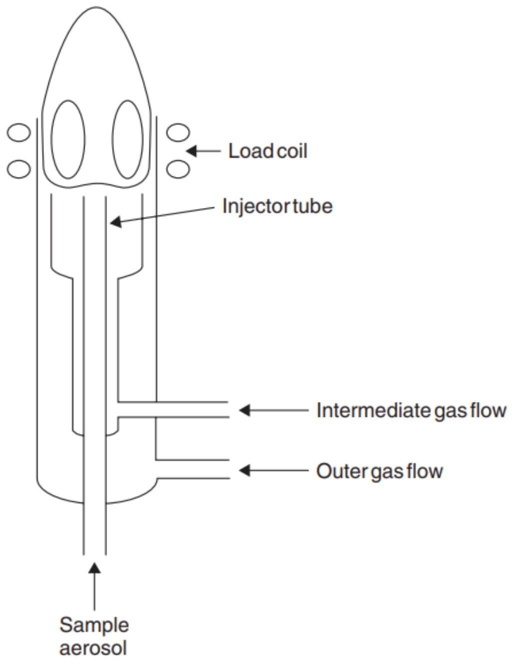


Figure 6. Diagram of a plasma torch, from Dean's "*Practical Inductively Coupled Plasma Spectroscopy*" [38]

As for ICP-MS, the change lies in the detecting aspect, where all the ions from the sample and the carrier gas are transferred into a mass spectrometer and are calculated in conventional mass/charge ratio. The accessibility and improved detection limits make ICP spectroscopy techniques useful for the project, their multi-elemental analysis capabilities are exploited in this research, however, like all analytical techniques, these also have their drawbacks. Sample preparation is perhaps the most inconvenient aspect, compared to XRF and NAA, samples from the excavation had to be taken, documented, dried and ground to homogenise each sample, and undergo digestion afterwards in order to be introduced into the system through a nebuliser. There are variations to this operation which overcome this, such as laser ablation ICP-MS (LA-ICP-MS) [39], which significantly reduces preparation time, however, compromises quantification capabilities and complicates its process [40,41]. Nevertheless, the regular ICP-MS technique should yield relevant data at the cost of time, which seems most suitable to this research.

Previously ICP-OES and ICP-MS were used to analyse samples from this excavation, these were done specifically for detecting lead. In the ICP-OES survey results, trace amounts of unexpected gold and mercury were found. This altered the ICP-MS protocol slightly, with an added standard of gold and mercury used, however, these were expired at the time, and the results yielded were inconclusive and incomparable between batches due to a new set of calibration standards made for each batch. These problems and downfalls made the results relatively redundant, however helped pave and build the method for this project [26].

1.3.2.1 ICP-MS sample preparation

Sample preparation processes for ICP analysis include soil decomposition or extraction. The most common decomposition method is soil digestion – as the title suggests, it destroys the sample matrix and liberates the metals. In extraction procedures, metals are removed from the matrices and these are often associated with speciation, where specific oxidation states or organometallic compounds of trace metals are extracted. These techniques are usually employed when the need to detect certain toxic forms of the metals occur, ethylenediamine tetraacetic acid (EDTA) extraction is one such example [38,42].

Soil digestion methods vary from open vessel digestion to microwave-assisted digestion, but the theory remains largely the same, an acid and an external heat source is utilised to decompose the sample matrix, thus liberating the metals of interest from the soil. Different acids can be used, each with their own merits and drawbacks. The most commonly used acids for soil digestion are hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), perchloric acid ($HClO_4$) and hydrofluoric acid (HF). The pros and cons of each are well documented by Dean in *Methods for Environmental Trace Analysis,* AnTS Series [43], 2003, and the resulting digested sample can be filtered and handled accordingly before analysis. Open vessel digestion however contains two major drawbacks, one being it is a much more time-consuming process. In microwave-assisted digestion, the added pressure from the closed Teflon tubes speed the digestion process significantly, making a digestion cycle last around 75 minutes as opposed to the 18 hours required for an open vessel digestion.

The second drawback is an increased amount of both samples and digestion acid are required for open vessel digestion [44,45]. However, the results from the subsequent analysis shows good agreement from both preparation technique.

For this project, microwave-assisted digestion is chosen as the sample preparation method, it is demonstrated as efficient and provides results consistent with open vessel digestion. Digestion is chosen over extraction mainly due to speciation being not needed, as this project only wants to quantify and all metals species we are interested in, similar to Cook *et al*.'s study, zinc, copper and lead are chosen, and gold and mercury were also of interest from previous ICP survey results.

2 AIMS & METHODOLOGY

2.1 Aims

The aim of this project is to identify and quantify any metals of interest present in the soil samples collected from the Ribchester Revisited project. These include alloying elements such as zinc (Zn) and copper (Cu) which make brass, as well as previously mentioned potential precious metalworking elements such as gold (Au) and mercury (Hg). Lead (Pb) was a widely used metal at the time due to its versatility and simplicity. Pb is also added to objects occasionally prior to casting, due to its ability to lower melting points, easing some pouring processes. The presence of Pb would be of note if any were found, from specific context of soil, as it could date activities later than previously imagined [46,47]. Although tin bronze was more widely used than brass, higher levels of Zn is present in brass (approximately 18%) than tin (Sn) in bronze (approximately 9%), therefore any brass present will be easier to detect [48]. In addition, Zn's compatibility with the other elements of interest in an ICP-MS standard solution over Sn's was also considered, and Sn was not investigated in this study. According to Healy (1978), Zn ore was not prominent in Britain, and any found could indicate items containing Zn were imported to this part of the empire [49].

A further aim for this research is to establish a reproducible method for future works of this nature, building on top of previous methods, as projects like Ribchester Revisited are still ongoing.

