# Lowering Levels of Heritage Crime via Novel Chemical Procedures

A Doctoral Thesis

By

Richard Wilson

Supervisors:

Dr Paul Kelly

Dr Louise Grove

Dr Mark Monaghan

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

Department of Chemistry

Loughborough University

Loughborough

Leicestershire

LE11 3TU

## Acknowledgements

There are many people to thank for their help both professionally and personally over the last 4 years. Firstly, to my supervisors Dr Paul Kelly and Dr Louise Grove, your support and input has been invaluable throughout, and I will be eternally grateful for the opportunity you gave me. I would also like to thank Dr Mark Monaghan for stepping into the breach in my final year, and taking such an interest in the work that was being done.

I would also like to take the opportunity to thank Pauline King for putting up with me in lab for 3 years. The lab itself was a great place to work for 3 years, so thank you to Beth and Lloyd for being great friends throughout and making it all so enjoyable, inorganic truly is winorganic.

Thanks must also go to Mark Harrison at Historic England, Rob King for both his help at Foster and Freeman, and for his weekly anecdotes, as well as everyone who completed the survey.

This PhD would have been impossible without a weekly pub quiz to keep my mind active, so thanks must also go to Matthew Healey and Moira Lane for their key contributions to this.

Away from the department I have offloaded stresses and worries on many people, and each of those deserve thanks, so a big ‘cheers’ to all the boi’s, Cram, Lynch, Jon, Sam, Forster, Danny, Goo, Gracey, Greg, Tog Dog, and Carl, you are all chicken legends.

Emma, thank you for listening to me stress and worry so much, you are an absolute star.

Finally, and most importantly, I have to thank my Mum, Dad, and Emily. More than anyone else, you have supported me emotionally (and financially!) through what have been tough times on occasion and I would never have got this far without you. For the 1am phone calls, the dog adoption, the transport to Mansfield games, and a million other things, I thank you from the bottom of my heart. You will never quite understand what your support has meant.

To everyone above, and anyone I may have forgotten, thank you again!

# Contents

## Abstract

The work reported here focused on developing innovative ways of addressing heritage crime, and by doing so, protecting and preserving the historical assets found nationwide. The interdisciplinary focus, linking chemistry and criminology was imperative, and this connection is a novel way in which the issue of heritage crime can be addressed.

A survey was completed noting the key issues faced, and helped develop and report an understanding of the general attitudes towards heritage sites across the country. The results obtained here facilitated the chemistry research from this point, channelling the investigations in the appropriate pathway, as well as justifying the work done from that point onwards.

A large focus during the course of the research was that of metal theft. With this in mind, there were subsequent attempts to develop a novel and non-invasive technique, which could help lower levels of such crime at heritage sites. Early work concentrated on detecting trace levels of metals commonly found at heritage sites such as copper and lead, and their interaction with the surface of the skin. The metals were shown to form characteristically coloured complexes when reacting with components of the skin itself, thus confirming an individuals recent contact with the relevant metal.

This work progressed further via analysis of the metal itself post contact with a human finger. Again, remaining non-invasive was imperative, and a technique focusing on the development of fingerprints from the surface of copper and its alloys, via utilization of gelatine lifters, was studied extensively. Optimizing this technique via a study on the effects of the environment a piece of metal was stored in prior to development via rubeanic acid solution further developed the understanding of this method. Desiccation and the resultant reduction in humidity proved to be effective in enhancing the quality of fingerprint produced. This also had potential impact outside of the heritage crime focus, with fingerprint development from surfaces such as bullet casings being a particularly noteworthy example.

Studies relating to why a change in environment enhanced the quality of fingerprint developed were conducted, with several fingermark constituents being shown to react with rubeanate solution.

Because of high theft levels highlighted within the survey, efforts were made to produce information regarding stone samples found in a range of different environments. Laser induced breakdown spectroscopy (LIBS) was used as a method of non-invasively analysing loose material from several gravestones removed via the gelatine lifters. As well as producing information unique to each piece of stone analysed, this also highlighted a novel use of the analytical equipment itself.

# Chapter 1 – Introduction

## 1.1 Heritage sites

A heritage site is defined as a place of physical or cultural significance. There are 1073 World Heritage Sites designated by UNESCO, and thousands more with different classifications[1]. In 2015, around 40 million people over the age of 16 viewed heritage sites according to Heritage Counts[2], underlining significant interest in cultural and historical tourism. This also provides impetus for the clear need to protect sites of cultural and historical significance for current and future generations. Aside from World Heritage Sites the other classifications that a site can include are[3]:

- Listed Buildings
- Scheduled Monuments
- Scheduled Parks and Gardens
- Conservation Areas
- Protected Marine Wreck Sites
- Registered Battlefields

Specific pieces of legislation and conditions relate to the different sites and consequently there are various kinds of criminality associated with each. Listed buildings are commonly victims of metal theft[4] (as shown in fig 1), due to the large amounts of metal that can be found on site, whilst scheduled monuments and parks and gardens suffer from illicit metal detecting and anti-social behaviour[5]. Each can affect the public's enjoyment of heritage sites, and increased crime levels could theoretically reduce number of visitors at these historic locations[6]. Different laws protect all these and with that, the branch of crime most affecting them can vary.

**Figure 1 – A church roof which has been a victim of lead theft**[7]

Listed buildings are graded based on their age and historic value. Those that are graded I or II* (the most precious grades) are also those which are most frequently targeted by criminals[5]. As noted above, metal theft in particular is a large scale problem at listed buildings. This can be metal which is used both practically and therefore less specific to a site's cultural importance, or that housed with historic significance. The latter is where the research to be outlined here aims to focus, by developing some method of detection, which can help lower the increasing levels of such crime. It is clear that even our most valuable assets are vulnerable to crime, with prevention of paramount importance.