2.2 Methods

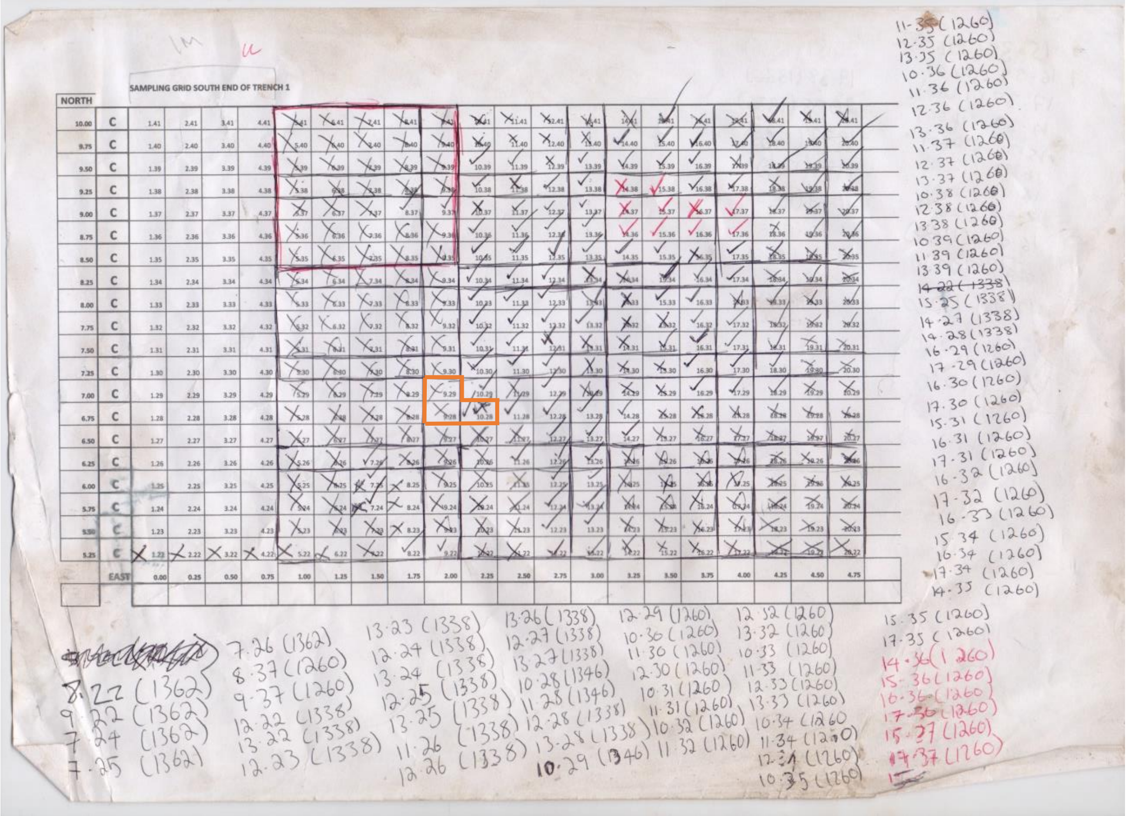
2.2.1 Sampling and excavation

The sampling method was relatively simple – it follows conventional archaeological soil recovery protocols [50], including a detailed grid system (see appendix 6.3), documenting where each of the samples came from within the trench. The spacing between each sample was 25 cm and there were some obstructions in the form of rocks preventing recovery of soil at every point in the grid system. As this is not the first excavation, the topsoil was already removed, and context numbers were given to locales which had similar characteristics i.e. depth or geology. The grid was organised in lines and each sample was from a point on a line. The lines followed a georeferenced x-axis of eastings, and the spots correspond to the y-axis of northings, these in turn correspond to the British OS national grid. For example, sample 21.40 (1215) came from line 21, spot 40 with the context of (1215), which is of similar geology and depth as other samples with the same context number.

A control soil sample was taken from the site of the trench, which was not only away from any potential workshop, it was also deep enough to be free of any anthropogenic contamination and can be considered a geology soil sample.

In total, including the control soil sample, 351 samples are processed and analysed.

It is also of note that the reference for the three soil samples from the clay hearth are 10.28, 10.29 and 11.28, and they share a context of (1346) (see fig.7).



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15·36 (1260)
16·36 (1260)
17·36 (1260)
15·37 (1260)
17·37 (1260)

Figure 7. An example of the grid square sheets, highlighted are the three locations where samples of the clay hearth was excavated with the context of (1346)

The amount of soil contained in each sample varied drastically, though none weighed more than approximately 50g before drying. Since the geology varied across the site, samples (especially those mainly composed of clay) were dug with a trowel and tended to be larger in size and weight.

2.2.2 Initial sample preparation

The recovery of the samples was completed in July 2017, and sample preparation began at the end of 2017, with drying and grinding of the samples taking place first. Samples were separated into individual plastic containers that were decontaminated and cleaned with nitric acid (made from analytical grade concentrated HNO_3) diluted with deionised water, they were labelled and put into an oven set at 100˚C for approximately 2 hours. Once dried, the samples were ground using a marble pestle and mortar to homogenise the sample. The pestle and mortar were also cleaned in-between uses with the same dilute HNO_3. This process was completed for all of the samples before proceeding to the microwave digestion.

2.2.3 Microwave-assisted digestion

To digest the samples, protocols set out by Dean J. in 2005 were roughly followed but optimised according to manufacturer’s guidelines. 0.1g of the sample was weighed out with ±0.05g error and 10ml of analytical grade 75% HNO_3 added to the Teflon vessels of the microwave digester. The device was then set with the following parameters: ramp to 150˚C in 10 minutes, hold for 10 minutes, ramp to 180˚C in 10 minutes, hold for 20 minutes and allowed to cool afterwards. To establish a protocol that could be reused with other microwave instruments, this same procedure was carried out in two different brands of microwaves: Anton Paar’s “Multiwave GO” and Milestone’s “ETHOS EZ Microwave Digestion System”. Parameters were checked to be within both manufacturers’ guidelines, and 10 of the samples were digested in both microwave systems. After checking the results were consistent (see table 2.), most of the samples were digested in the Milestone “ETHOS EZ” microwave due to accessibility.

2.2.4 ICP-MS analysis

The ICP-MS used is the Thermo Fisher X series I. The ICP-MS protocol was reused from the previous UCLan project as follows: digested samples were cooled and diluted by adding 0.1ml of digest in 10ml of 1% HNO_3 (100µl of sample + 9900µl of HNO_3). The 1% HNO_3 was made from analytical grade 75% HNO_3 and nano-pure water. These are then loaded into the ICP-MS autosampler, preceded by a blank of 1% HNO_3 (the same as the one used to dilute the samples) and a series of calibration standards. The calibration standards were bought from SPEX CertiPrep Eu. The stock standard solution had a concentration of 100ppm in a 5% HNO_3 matrix. This was diluted by the same 1% HNO_3 first to 1000ppb, and was further diluted for the calibrations. These were ordered in ascending concentrations at levels of 20ppb, 50ppb, 100ppb, 200ppb, 500ppb and 1000ppb after the blank. The amount of standards made were to last throughout the project, as using the same standards would allow comparability between batches. The stock standard was a custom multi-element standard, which contained Zn, Cu, Pb, Hg and silver. A separate Au standard had to be bought due to the incompatibility of all these elements in the same standard, and unfortunately it had a different stock concentration as well as matrix, (10ppm in a 2% HCl matrix), and this was used in the same dilutions later.

Each sample and standard ran three times and an average calculated, with standard deviation σ included in the tables in the appendix.

*A series of revisions in methods are introduced for the analysis of Hg and is discussed in the results chapter 3.1.1.

3 RESULTS AND DISCUSSION

3.1 Results and data

All results and raw data are in the appendix, with results of Cu, Zn and Pb displayed as heat maps made in MS Excel (fig. 8, 10, 12) and subsequently QGIS (fig. 9, 11, 13), according to the same grid reference employed in sampling. Silver was entirely absent as seen in the raw data and thus not processed in the same way. The lack of Au and Hg data resulted in a similar lack of visual representation.

In the Excel maps each spot has a corresponding dilution corrected concentration with the unit of ppb. For lines 23 and 37 duplicates were taken from the same grid reference but had different context numbers, hence the absence of some data along these lines.

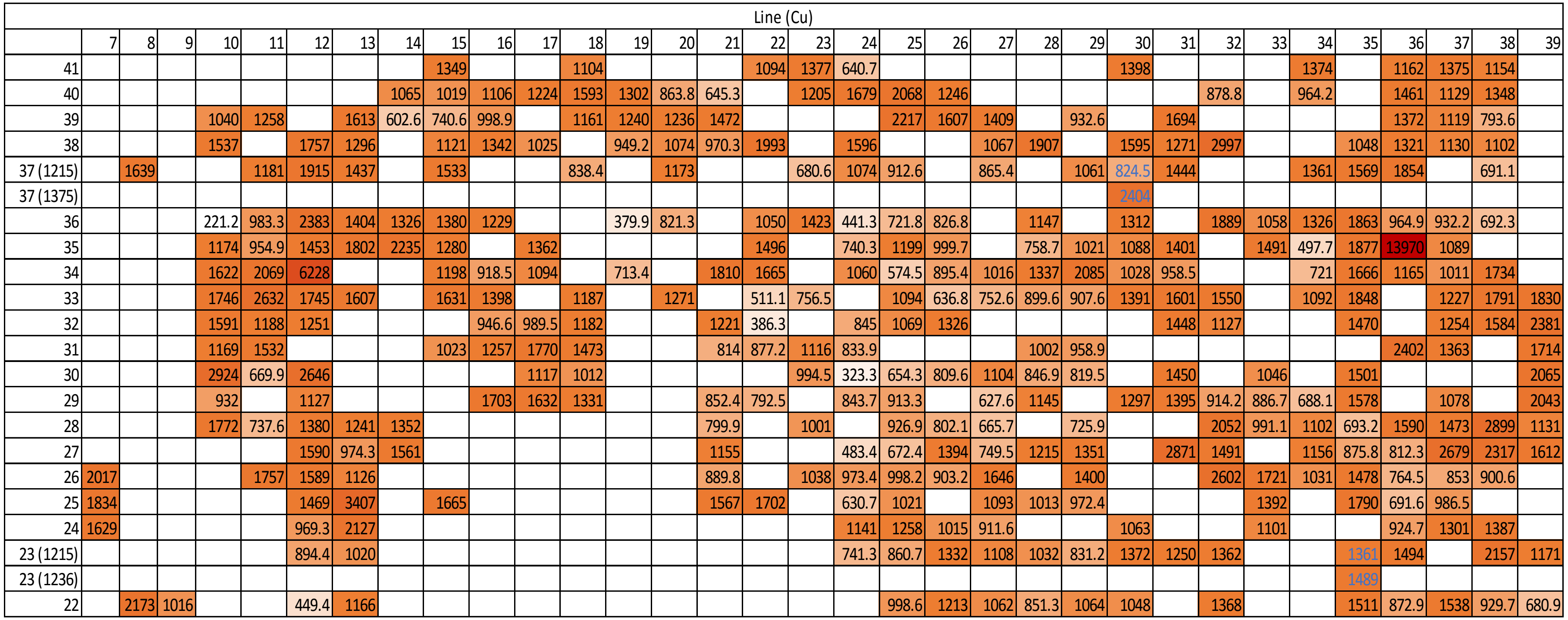
This spreadsheet was converted into a .csv file (comma-separated values) in order to generate a heat map that overlays over an aerial drone photograph of the excavation trench using the QGIS software [51]. Each label represents a percentile of the data, with 0% as transparent, followed by 25% (orange), 50% (yellow), 75% (green) and 100% (blue).

Due to a software error, data collection for sample 15.31 in batch 2 (appendix 6.1.2) was interrupted. It was re-run with the revised methods meant for Hg as it was also near the samples which came back with relatively high Hg concentration (appendix 6.1.11 and 12). The results from these batches for Pb are displayed below in table 1. This also works as data validation across methods.

Table 1. Data of re-runs from appendix 6.1.11 and 12 for Pb

Grid Reference	6.1.2 run (ppm)	6.1.11 run no. 1 (ppm)	6.1.11 run no. 2 (ppm)	6.1.11 run no. 3 (ppm)	6.1.12 run (ppm)	Standard deviation (σ)
15.31	n/a	2.591	2.336	3.766	1.933	0.788
15.35	4.713	3.995	4.092	4.389	4.124	0.291
15.36	1.931	1.957	2.461	2.171	1.816	0.255
16.34	1.390	1.624	1.560	1.699	1.349	0.150
16.36	0.946	0.809	0.813	0.903	0.618	0.126

3.1.1 Heat maps showing copper distribution



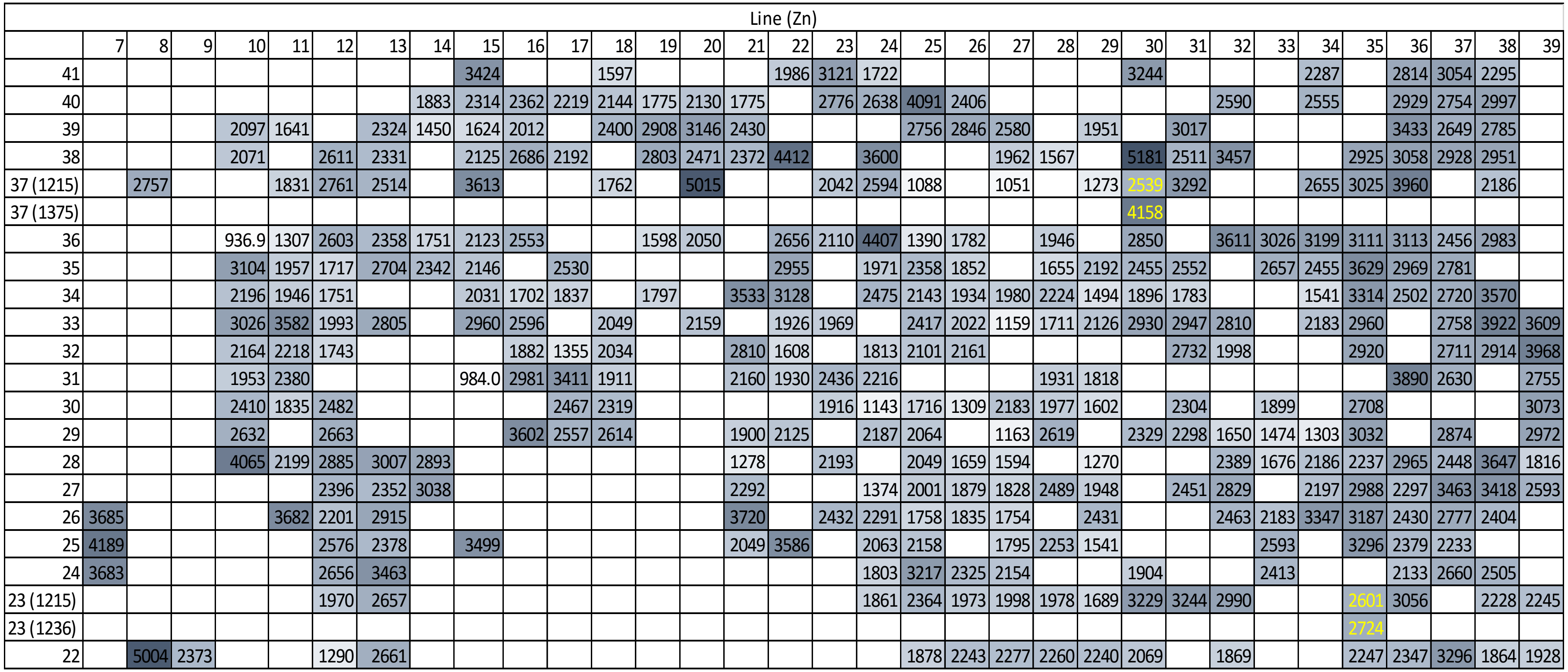
	Line (Cu)																																
	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39
41									1349			1104				1094	1377	640.7						1398				1374		1162	1375	1154	
40								1065	1019	1106	1224	1593	1302	863.8	645.3		1205	1679	2068	1246						878.8		964.2		1461	1129	1348	
39				1040	1258		1613	602.6	740.6	998.9		1161	1240	1236	1472				2217	1607	1409		932.6		1694					1372	1119	793.6	
38				1537		1757	1296		1121	1342	1025		949.2	1074	970.3	1993		1596			1067	1907		1595	1271	2997			1048	1321	1130	1102	
37 (1215)		1639			1181	1915	1437		1533			838.4		1173			680.6	1074	912.6		865.4		1061	824.5	1444			1361	1569	1854		691.1	
37 (1375)																								2404									
36				221.2	983.3	2383	1404	1326	1380	1229			379.9	821.3		1050	1423	441.3	721.8	826.8		1147		1312		1889	1058	1326	1863	964.9	932.2	692.3	
35				1174	954.9	1453	1802	2235	1280		1362					1496		740.3	1199	999.7		758.7	1021	1088	1401		1491	497.7	1877	13970	1089		
34				1622	2069	6228			1198	918.5	1094		713.4		1810	1665		1060	574.5	895.4	1016	1337	2085	1028	958.5			721	1666	1165	1011	1734	
33				1746	2632	1745	1607		1631	1398		1187		1271		511.1	756.5		1094	636.8	752.6	899.6	907.6	1391	1601	1550		1092	1848		1227	1791	1830
32				1591	1188	1251				946.6	989.5	1182			1221	386.3		845	1069	1326					1448	1127			1470		1254	1584	2381
31				1169	1532				1023	1257	1770	1473			814	877.2	1116	833.9				1002	958.9							2402	1363		1714
30				2924	669.9	2646					1117	1012					994.5	323.3	654.3	809.6	1104	846.9	819.5		1450		1046		1501				2065
29				932		1127				1703	1632	1331			852.4	792.5		843.7	913.3		627.6	1145		1297	1395	914.2	886.7	688.1	1578		1078		2043
28				1772	737.6	1380	1241	1352							799.9		1001		926.9	802.1	665.7		725.9			2052	991.1	1102	693.2	1590	1473	2899	1131
27						1590	974.3	1561							1155			483.4	672.4	1394	749.5	1215	1351		2871	1491		1156	875.8	812.3	2679	2317	1612
26	2017				1757	1589	1126								889.8		1038	973.4	998.2	903.2	1646		1400			2602	1721	1031	1478	764.5	853	900.6	
25	1834					1469	3407		1665						1567	1702		630.7	1021		1093	1013	972.4				1392		1790	691.6	986.5		
24	1629					969.3	2127											1141	1258	1015	911.6			1063			1101			924.7	1301	1387	
23 (1215)						894.4	1020											741.3	860.7	1332	1108	1032	831.2	1372	1250	1362			1361	1494		2157	1171
23 (1236)																													1489				
22		2173	1016			449.4	1166												998.6	1213	1062	851.3	1064	1048		1368			1511	872.9	1538	929.7	680.9