## 1.2 Heritage crime

Heritage crime is defined as '*any offence which harms the value of heritage assets and their settings to this and future generations*[5][8].' This is a broad definition however, and when considering this form of crime on a more international scale can be condensed into more specific branches. Much of the focus here has been on art theft and the illegal trade of archaeological objects[8]. Issues like looting and global trafficking of items are more problematic abroad than within England, and so will not be the focus of as much attention to those that can provide definitions of heritage crime like Historic England. It is important to note these issues in a global context however, to fully appreciate the scale of the problems facing heritage assets and efforts to protect them. It is hoped that potential methods of tackling heritage crime on a national scale, can also have an influence on protecting international assets. The attempts to protect stone discussed later in this report a notable example of this. Upon reviewing the evidence, it is easy to see why heritage assets are the victim of such offences. A small amount of protection for a large amount of valuable material makes heritage sites an easy target for thieves. Coupling this with the difficulty in proving the provenance of a potentially stolen item further highlights the necessity in improving the current levels of protection and detection. This is not limited to opportunistic acts. More organised criminals commonly target heritage sites, most commonly churches within this country. This will generally involve a large group stealing a vast amount of copper or lead to sell on illegally. This group will have a much more in depth understanding of the scrap metal industry, and hence are generally difficult to trace as a result. It was hoped that the introduction of the Scrap Metal Dealers Act 2013 would deter such criminal acts, and there is evidence to suggests that this has indeed had a positive effect on the reduction of such crime[9]. This is by no means the end of the battle however, and it could be a case of a temporary decline whilst criminals adjust to new acts before the levels of metal theft rise again. Historic England have suggested that stolen metal could be sold abroad to bypass said act. On an international scale, the issue of heritage expands yet further. As was noted by Winter[10], in countries with political turmoil and military conflict, heritage assets are at grave risk of destruction. The destruction of cemeteries and mausolea are cited here, and there are other noteworthy examples of this being the case[11][12]. Whilst there are parallels and links between heritage crime within this country and abroad (such as stolen metal being sold abroad to avoid the restrictions set up via the Scrap Metal

Dealers Act), there are also problems surfacing abroad that are not as problematic within this country and the western world in general. One of the key reasons for this is the different levels of urbanization that has occurred elsewhere in the world. This process results in a fine line with regards to heritage assets. Whilst in most instances, the heritage of a country is celebrated and acts as a tourism tool, there are other occasions where it is criminally ignored and destroyed with the rise of urbanization[13].

A key reason for the increase in theft at places of heritage significance is the amount of precious metals and stones that are regularly found there. With increases in the price of metals[14] and gemstones[15] there is clearly going to be an increased desire for those that are criminally active to steal, and therefore sell, such materials. Gemstones in particular are a material that has increased in value in recent years and is now, according to some reaching new economic classes. The search for new areas where such valuable assets can be found has been likened to a *'gold rush*[15]*'.*

The reason such metals and gemstones are increasing in price is a result of several factors. The unpredictability of many currencies as well as a high demand for certain precious metals like gold[16] add up to the desirability which threatens the metals and stones and the sites which they are located in.

What sets heritage crime apart from other crimes, is that not only do the crimes affect people in the present, they also affect future generations whom can no longer enjoy the historic setting which such sites highlight, an attitude mirrored by Alder et al. *'A major aspect of the harm in terms of plunder of cultural heritage material consists of the loss to human knowledge about our past that results from the destruction of heritage sites*[17]*'*. Some commentators even go as far as saying '*the destruction of cultural heritage should be treated as a violation of human rights'*[18]. Nowhere is this clearer than with lead theft on church roofs. As well as being an immediate financial burden, these often requiring fundraisers to fix rain damage inside[19]. This goes further however, with regard to the damage caused to future generations. When replacing said metal is deemed too much of a financial burden, the decision is sometimes made to replace lead with other, less valuable metals, like steel[20]. In the short term this is no doubt beneficial, and even listed as an option by Historic England as a solution to lead being stolen[21]. Often, the damage perpetrated against these sites is time consuming and expensive to repair, if indeed restoration is at all possible. In the long term though, a historic feature has been forcibly altered in order to protect it against crime. This further reiterates how problematic crimes committed against these areas of cultural significance can be, and there necessity in being prevented[22]. Maintaining as much of a country's history as possible is very important. An example perhaps less obvious, but certainly worth noting is the contribution heritage sites make to the economy that comes with tourism which such sites attract. UNESCO estimate that the financial benefit of World Heritage Sites to the UK can be valued at £61.1 million per year. Historic England state that in England in 2014 alone, they received more visitors than museums, theatres, or sports events, and that heritage sites create and fund many jobs throughout the country[23]. This further emphasises the long term effects that can occur as a result of heritage crime, and highlights why such efforts are being made to protect these assets.