Figure 8. MS Excel heat map showing distribution of Cu with grid system from the excavation

Control soil: 182.9 ppb

Figure 9. QGIS heat map showing concentrations of Cu overlaying an aerial photo of the trench (marked is the location of the hearth)

3.1.2 Heat maps showing zinc distribution



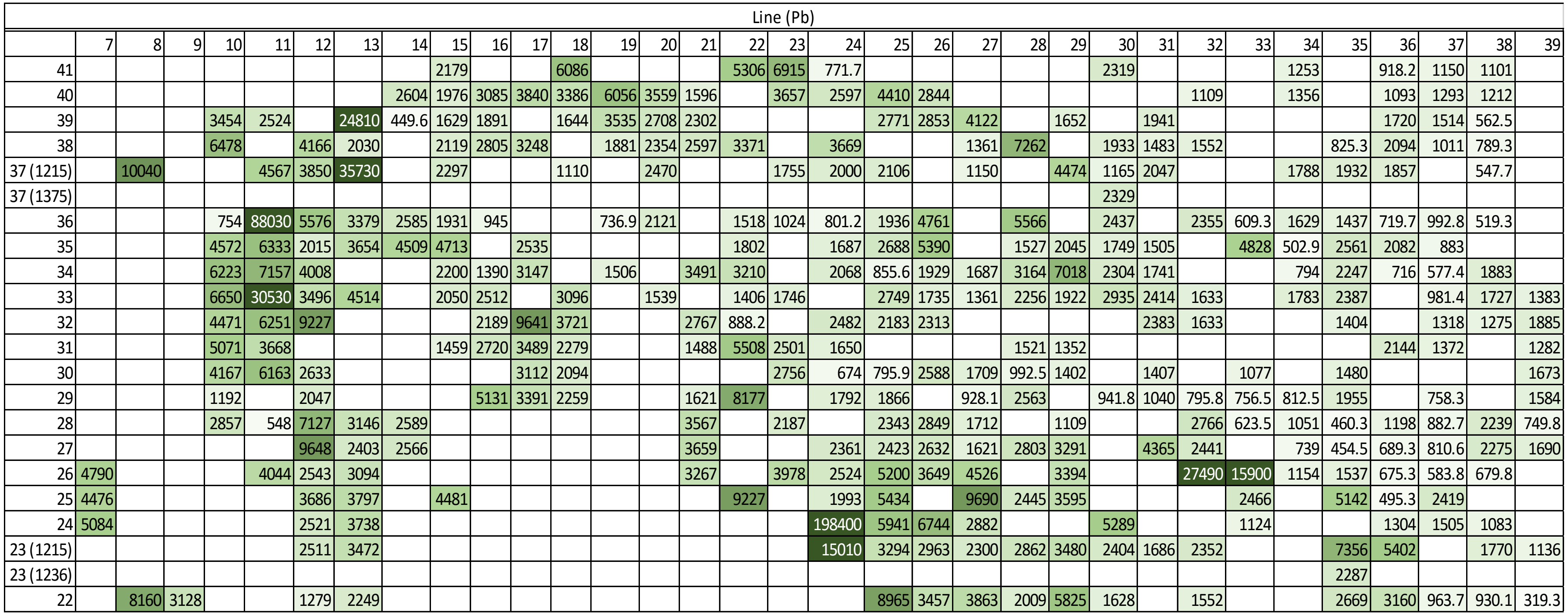
	Line (Zn)																																
	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39
41									3424			1597				1986	3121	1722						3244				2287		2814	3054	2295	
40								1883	2314	2362	2219	2144	1775	2130	1775		2776	2638	4091	2406						2590		2555		2929	2754	2997	
39				2097	1641		2324	1450	1624	2012		2400	2908	3146	2430				2756	2846	2580		1951		3017					3433	2649	2785	
38				2071		2611	2331		2125	2686	2192		2803	2471	2372	4412		3600			1962	1567		5181	2511	3457			2925	3058	2928	2951	
37 (1215)		2757			1831	2761	2514		3613			1762		5015			2042	2594	1088		1051		1273	2539	3292			2655	3025	3960		2186	
37 (1375)																								4158									
36				936.9	1307	2603	2358	1751	2123	2553			1598	2050		2656	2110	4407	1390	1782		1946		2850		3611	3026	3199	3111	3113	2456	2983	
35				3104	1957	1717	2704	2342	2146		2530					2955		1971	2358	1852		1655	2192	2455	2552		2657	2455	3629	2969	2781		
34				2196	1946	1751			2031	1702	1837		1797		3533	3128		2475	2143	1934	1980	2224	1494	1896	1783			1541	3314	2502	2720	3570	
33				3026	3582	1993	2805		2960	2596		2049		2159		1926	1969		2417	2022	1159	1711	2126	2930	2947	2810		2183	2960		2758	3922	3609
32				2164	2218	1743				1882	1355	2034			2810	1608		1813	2101	2161					2732	1998			2920		2711	2914	3968
31				1953	2380				984.0	2981	3411	1911			2160	1930	2436	2216				1931	1818							3890	2630		2755
30				2410	1835	2482					2467	2319					1916	1143	1716	1309	2183	1977	1602		2304		1899		2708				3073
29				2632		2663				3602	2557	2614			1900	2125		2187	2064		1163	2619		2329	2298	1650	1474	1303	3032		2874		2972
28				4065	2199	2885	3007	2893							1278		2193		2049	1659	1594		1270			2389	1676	2186	2237	2965	2448	3647	1816
27						2396	2352	3038							2292			1374	2001	1879	1828	2489	1948		2451	2829		2197	2988	2297	3463	3418	2593
26	3685				3682	2201	2915								3720		2432	2291	1758	1835	1754		2431			2463	2183	3347	3187	2430	2777	2404	
25	4189					2576	2378		3499						2049	3586		2063	2158		1795	2253	1541				2593		3296	2379	2233		
24	3683					2656	3463											1803	3217	2325	2154			1904			2413			2133	2660	2505	
23 (1215)						1970	2657											1861	2364	1973	1998	1978	1689	3229	3244	2990			2601	3056		2228	2245
23 (1236)																													2724				
22		5004	2373			1290	2661												1878	2243	2277	2260	2240	2069		1869			2247	2347	3296	1864	1928

Figure 10. Heat map showing distribution of Zn with grid system from the excavation

Control soil: 877.3 ppb

Figure 11. QGIS heat map showing concentration of Zn (marked is the location of the hearth)

3.1.3 Heat maps showing Pb distribution



	Line (Pb)																																
	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39
41									2179			6086				5306	6915	771.7						2319				1253		918.2	1150	1101	
40								2604	1976	3085	3840	3386	6056	3559	1596		3657	2597	4410	2844						1109		1356		1093	1293	1212	
39				3454	2524		24810	449.6	1629	1891		1644	3535	2708	2302				2771	2853	4122		1652		1941					1720	1514	562.5	
38				6478		4166	2030		2119	2805	3248		1881	2354	2597	3371		3669			1361	7262		1933	1483	1552			825.3	2094	1011	789.3	
37 (1215)		10040			4567	3850	35730		2297			1110		2470			1755	2000	2106		1150		4474	1165	2047			1788	1932	1857		547.7	
37 (1375)																								2329									
36				754	88030	5576	3379	2585	1931	945			736.9	2121		1518	1024	801.2	1936	4761		5566		2437		2355	609.3	1629	1437	719.7	992.8	519.3	
35				4572	6333	2015	3654	4509	4713		2535					1802		1687	2688	5390		1527	2045	1749	1505		4828	502.9	2561	2082	883		
34				6223	7157	4008			2200	1390	3147		1506		3491	3210		2068	855.6	1929	1687	3164	7018	2304	1741			794	2247	716	577.4	1883	
33				6650	30530	3496	4514		2050	2512		3096		1539		1406	1746		2749	1735	1361	2256	1922	2935	2414	1633		1783	2387		981.4	1727	1383
32				4471	6251	9227				2189	9641	3721			2767	888.2		2482	2183	2313					2383	1633			1404		1318	1275	1885
31				5071	3668				1459	2720	3489	2279			1488	5508	2501	1650				1521	1352							2144	1372		1282
30				4167	6163	2633					3112	2094					2756	674	795.9	2588	1709	992.5	1402		1407		1077		1480				1673
29				1192		2047				5131	3391	2259			1621	8177		1792	1866		928.1	2563		941.8	1040	795.8	756.5	812.5	1955		758.3		1584
28				2857	548	7127	3146	2589							3567		2187		2343	2849	1712		1109			2766	623.5	1051	460.3	1198	882.7	2239	749.8
27						9648	2403	2566							3659			2361	2423	2632	1621	2803	3291		4365	2441		739	454.5	689.3	810.6	2275	1690
26	4790				4044	2543	3094								3267		3978	2524	5200	3649	4526		3394			27490	15900	1154	1537	675.3	583.8	679.8	
25	4476					3686	3797		4481							9227		1993	5434		9690	2445	3595				2466		5142	495.3	2419		
24	5084					2521	3738											198400	5941	6744	2882			5289			1124			1304	1505	1083	
23 (1215)						2511	3472											15010	3294	2963	2300	2862	3480	2404	1686	2352			7356	5402		1770	1136
23 (1236)																													2287				
22		8160	3128			1279	2249												8965	3457	3863	2009	5825	1628		1552			2669	3160	963.7	930.1	319.3

Figure 12. Heat map showing distribution of Pb with grid system from the excavation

Control soil: 149.4 ppb

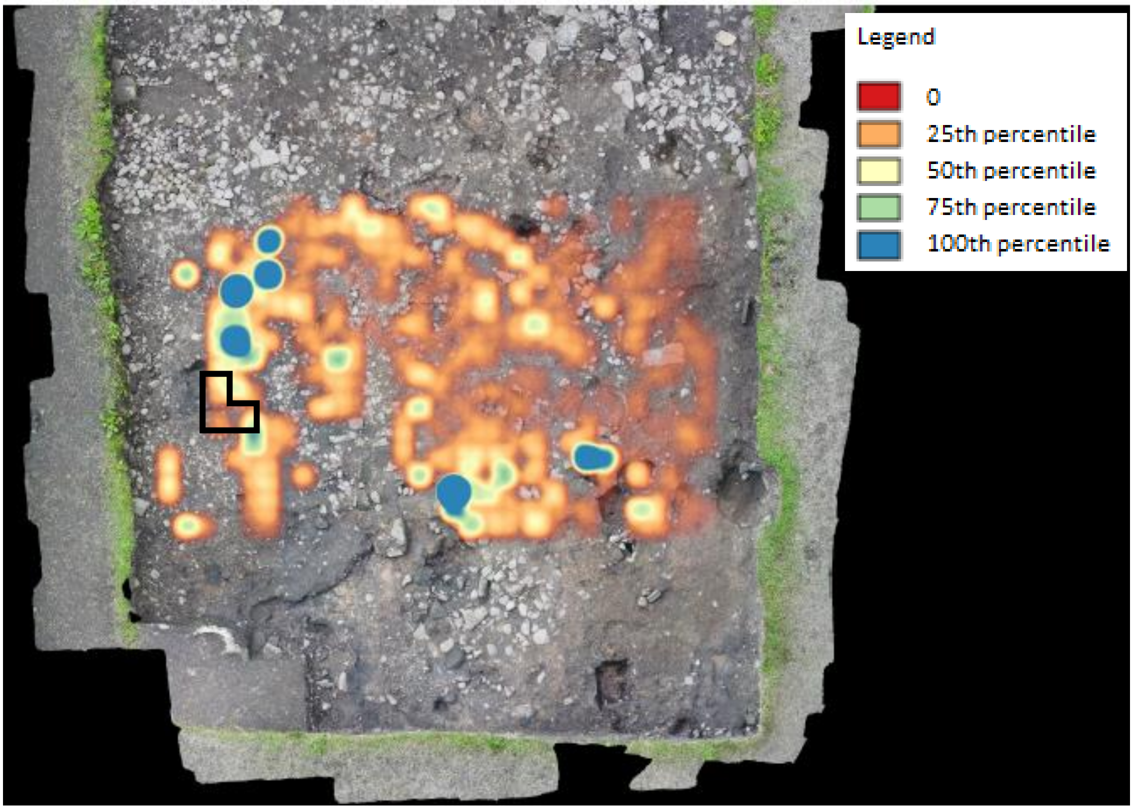


Figure 13. QGIS heat map showing concentration of Pb (marked is the location of the hearth)

3.2 Experimental evolution and discussion

Batches of samples were analysed using the ICP-MS using the methods outlined previously, and the first tests were to compare the digestion microwaves and if the same protocol can be used in different microwaves to yield similar results.

The table below shows the ICP-MS analysis of the samples that were digested in both of the microwaves. They are largely comparable with a few unexplained anomalies, namely in 8.22 and 8.37’s Pb concentration. The error for 8.37’s other elements results are not so severe, suggesting an anomaly within the detection of the Pb, a re-run of this could have remedied the difference, however this was overlooked and was not completed. Concerning 8.22, the standard deviations are relatively high across the three elements, which could be due to a discrepancy in the digestion method, including the amount of sample weighed or the amount of acid used. However, the other results agree with each other. These samples were not chosen with any specific criteria, and silver is omitted from this table for a complete absence across all samples. The results from this method are in appendix 6.1.1 to 6.1.11.

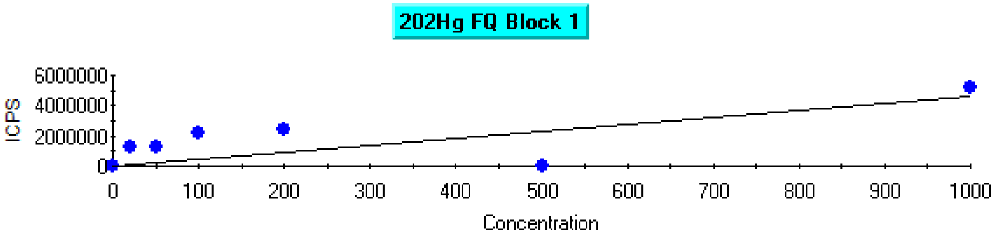
Microwave A is the Anton Paar’s Multiwave GO and microwave B is the Milestone’s ETHOS EZ digestion system.