In 2015, English Heritage branched into separate groups, with English Heritage being entrusted with the role of looking after over 400 state-owned historic sites across the country, and Historic England becoming the regulatory arm of this group, whom appoint trustees to the board[24]. In 2009, the phrase 'heritage crime' was devised as a way of shining a spotlight on the damage that was being caused at the countries historic sites throughout the country. Steadily over time, its use has increased and it now seems to be widely accepted throughout the community involved in facing up to the problem, including the police, academics, volunteers, and owners of such assets. To progress even further it is important that use of the term progresses to more general use, and a key aspect of this will be the use of it in the media. This is another area showing promise and improvement, with well-known websites using it in their headline[25]. The terminology itself is relatively modern, not previously being separated into its own branch, merely being included as just 'crime' or as theft of cultural objects[22]. This is one area which has shown great improvement in recent years, and has resulted in increased public awareness, something of vital importance when tasked with protecting such important sites. However there are still potentially improvements to be made in this area, highlighting why projects like this are of such importance. One such example is the lack of any legislation specifically mentioning 'heritage crime'. Whilst being focused on, all of the specific crimes that occur on site come under a more general banner such as The Theft Act 1968 or The Criminal Damage Act 1971 which are both commonly utilized. There is other legislation also related to the prevention of what is now classified as heritage crime, most notably the Ancient Monuments and Archaeological Areas Act 1979, the Protection of Military Remains Act 1986, and the Planning (Listed Buildings and Conservation Areas) Act 1990. Having specific, heritage crime, legislation will be another key step in the efforts to raise awareness of and lower levels of heritage crime long term. This aim is noted in the Memorandum of Understanding (2011) drawn up between Historic England, the Police, and the Crown Prosecution Service[26].

The types of crime perpetrated against these settings can vary, and include theft of metal or architectural material, looting, smuggling and arson. What is common throughout though, is the resulting financial strain and destruction. The general attitude of police and academics towards heritage crime are slowly changing, with the introduction of action groups like ARCH (Alliance to Reduce Crime against Heritage) and a Memorandum of Understanding (2011), which is a general guide to aid understanding and co-operation between all parties involved in such circumstance. The Police, The Crown Prosecution Service, Historic England, and a growing number of local authorities have signed this. This has now advanced further on a global scale, with the first instances of heritage crime being classed as a war crime occurring[27]. This is a hugely important step as it highlights the wide reaching consequences which can, and do occur as a result of this form of crime.

Conversely, despite this progress, there is still room for improvement when it comes to the attitude of a large degree of the general population. It is very important to improve this as much as possible so there is a greater awareness of what constitutes a crime, and the long term effect it can have at heritage sites. The developments so far are significant in raising the profile of heritage crime. There is, however a great deal of work still required in order for the levels to be lowered sufficiently. The majority of the work done in order to reduce and prevent such crime, concentrates on deterrence rather than detection. This is particularly evident with crimes such as illicit metal detecting, where conversations with the offender themselves as well as those who detect legally has helped analyse the thought process of those who commit said violation[28]. Despite current efforts however, crime is always going to exist, and with it, the need for detection remains.

A survey commissioned by English Heritage in 2011 suggests that crimes against heritage sites are on the increase. The research done showed that in the year ending 2011 17.9% of those who own heritage assets recalled a crime occurring on site. The results also suggested that there are around 60,000 cases of criminal damage to heritage assets each year in England alone[5]. This work has been further emphasised by a survey completed at the start of this project which indicated that 50% of those questioned had experienced heritage crime at their most relevant site within the year ending 2013[29]. What this appears to suggest is that the national strategies that have been attempted thus far have achieved limited success. Whilst there have been some instances of current practices showing a degree of success (such as the Scrap Metals Dealers Act 2013), the problems still clearly exist and whilst they do there is still clearly the need for research like that outlined here, to exist.

The next question is what form of heritage crime is the most problematic. Both surveys and the consensus amongst those relevant, points towards metal theft as being clearly the greatest threat to heritage sites in this country. There are of course variations however between each type of heritage site. Listed buildings are especially prone to metal theft, probably due to the higher amounts of copper and lead found at such properties, metals that are very appealing to metal thieves due to their high selling price[30], because of both their practical and decorative function.

There are also examples of crime that whilst not specific to heritage sites, certainly do spoil the public's enjoyment when visiting these places. Ranging from graffiti and vandalism in general, to anti-social behaviour (12.3% of heritage sites being affected by this[5]), something which is especially problematic at scheduled monuments (perhaps because of a lack of awareness as to a monuments significance).

Crime is prevalent at all forms of heritage site. Registered Parks and Gardens for example, whilst perhaps not having the same amount of financially valuable material as listed buildings or scheduled monuments, do provide a setting for various other crimes to occur, be that illicit metal detecting, or vandalism and anti-social behaviour. It is thought that Registered Parks and Gardens are actually the heritage sites where ***most*** crime occurs, but the difficulties in obtaining data regarding such isolated sites means genuine statistics are hard to come by, a common complication facing those tasked with analysing heritage crime.

### 1.2.1 How are we tackling heritage crime?

The methods of lowering levels of heritage crime can be classified in two groups, prevention and detection. Prevention would include legislation currently in place to prosecute those committing such offences. Because of a steady increase in media attention towards heritage crime, coupled with the increasing levels of criminal activity occurring at such sites, new legislation such as the Scrap Metal Dealers Act (2013) has been enacted. This aims to raise the standards of trading across the scrap metal industry. Scrap metal dealers are required to identify traders selling metal to them, meaning in theory that the entire process has a higher level of professionalism and a reduced chance of undetected criminality. This is not the first law relating to the protection of heritage sites. As far back as 1979, the introduction of the Ancient Monuments and Archaeological Areas Act (1979) had a clear aim to lower levels of crime, and hence protect, our cultural assets for this and future generations. Section 42 of this Act had a focus on lowering the levels of illicit metal detection by restricting the use of a metal detector in a protected place without the consent of English Heritage. By maintaining a control over such procedures, the amount of material removed is both monitored and kept to a sensible level.

The act ensures that recovered items of cultural or physical significance are kept by those tasked with ensuring they can be displayed to the public rather than stolen and removed from the public's awareness.

A noteworthy feature regarding the legislation is the variety of sites in need of protection. Due to this contrast, there are laws affecting scheduled monuments like that noted above, which are not relevant to other heritage sites. As a result, other laws are required, and one such example was the introduction of Planning (listed building and conservation areas) Act 1990. This focuses on listed buildings, if the crime is to:

*Execute or cause to be executed the demolition of listed buildings or works to alter a listed building which affect its special interest, without building consent*[31].

The failure to comply with a condition attached to a listed building consent would result in a fine (not exceeding £20,000) or a maximum of 2 years in prison. There are laws like this that are very specific to tackling heritage crime, but there are also laws that are put in place to lower crime generally, but clearly have an effect on heritage crime. This is true of the Scrap Metal Dealer's Act 2013 lowering levels of metal theft, and is true of legislation such as the Anti-social Behaviour, Crime and Policing Act 2014. This seeks to introduce simpler, more effective powers to tackle anti-social behaviour that provide better protection for victims and communities. Anti-social behaviour is a clear problem at places of cultural significance geared towards the visiting public. Once it becomes too great a problem, visiting numbers fall and the potential for crime will increase. Reasons like this emphasise how important such legislative measures are in preventing such crime from occurring in the first place. Relevant laws being in place is just the first step towards ensuring sufficient protection of heritage settings throughout the country however. Perhaps one of the greatest issues facing such locations is the lack of public awareness of several sites actual historic and cultural significance, and with that a lack of understanding of how and why they need to be protected.

### 1.2.2 Action groups and programmes

One of the largest problems surrounding metal theft is the 'domino effect' that occurs when lead roofing is stolen and flooding is the result[32]. Highlighting why this is so harmful is of great importance to the police and Historic England in their efforts to reduce levels of metal theft. Promoting protection of heritage sites is done by a variety of means. One such practice is the development of such umbrella groups like ARCH (Alliance to Reduce Crime against Heritage) formed in 2011, whose sole focus is, through conferences and training events, to take forward initiatives to tackle heritage crime and galvanise local action[33]. Via such methods, the group provides a means of discussing priorities, sharing information regarding heritage crime, carrying out training, highlighting best practice, and making local contacts[33]. The importance of such groups is key in raising awareness of heritage crime, especially towards those who are in a position to help alleviate such concerns. Campaigning groups have a clear interest in reducing heritage crime, working in conjunction with police forces as well as academics and volunteers focused on the social effect of such offences. What has become clear from the work done by such bodies is the passion many people have in protecting heritage sites, something which forms the core of the efforts to safeguard them. Benefits of this are varied, one such example being the simple process of cooperation and support when dealing with crime, arguably resulting in an increased likelihood of crime being reported and dealt with in the correct manner. By having a clearer idea of who to contact and when, the knowledge of all involved will surely begin to increase, as experts in each field can pass on their knowledge more effectively. Also of great importance is the more clearly defined roles and responsibilities that the Memorandum of Understanding highlights[26]. This also makes it far clearer as to what constitutes a heritage crime, an area that has caused problems before, where ignorance has resulted in criminal offences occurring without the full ramifications being apparent to the perpetrator of the offence. This is most common with crimes like illegal metal detecting, in cases where the historical significance of a location is unknown to the individual on the site itself. This has resulted in better training for those tasked with lowering levels of heritage crime, and clearer sentencing guides for the Crown Prosecution Service to use when prosecuting those who commit such offences[6]. Both have resulted in improvements of recording data, and higher levels of knowledge being shared throughout the community. Over 100 member organisations signing up to ARCH within 2 years have highlighted the positive work done so far. This no doubt has the potential to be an effective force, as the collaborative efforts of a group have a much greater chance of success in lowering levels of such crime than each group working towards a separate goal[22].

Historic England , the public body that is tasked with looking after the historic environment of England, have a key role to play in ensuring that the sites under their banner are protected, and the formation of action groups, with which they are involved is clearly of great importance. In addition to this, drawing attention to those sites particularly under threat, and hence in more urgent need of protection, is an area which Historic England has been focusing on. The introduction of 'Heritage at Risk[34]' in 2008 aimed to identify those sites at most risk of neglect, or inappropriate development (a heritage crime itself), issues which commonly run parallel to the levels of crime present at a given site. By identifying these 'at risk' sites, the aim of the group is to reduce this number via well-managed protection. This list of 'at risk' sites is updated annually and includes the most grand heritage sites, and the simplest ones, as well as taking all forms of crime into account. Introducing this measurement has had early success, with a third of those sites classified as being at risk in 2010, now being removed from this list due to an improvement in their circumstance. 2016 also has fewer entries into the ‘at risk’ register than in 2015 suggesting improvement. However, the struggle to fund protective measures means there is still plenty of work left. Nevertheless, with the steps outlined above, and a steady increase in publications regarding this issue, there is reason to be optimistic, in terms of improving the protection of such important assets.