Table 2. Results comparing prowess of the two microwaves (ref. appendix 6.1.1)

Grid Reference	Microwave A: Pb (ppm)	Microwave B: Pb (ppm)	Standard deviation (σ)	Microwave A: Cu (ppm)	Microwave B: Cu (ppm)	Standard deviation (σ)	Microwave A: Zn (ppm)	Microwave B: Zn (ppm)	Standard deviation (σ)
7.24	5.084	4.720	0.257	1.629	1.223	0.287	3.683	2.740	0.667
7.25	4.476	5.071	0.421	1.834	1.990	0.110	4.189	4.586	0.281
7.26	4.790	5.574	0.554	2.017	2.264	0.175	3.685	3.971	0.202
8.22	8.160	4.405	2.655	2.173	1.144	0.728	5.004	2.673	1.648
8.37	10.400	2.231	5.776	1.639	1.711	0.051	2.757	3.086	0.233
9.22	3.128	4.819	1.196	1.016	1.477	0.326	2.373	3.183	0.573
10.28	2.857	4.026	0.827	1.772	2.326	0.391	4.065	4.938	0.617
10.29	1.192	1.470	0.197	0.932	0.995	0.045	2.632	2.909	0.196
10.30	4.167	6.366	1.555	2.924	3.227	0.214	2.410	2.450	0.028
10.32	4.471	6.210	1.230	1.591	2.140	0.388	2.164	2.620	0.322

3.2.1 Mercury results and revision of methods

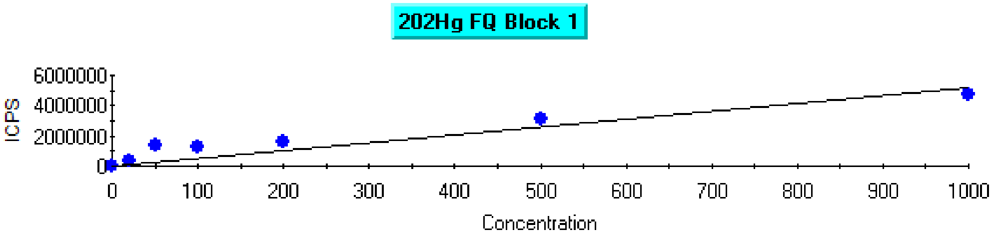
The results showed this method was sound for the analysis of Cu, Zn, Ag and Pb, however Hg seems to behave very differently. Re-runs and further batches indicated similar problems are occurring, specifically Hg was not detected as intended, both in the standards as well as the samples, as shown in fig. 14 – 16 (appendix 6.1.1 – 3).



Intercept CPS=154.667983 Intercept Conc=0.033861
Sensitivity=4567.786872 Correlation Coeff=0.684808

Label	Defined	Measured	Error	Mean CPS	% Error
blank	0.000	-0.000	0.000	154.67	0.00
20ppb	20.000	277.743	257.743	1268825.24	1288.71
50ppb	50.000	288.684	238.684	1318803.39	477.37
100ppb	100.000	470.001	370.001	2147020.38	370.00
200ppb	200.000	530.796	330.796	2424717.01	165.40
500ppb	500.000	-0.034	500.034	0.00	100.01
1ppm	1000.000	1129.769	129.769	5160696.63	12.98

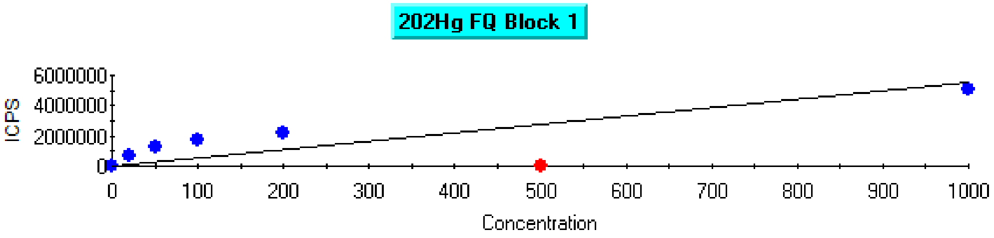
Figure 14. Calibration line of Hg for batch 7.24 - 13.27



Intercept CPS=494.680221 Intercept Conc=0.095313
Sensitivity=5190.039811 Correlation Coeff=0.964436

Label	Defined	Measured	Error	Mean CPS	% Error
blank	0.000	-0.000	0.000	494.68	0.00
20ppb	20.000	68.645	48.645	356764.62	243.22
50ppb	50.000	273.620	223.620	1420592.27	447.24
100ppb	100.000	252.539	152.539	1311183.57	152.54
200ppb	200.000	301.582	101.582	1565714.83	50.79
500ppb	500.000	601.209	101.209	3120792.39	20.24
1ppm	1000.000	901.671	98.329	4680205.50	9.83

Figure 15. Calibration line of Hg for batch 13.28 - 19.36



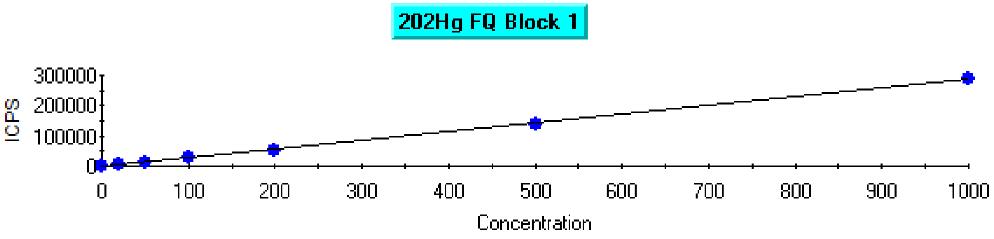
Intercept CPS=993.387638 Intercept Conc=0.180568
Sensitivity=5501.447120 Correlation Coeff=0.960787

Label	**Defined**	**Measured**	**Error**	**Mean CPS**	**% Error**
blank	0.000	-0.000	0.000	993.39	0.00
20ppb	20.000	120.059	100.059	661490.36	500.29
50ppb	50.000	226.264	176.264	1245770.25	352.53
100ppb	100.000	312.531	212.531	1720365.24	212.53
200ppb	200.000	396.180	196.180	2180559.20	98.09
500ppb	500.000	-0.181	500.181	0.00	100.04
1ppm	1000.000	928.696	71.304	5110167.93	7.13

Figure 16. Calibration line of Hg for batch 19.38 - 24.35

3.2.1.1 Revision 1: Au solution

With no success in changing parameters with the machine to remedy this error, a query to the manufacturers as well as their consultant was made. This resulted in some ICP-MS protocols being changed regarding specifically Hg in the standards. In order to stabilise the Hg ions, the modified protocol for analysing Hg was as follows: the previous setup remains the same, except 200ppb of Au solution was added to all samples, blanks, standards as well as wash solutions for the system. This method stabilised the Hg standard and the results can be seen in fig. 17 (appendix 6.1.11).



Intercept CPS=158.632521 Intercept Conc=0.552447
Sensitivity=287.145271 Correlation Coeff=0.999807

Label	**Defined**	**Measured**	**Error**	**Mean CPS**	**% Error**
blank	0.000	0.000	0.000	496.56	0.00
20ppb	20.000	17.278	2.722	5412.27	13.61
50ppb	50.000	44.669	5.331	13205.44	10.66
100ppb	100.000	88.542	11.458	25687.55	11.46
200ppb	200.000	193.363	6.637	55510.23	3.32
500ppb	500.000	487.141	12.859	139092.89	2.57
1ppm	1000.000	1009.224	9.224	287630.69	0.92

Figure 17. Calibration line of Hg with 200 ppb Au added

With further research, this method is in line with literature found, which details the chemistry behind this. It is theorised that Au (III) combines with all forms of Hg (elemental, organic and inorganic complexes) in solution as an 'amalgam' and keeps it stable in nitric acid [52].

This information came quite late into the project and the impracticality of re-running all previous samples was evident, therefore results from the previous method that showed an abundance of Hg were selected to be re-ran instead with the new method.

The results from this sparked another problem, as seen in fig. 18. This log graph shows carryover of Hg from the calibration standards into the blanks and subsequently the samples. This is especially evident in the mass-uncorrected counts in the blanks immediately after the calibration standards. This meant all data for Hg from the previous method (without the added Au solution) could be unreliable, as any detected Hg could be due to the carryover from the standards as opposed to from the digested samples. Upon further investigation, this phenomenon was also documented [52].