### 1.2.3 Media attention

Public awareness raised through the media plays a key role in raising the profile of heritage crime. This can often be done by drawing a positive, media attention, from the negative of the offence itself. This is especially apparent when the crime is committed against a place of emotional, as well as cultural and physical significance. Nowhere is this truer than with damage often committed against war memorials. As English Heritage point out, ‘*They stand at the heart of almost every community and it is estimated there are more than 100,000 throughout the towns of the UK*[35].’ This alone strongly suggests why war memorials seem to strike such a chord with the general public, and why, when crimes are committed against such places, it provokes a good deal of media attention[36][37][38]. It emphasises how much the public care about this issue, and tapping into this emotion, and desire to protect a country’s history is of vital importance. The issue of heritage crime gains further notoriety in the aftermath of the release of official statistics. An example of this includes the BBC article with the headline ‘metal theft in Sheffield rises by 72% over 5 years’[39]. Although this obviously stems from a piece of information that is merely highlighting metal theft in general, as opposed to theft of heritage metal, nonetheless it could be argued that its presence in the media could result in increased attention to any form of metal theft, including that at heritage sites.

With funding being one of the greatest obstacles facing the efforts to protect heritage sites, drawing attention to such issues through media attention (and protection groups like ARCH) is integral in lowering levels of crime. Increased media attention also has the potential to improve the situation at the heritage sites with the highest levels of crime. By increasing media attention shone on such issues, there is surely an increased chance of an upturn in the efforts of the local community in protecting these areas of significance.

However, this does not always happen, and as a result metal theft is continuing to happen. As will be seen in Chapter 2, a survey was conducted and revealed that copper and lead theft are of greatest concern to heritage professionals[29]. As a result, there will always be a clear need for the development of forensic techniques to detect those still committing offences in the face of such efforts. This is why the work being done here aiming to develop a novel detection method is of such importance, and the efforts made to work hand in hand with Historic England are necessary. The collaboration of innovative research and the primary group tasked with protecting heritage sites is an excellent step in the right direction in terms of tackling such levels of crime. Those who commit such offences are rarely deterred by the threat of the sentence as the reward of crime often outweighs the risk of jailtime. The type of individual committing such offences also suggests a decreased concern at jail time compared to the average individual[40]. They are instead dissuaded from committing a crime by the threat of detection. This project aimed to offer a significant improvement in the current techniques available to those tasked with catching those committing heritage crimes. Whilst noting that improved forms of detection offer a valid way of attempting to reduce crime, it was believed that this project could contribute to the efforts in place to lower levels of this type of offence.

### 1.3 General metal theft

Based on the existing evidence, there is little doubt that metal theft is clearly the most widely reported issue facing our heritage sites across the country[22][29][41]. Whilst offences like anti-social behaviour are also common, the direct effects that metal theft has on an asset in use may suggest an increased level of awareness of when a crime has been committed, and an increased likelihood of reporting the criminal act.

The extent of this problem was emphasised by recent results published by the Association of British Insurers which state that as of 2012, each week there are over 1000 metal theft cases, and, relating to the issue of heritage crime[42]. It also states that each week approximately 23 churches are attacked by metal thieves, an issue, which can cause a 'domino effect' resulting in several other financially and culturally destructive scenarios. Churches are particularly threatened with regard to metal theft[43]. The presence of lead roofing, as well as often housing decorative items, identifies churches as 'easy targets' to thieves. Results published by the Church of England in 2011 further highlight this, stating an increase in claims of metal theft on insurance from 10 in 2003 to 1763 in 2010[44]. When metal is stolen from churches, the effects are often severe. Due to commonly being under insured, if at all, funds to replace the metal are difficult to come by, relying on worshipers to donate to replace stolen materials. Cheaper alternatives, for example stainless steel, are a possibility but can detract for the historical integrity of a site so are not often a favourable solution.

As with many materials, the levels of theft can often mirror a sudden increase in demand side-market fluctuations. There is evidence that this is also true with metals, specifically for the purpose of this work, copper and lead. Sidebottom et al discuss the positive correlation between copper prices and levels of copper theft[30]. As the price increases, so to do the financial gains in selling stolen metal. As a result a sudden increase in the demand for the metals could well result in spikes of this crime occuring. The demand for such metals far exceeds the supply, and hence the of the metal increases, and with that so will the temptation to commit the offences, and the frequency in which, the offences will be committed. It also makes the replacement of the metal stolen even more financially difficult for the victims of the crime, making the whole process a vicious cycle. The introduction of legislation such as the Scrap Metal Dealers Act (2013) aims to ensure that with the inevitable fluctuations in demand, the levels of crime remain as low as possible, but this is a difficult task, and so as many methods as possible to stop such crime are required. Figure 2 highlights the relationship between lead price and the amount of insurance claims over a four year period.

**Figure 2 - Graph comparing the trading price of metals with the levels of insurance claims**[45]

The survey discussed in chapter 2 highlighted copper and lead as the largest concern to heritage professionals. This was based on answers from a group of people relevant to heritage crime, with the survey sent online to approximately 200 heritage site managers and volunteers via email, and those relevant to this subject area. It included members of the Police Force, relevant academics, tenants, volunteers, and people working within Historic England itself, and yielded 76 responses. This suggest a clear knowledge of the issue which may not be as evident within the general public, however there is still the potential for slight bias, just based on the media attention that is more apparent with some issues than others, meaning metal theft may have been given precedence over other issues on occasion.

Another possible issue is that respondents only answered based on their one most relevant heritage site, rather than multiple ones. This means some materials, which are rarer, may not have been noted nearly as much as those found on nearly every heritage site, copper and lead being the two main examples. This perhaps means the results are not as dominant towards these two particular metals as the survey results suggest. Other evidence reported does may the case that copper and lead are the metals under greatest threat however, so this is likely not the case.

Primarily this will be because they both have both a practical as well as decorative function, with copper being used in piping, and lead in roofing, making these metals very accessible to potential thieves. Such a wide range of capabilities will also increase the value and demand for said metals. Other metals stolen include alloys of copper, particularly brass and bronze, which gives rise to potential methods of detection having a crossover with several metals at once. Obviously there are several other metals not mentioned that also contribute significantly to the high numbers of such metal theft, gold and silver being two examples.

The extent of metal theft in the years preceding 2013 acted as an impetus to the passing of the 2013 Scrap Metal Dealers Act. Within the first year this appeared to help drop levels of metal theft by a third (from 60,000 to 40,680 in 2013/2014)[46]. The improvements coming from the punishment of those trading without a license, giving thieves much less option of selling stolen goods.

There is evidence emerging however, that raises concerns that this immediate decrease has been followed by a sharp increase in levels of metal theft[47]. The reason behind this is not known for certain, but it could be displacement of the crime from one metal to another, or that initially, the theft of metal had simply shifted to another material all together (such as stone) before criminals adjusted to the new measures and resumed their theft of metals. This is a common criticism of situational crime prevention. Whilst efforts to lower crime are commendable, it often appears to be the case that crime will often displace, be that to another location, or as is the case with this research, pointing to another material[48]. This is especially true of the more organized criminal groups, which commonly target stealing metal in bulk. It is theorized that it takes time for criminals to adjust to new laws, so in the immediate aftermath of the introduction of new acts there is a drop, however after time they adjust, and with that, crime levels increase again, in a case of crime rates regressing to their mean[49][50]. In the case here, what appears to be the greatest reason for this is the shift from opportunistic theft, to more organised efforts to commit such offences. The police themselves and several media sources have indicated that the main problem of metal theft generally stems from organised crime groups[51], however others argue that these statistics are flawed and only a small percentage of such crime is committed by organised crime groups, with the majority coming from those with little/no previous conviction of metal theft[52]. There is debate that rather than 'solving' the problem, the introduction of the Scrap Metal Dealers Act merely 'suppressed' levels whilst criminals adapted to the introduction of this new legislation[47]. This could be via any range of techniques, and as of yet there is very little information regarding why such an increase has occurred, but some theories include selling stolen metal abroad where there are fewer restrictions to illicit sales, stemming from lighter regulation[53]. Another possibility is the limitations of the Scrap Metal Dealers Act 2013 itself, such as the lack of power to search for the police to use to their advantage in their attempts to find metal thieves. What is also notable is the economic factors that can have an affect. With cuts to police budgets[54], operationally, they will be more selective about the areas of particular concern and where their focus is[55]. With this, there could be concerns that the work done and the progress so far could be halted. Although metal theft is clearly an issue beyond that within a heritage context, it is without doubt relevant, and the largest scale form of crime being committed against areas of cultural and physical significance, the levels of which need to be lowered. Whilst such problems persist, there is clearly the market for novel forms of research into detecting and/or preventing those committing such crime. With this gap in both the knowledge base, and, in particular the practical aspect of policing heritage crime, comes the need for research to develop and progress this to the next level in terms of both awareness and techniques which are being designed specifically with the lowering of heritage crime levels in mind.

## 1.4 Stone theft

As a result of the high levels of metal theft, and the fact that it clearly appears to be the greatest threat to heritage sites, the issue of metal theft is fairly well known, especially in comparison to other forms of theft that can occur, particularly at heritage sites. However, there is increasing public awareness of other, less common issues. One of the prime reasons for this is the media attention that has focused on this threat[56][57][58]. Perhaps the best illustration of this is stone theft. Several articles have been published in well-known media outlets highlighting this issue and hence increasing the public awareness on what is possibly a surprising material to have such high levels of theft. A reasonable argument could be put forth that it is this lack of knowledge which increases the threat of stone theft, with certain acts of theft occurring in broad daylight[59] and the effects the theft going on to cost the sites in question thousands of pounds in replacement. This is money that is rarely readily available, and the arrival of such unwanted costs (the 19 slabs stolen in this case cost £2000 to replace) are what can cause long last damage to such historic sites. Recently, stones from the memorial site for the soldier Lee Rigby were stolen[60] and the resulting media attention was trending on Twitter and received attention on Facebook.

Whilst this specific case had so much attention because of the emotive nature of the site, it is important to note the lengths criminals will go to in order to get hold of these paving slabs. What is most worrying about such theft is the ease in which perpetrators are committing the crime, and the great difficulty there is in replacing certain stone when stolen. This is particularly problematic in listed buildings, where specific types of stone are required and like for like replacements are difficult to achieve or expensive.

**Figure 3 - Stone stolen from the Lee Rigby memorial in 2016**[61]

There is a belief amongst some that stone is being 'stolen to order.[62]' Couple this with the fact that stone is very easy to sell, both online and at markets, and it is very easy to see why levels of stone theft are high. On one side there is the simplicity of selling common stone in bulk, but there are also examples of rarer stones, commonly found at heritage sites, being able to fetch a reasonable price. With both common and rare options being available at heritage sites, and perhaps not as well guarded as other materials, it is easy to see why they are an attractive proposition for thieves. What is less clear however is why levels have risen recently, as, unlike in the case of metal theft, it did not stem from a rise in the cost of stone. It could simply be a case of criminals realising the potential selling value of an item that has never previously been looked at as valuable, as well as understanding how easy materials like this are to sell in the first place. There is also the chance that increased media attention regarding theft of stone has resulted in an increase in value of stolen stone and hence a greater level of theft. Another possibility is that the introduction of acts preventing the selling power of materials like metal could have resulted in a 'shift' of heritage crime towards materials that have much less protection, such as stone. Because of this increase in stone theft, there is a clear need for the current processes of linking an individual, to stone and brick, to be developed further. This is only added to when considering the issue from a wider perspective than heritage crime. Developing new methods of detection from the surface of brick and stone is of great interest within the forensic community with examples such as the London riots emphasising the necessity in expanding the current techniques of detection[63]. Where this does differ from heritage crime though, is that in this case, the only requirement would be to lift fingerprints from a brick surface. Whereas when the brick or stone is from a place of historical or cultural significance, the history of the stone dictates that any chemical contact would be as good as damaging it. As a result developing a method of detection that requires little to no chemical treatment or destruction of the material is vital. This is another example of why a project solely focusing on these materials from a heritage context is of great importance. They have unique requirements and circumstance, and with that comes the need for very specific aims and techniques.