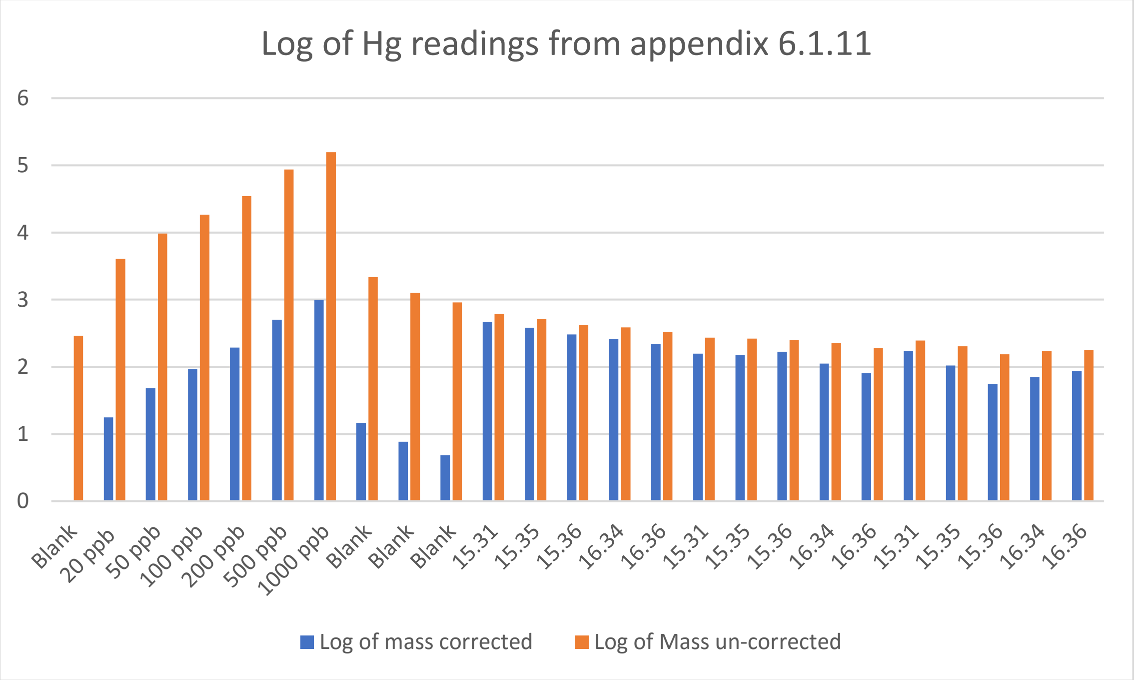
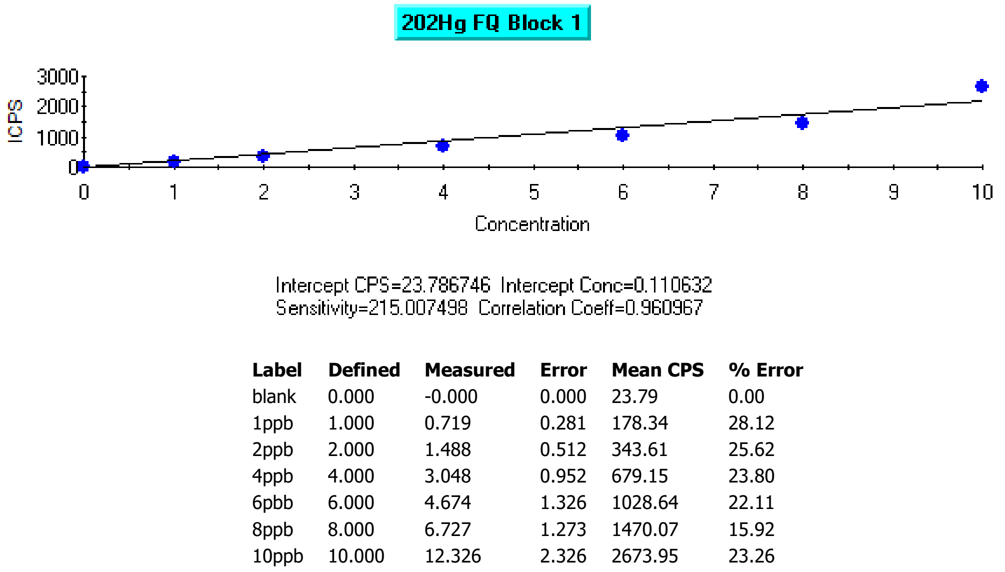


Figure 18. A log graph of the results from the run with "high Hg concentration" (appendix 6.1.11)

3.2.1.2 Revision 2: lower concentrations

This prompted another revision over the methods for analysing Hg, which dialled back the concentrations of the calibration standards as: 1ppb, 2ppb, 4ppb, 6ppb, 8ppb and 10 ppb. The result of this is shown in fig. 19 and table 3 (appendix 6.1.12).



Intercept CPS=23.786746 Intercept Conc=0.110632
Sensitivity=215.007498 Correlation Coeff=0.960967

Label	Defined	Measured	Error	Mean CPS	% Error
blank	0.000	-0.000	0.000	23.79	0.00
1ppb	1.000	0.719	0.281	178.34	28.12
2ppb	2.000	1.488	0.512	343.61	25.62
4ppb	4.000	3.048	0.952	679.15	23.80
6pbb	6.000	4.674	1.326	1028.64	22.11
8ppb	8.000	6.727	1.273	1470.07	15.92
10ppb	10.000	12.326	2.326	2673.95	23.26

Figure 19. Calibration line of Hg with new standard concentrations

Table 3. Table showing both mass uncorrected counts and concentration of new calibration standard and subsequent blank (appendix 6.1.12)

Sample	Hg uncorrected counts	SD (σ)	Hg concentration (ppb)	SD (σ)
Blank	24.0000	0.073	0	16
1ppb	166.668	0.073	0.719	14.048
2ppb	293.338	0.366	1.488	60.709
4ppb	573.351	0.254	3.048	34.022
6ppb	880.043	0.371	4.674	76.323
8ppb	1248.086	0.545	6.727	115.185
10ppb	1448.115	0.720	12.330	48.505
Blank	54.667	0.044	0.189	8.327

Both problems regarding the difficulty of analysing Hg (instability and carryover) had been remedied, however, each solution brought a new challenge along. Firstly, and quite obviously, the addition of 200ppb of Au solution into the entire ICP-MS system as well as each sample would mean the inability to analyse existing Au in the samples, which was a metal of concern to this project. Secondly, the reduced concentration of the calibration standards had introduced a degree of error in the accuracy of quantifying concentrations that were above the 10ppb standard i.e. the mass uncorrected counts of various elements of some samples exceeded the counts of the most concentrated standard. An example of this is 15.36’s Pb count is 48,212.856 and the 10ppb standard Pb count is 31,345.951 (appendix 6.1.12).

The solution to the first problem is equally apparent: to analyse for Au and Hg (along with the other elements present in the standards) separately, a good way in the context of this project would have been to run all the samples without studying Au to begin with, and only analyse samples which resulted with Hg being present with Au, as we are interested in potential fire-gilding. The solution to the second problem is also simple, though may not be as effective. One could increase the dilution factor, for this project, from 100 to 1000, this would ensure the elements’ counts would fall within the range outlined by the standards, however this introduces its own kind of risk, as any pipetting error regarding sample dilution is thus amplified ten times. Furthermore, this may reduce the concentration of the already low and volatile Hg, making it even harder to detect.

3.2.2 Further revision of methods: cooling and sensitivity

Another complication with the Hg analysis, and it involved the setting of the ICP-MS, namely the cooling function on the nebuliser of the machine, which, when turned on, increases the sensitivity of the ICP-MS. In between batch 5 and 6 (appendices 6.1.5 and 6.1.6 respectively), a change to the cooling setting was carried out without the author’s knowledge, hence a difference in sensitivity in the form of a decrease, though the results continued to appear as normal, this was overlooked until further batches. As a result, the batch containing the control soil ran with both cooling and without. It is assumed that the data are still comparable since the reduced sensitivity also affected the calibration standards of those batches, and the counts for all the data (sample and standards) should be lowered by the same factor where cooling was turned off.