### 1.4.1 Other materials

Whilst stone appears to be the most notable ‘new’ item of interest for those intent on stealing a country’s heritage, it is by no means the only material under threat aside from metal. The survey discussed in chapter 2 included several materials that, whilst not the most common, still require protection, but are not as well known, as in many instances they are grouped under one banner of ‘architectural materials’. These include paintings, fabrics, books, and alabaster. Items being damaged as well as stolen is also an area where the development of a detective measure would be of significant value. Such assets as tiles, fireplaces, and milestones[22] have been reported as being harmed at heritage sites, all of which would be hugely benefited from a suitable detective techniques.

### 1.4.2 Other branches of heritage crime

There are many examples of heritage crime that, whilst clearly problematic, perhaps are more of an issue to be looked at from a preventative standpoint as opposed to a detective one, which this research is most likely to focus on. Despite this, they are worth mentioning, just highlight further the extent of heritage crime. Many of these are crimes that whilst not specific to heritage crime, do commonly occur at heritage sites. It is also noteworthy how different forms of crime affect each different types of asset. Scheduled Monuments and Scheduled Parks and Gardens are particularly victims of anti-social behaviour, a type of crime including littering, drug abuse, or intimidating behaviour. A form of anti-social behaviour that could be looked at in a detective manner is graffiti, by analysing paint samples for example.

One of the greatest problems facing heritage assets on a global scale is the lack of specificity regarding the forms of offence heritage crime can take. This is especially clear with examples such as art crime. The broad term of 'art crime' is yet to fully go away, with 'art crime' still being used rather than being more specific depending on what form of crime this is. This is merely an umbrella term, which takes into account a range of different offences including theft, fraud, looting, and trafficking. One such example of this is the theft of the bronze Wenlock Jug[64] which can be classed as both 'art crime' and 'metal theft'.

As of 2013 theft of art and antiques was estimated at £300 million, second only to the illicit drug trade in terms of the most lucrative trades for organised crime in the UK[65]. This is an area that does have links with chemistry, with forensics being used to prove forgeries and increase cultural preservation[66]. This began as long ago as the late 19th century, with the analysis of pigments a clear example of chemistry being used to help prove the value of items, and in turn act as a taskforce to deter heritage crime, even before this term was first coined. Forensic evidence being used to prove the legitimacy of art occurred throughout the 20th century. One of the first such instances being in the 1920s when x-radiography proved a piece of art was not an actual Da Vinci, but instead a fake[66]. With the introduction of carbon dating in the 1940s, the links between art crime and chemistry grew as this method was another tool to prove the history of artwork[67]. Over the decades, this has now progressed to techniques such as micro Raman spectroscopy and X-ray fluorescence spectroscopy being used as a method of non-invasively analysing artwork. The development through the decades emphasises a constant need for improvement and new techniques to be developed for such work, with the introduction of non-invasive techniques highlighting a greater respect for the history of the item itself as well as the desire to prosecute criminals.

This lack of 'categorization' is perhaps another reason for previous difficulties in obtaining information regarding heritage crime. Until recent years, there was little differentiation between the types of crime occurring at heritage sites. Classifying each differing form of crime is important to understand what areas need to be tackled, and the gradual introduction of such procedures has enabled specific areas to receive the necessary focus, be that socially, or scientifically.

Two of the largest problems both arise from a lack of awareness and ignorance towards our heritage assets. These are unauthorised metal detecting and unauthorised alterations to those owning or living in listed buildings. Issues like this are those that are likely to be affected by the promotion of awareness targeted by ARCH, and increased media attention. There are arguments however that this media attention can actually have a negative impact by encouraging people to search for more materials[68]. The difficulty in keeping track of such crime is further highlighted in a report by Gill in 2010. He notes that some material is passing directly abroad, with individuals in metal detecting club even being accused of directing such goods abroad[69]. This echoes criticism of the Scrap Metal Dealers Act 2013, which has been accused of not preventing the movement of stolen metal abroad.

Whilst this project will not directly influence said issues, the attention such work can receive has the potential to have more far-reaching consequences.

What is indisputable is the wide range of assets that are in need of protection at heritage sites worldwide. There are clear examples of noteworthy work being done attempting to highlight this issue, and in turn lower the levels of crime effecting such historic locations. This thesis is another example of the novel work being completed which is addressing this particular issue. By linking chemistry and heritage crime, this unique and multidisciplinary project looked at the problem from a social science viewpoint, and then sought to address the relevant problems via research in a laboratory environment. The introduction of techniques discussed here, as well as the existence of such a project in the first place clearly highlights the progress that is occurring in this particular field, whilst also noting the necessity for improved tools to lower current levels of heritage crime.

## 1.5 Chemistry and heritage crime

Until now, there has been a notable lack of knowledge in terms of the link between chemistry and heritage crime, further highlighting the unique importance of such work. However, there are some offences occurring on heritage sites that have been analysed chemically, and are now being used at many such sites around the country.