3.3 General discussion of all results

From the results yielded and a visual representation presented, one can infer and identify the type of metalworking conducted in *Bremetenacum* after the end of Roman occupation. To start, the control soil was found to contain a trace amount of Cu and Pb (around 150ppb for both), and a slightly higher amount of Zn (877ppb), the negligible amount of Hg and silver indicate the lack of these elements in the area.

3.3.1 Copper

The levels of Cu around the forge area as well as the surrounding clay floor proves to be inconclusive. The levels across the analysed soils fluctuate tremendously and are all higher than the control sample. It is apparent that there is a more concentrated zone of Cu north of the forge (see fig. 9), which is indicative of cleaning out a hearth, similar to the Birdoswald smithy [20,23]. However, since the east of the excavated area also has high concentrations of Cu, this only coincides with the expectations of Roman uses of Cu, in the forms of bronze and brass, quite extensively and at times high purity Cu was produced [46,47]. It is known that Cu-containing objects and artefacts have been excavated and documented from the forts [13], both within its vicinity and in the extramural complex, these artefacts could have caused the few spikes in the data such as sample 36.35 (1215). Since the departure of Romans however, it remains unclear whether activities of working or repurposing Cu are found in this area as it is impossible to discern between works and use of this metal.

3.3.2 Zinc

Concerning Zn, the local geology already had a trace amount of Zn according to the control soil sample, still all the samples analysed showed a higher concentration than the geology of the area. There are no obvious patterns regarding the location of the forge. However, towards the east of the trench is where a higher concentration of Zn was detected. From this experiment, it is inconclusive to determine if Zn was worked in this forge, partially because the concentrations do not concur with the Cu (see disparity in patterns of concentrations between fig. 9 and 11), and Zn is not expected to be found outside of an alloy of brass [46,47,49]. It is however, strong evidence of an abundance of Zn-containing items used around this part of the fort, or, if not utilised, deposited via refuse from the occupants.

3.3.3 Silver

As for silver (Ag), only negligible amounts were found throughout the project, most samples showed amounts similar to that of the control soil, therefore no evidence regarding uses related to this metal was found around the fort, let alone works with silver.

Batch 11 (appendix 6.1.11) seems to have encountered an error in detecting silver, as a severe case of carryover has occurred, this could be due to the addition of the Au solution in an attempt to stabilise Hg. This incident raised the concentration of Ag in subsequent samples inaccurately and is particularly apparent in the blanks immediately following the 1ppm standard. This seemed to have remedied itself in batch 12 (appendix 6.1.12) when the concentrations of the calibration standards were lowered.

3.3.4 Gold and mercury

Au and Hg were of particular interest due to a previous ICP-OES survey run that hinted to their presence, if confirmed, the archaeological importance would be truly immense. However, after many revisions to the methodology, Hg was not detected, even in the charcoal spread area where it would most likely show up around the context of (1260) (appendix 6.1.12). An attempt was made to analyse other key areas with all revised methods: the six samples chosen were the three samples from the clay hearth; with three digested with the Multiwave Go system (10.28, 10.29, 11.28); and two digested with the ETHOS EZ system (10.28, 10.29). The control soil completes the set of six samples that were to be examined. Four runs in total were planned, two of the runs to analyse Au with and without cooling with a Au calibration range from 20ppb to 1000ppb (the same as most of the other runs). The other two runs were to analyse Hg using the final method devised, with a reduced calibration range (1ppb to 10ppb) and the addition of 200ppb of Au solution to stabilise Hg in the standards and the samples. Unfortunately, several ICP-MS hardware problems were encountered, and no data was collected.

3.3.5 Lead

Finally, and the last of the elements that were analysed successfully, Pb. The concentrations of Pb at the excavated area around the forge show significantly higher amounts than that of the control soil, there are also several hotspots where concentrations of Pb were higher towards the east of the site, tapering off towards the edge of the excavated area (refer to fig. 13). Interestingly, the samples from the forge itself show a slightly lower amount of Pb than its surroundings, which is reminiscent of the finds at the Birdoswald *fabricae*. It was suggested previously by Wilmott and McDonnell that it is safe to assume the forge areas will be cleaned, no matter how temporary the forge itself is, with refuse and slags left around the immediate vicinity of the smithy [20,23]. This could be an example of such a scenario, and the lower amounts of Pb away from the hearth suggests something similar.

3.4 Metalworking clay hearth

With this information, the possibility that this hearth was used as a workshop smithy has increased and it was likely used as a temporary *fabrica*, specifically with works surrounding the use of Pb and none of the other elements investigated. The similarities of characteristics between this site and the ones in Birdoswald cannot be overlooked: the location within the fort; the size and lack of intricacy of its foundation; the dating of the setup as well as the overall similarities between the two forts suggest these were used by occupants after the Roman retreat. More importantly, one of the metals used in the *Bremetenacum* hearth is now identified as Pb.

4 CONCLUSION AND FUTURE WORKS

4.1 Metalworking in the clay hearth of *Brementenacum*

As mentioned, the clay hearth was most likely a smithy used to work Pb after the abandonment of the fort's previous owners. With the province discarded, and supplies no longer arriving on British shores, it is logical for those who remained behind to have had to repurpose and reuse metals that were left within the fort. As Pb was a soft metal that was easy to work with, it was widely used by Romans and other Europeans alike [46,47]. The basic forge and potential small-scale workshop could suggest a less seasoned smith was working with these manageable materials, the purposes of the crafts are left unknown, with a variety of possibilities to pick from, be they pipes, containers or cookware. It is unwise to conclude the purpose of this hearth as definitely not a domestic hearth, as future excavation evidence could contradict finds from this work, and perhaps other explanations could come to light which change how the functions of the hearth are viewed.

4.2 'Post-Roman' activities

The shift in opinions regarding how rapidly Roman settlements were deserted towards the start of the fifth century is apparent [1,2,16,18], this work however, unless contradicted in the future, sheds light on more widespread 'post-Roman' activities across Roman settlements than previously imagined, and offers an explanation as to how those who remained in these towns coped with the discontinuation of Roman supplies. It is likely other small-scale activities by residents who did not immediately abandon this fort would have been conducted, and future excavations could unearth more evidence consolidating this idea of a more concrete post-Roman period.

4.3 Future works

This project has devised strong methods for the analysis of anthropogenic metals in soil samples associated with metalworking in Roman Britain using ICP-MS, especially with regards to Cu, Zn and Pb. The revised method to analyse Hg appears to have promising potential, which could prove to be an asset in archaeologists' range of chemical analytical techniques given rigorous testing. It would be of particular interest to re-analyse the samples with a Sn standard and observe the relationship of distribution of Sn to Cu, which could shed light on if bronze was made or repurposed. If the methods employed are tested further and remain successful, they could be applied to other similar sites, namely with the samples previously excavated at Birdoswald. Since the nature of those workshops were never identified, it could provide further insight into life in post-Roman Britain within Roman settlements.

With regards to *Brementenacum*, it is an ongoing archaeological site, and if further hearths are located, this method could aid in the identification of metalworking activities once again, and the protocols could be refined and streamlined as necessary.

The samples that were dried and ground are still in safe keeping of the university, naturally these could be utilised to validate methods employed in this thesis, and other experimental methods could be employed in order to determine the extent that the results agree with each other. Newer instrumental advances such as LA-ICP-MS could be one such method, and if the resulting data agree, could cut down initial sample preparation time in future investigations.

Concerning the method itself, not only does it require validation and reliability checks with repeated ICP-MS runs, it could be developed further with additional elements in the standards depending on compatibility based on the elements involved. Other changes can occur regarding the digestion method, though results were yielded in this project, other compounds may be needed to be liberated from silica complexes and require total digestion, utilising hydrofluoric acid [36]. Further, the drying process can be changed to freeze-drying, employed with extraction as an alternative to digestion in order to minimise losses of very volatile compounds, as seen in Jagtap and Maher & Frena *et al.*'s studies [53,54].

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