Crimes like metal theft, which involve detection, as well as prevention, will clearly attract the attention of those in the scientific community. This is apparent by a considerable amount of research being completed, focusing on the very issue of metal theft[70][71][72]. One of the most well-known methods of tackling metal theft using chemistry, is forensic markers such as SmartWater[73]. This is a metal-based chemical that contains a forensic DNA code, that when applied to a surface maintains its intensity over time and can therefore be used to identify each unique metal surface. This is obviously of great use when identifying a thief, as if the metal is recovered, it can directly relate said person to the scene of the crime, and allow for the stolen metal to be placed back in its original home. The interest that Smartwater has garnered is clearly highlighted by the relationship which has been formed with the War Memorial Trust, which is now used to protect these Memorials countrywide[74]. These are important steps to make with regard to lowering the levels of crime committed against places of cultural or physical significance, but issues are still apparent, meaning alternatives must be looked at for when forensic taggants are unsuitable.

There are alternatives out there that are used on a lesser scale than SmartWater. These include simply imprinting an address on the metal, so when stolen it is easy to trace back to an original location[75] or a forensic grease which can mark both a piece of metal, and in turn a potential thief when contact is made[76]. Whilst all of these methods have merit, and are used at many sites throughout the country, there is still the need for improvement when it comes to pieces of metal that cannot be directly treated with chemicals, or be altered in any way, and to do so would harm the very value of the metal itself. Improvements are also required in terms of expense. Installing Smartwater can cost hundreds of pounds that is rarely available at heritage sites, and therefore a cheaper alternative is desirable. Therefore projects solely focusing on heritage crime have clear value and their importance is emphasised.

Metal theft is certainly an area of concern with regard to heritage crime, however it is by no means the only issue that is being focused on from a chemistry standpoint. Other materials are also stolen, and or damaged on heritage sites on an all too regular basis, and with this comes a need for new and novel methods of detection. Two of the most common materials are brick[77] and stone[58]. Based on the lack of protection such materials have when compared to metals with a higher perceived value, stone may be seen a surprising inclusion. However, there could be an argument made that the 'reputation' of stone as a material of less value means the efforts to protect it are behind those materials that have a higher historical rate of theft, like metals. It could also be argued that the introduction of the Scrap Metal Dealers Act 2013 has resulted in a 'shift' of this crime from metal to other materials like stone, as criminal adaptations are made. The survey in chapter 2, which was completed in 2014[29] also listed stone as a material recognised as under great threat, with it ranking as tied third most stolen material according to those asked (behind copper and lead). Feedback from Mark Harrison of Historic England has also backed up this belief that stone is a material under particular need of protection. As a result of this *'epidemic'* of stone theft that has occurred[57], there has been more focus on this area from a forensic viewpoint. As has been discussed by Davis et al, this also has worth beyond that of a heritage context when considering the riots in London for example and other such occasions where lifting fingerprints from brick, as well as historic stone would be desirable[63]. In comparison to many other surfaces, such as metal or plastics, there is very little information regarding the development of prints from bricks or stones. One of the earliest discussions was as recent as 1996 when Donche et al noted their efforts at developing latent prints from several different kinds of stones[78]. This was done with a degree of success using cyanoacrylate fuming, but less so with colloidal gold and physical developer. What is certainly worth noting however was the difficulties here that remain with regard to developing fingerprints from such surfaces. A highly porous nature, as well as a rough texture, make the surface very difficult to develop fingerprints from successfully.

As a result of this a method of detection that could be used to lower heritage crime, and also have a broader impact on crime levels in general regarding theft of stone, or any crime involving brick, would clearly be highly sought after.

### 1.5.1 Latent fingerprints

The research completed here has not only looked at the interactions between a person's hand and skin, but how they could be identified from this forensically. Fingerprints can be categorised into one of three types. Visual, plastic (indented), or latent[79]. Both visual and plastic/indented fingerprints can be analysed using the naked eye and suitable lighting. Visual fingerprints can be positive, where an image is formed by the contamination of another substance such as blood, or negative, where the impression of a fingermark is left in dust or soot. The non-invasive nature of being able to analyse means it is used whenever possible; however, it is rare that such fingerprints are left at the scene of a crime, instead being wiped away by the criminal. A more realistic situation and one that occurs commonly is the presence of latent fingerprints being left at the scene of a crime. A latent fingerprint is the most common form of evidence found, but these are often difficult to develop because of the wide variety of complex constituents present[80]. There are three sweat glands that make up the secretions of which these fingerprints are comprised. They are eccrine, sebaceous, and apocrine. Within these, are the inorganic and organic components that make up a fingerprint[81][82]. Apocrine glands are present on the groin, eccrine on the palms and soles of a person's feet, and sebaceous everywhere else. For this reason, eccrine and sebaceous material are the most commonly studied with regard to identification through fingermark analysis. Whilst sebaceous and apocrine glands are not present on the finger themselves, the regularity in which a person touches their face means that sebaceous material is usually present on a natural fingermark. When the skin touches a given surface, some of the material present in these fingerprints will be transferred, despite being 'invisible' to the naked eye. Developing an image of this latent fingermark, specific to each individual (with the exception of identical twins), is the focus of much study forensically.

| Source | Location | Inorganic Constituent | Organic Constituent |
|---|---|---|---|
| Eccrine Glands | Most of the body, but exclusive to palms of the hands and soles of the feet | Water (>98%)<br>Chloride<br>Metal ions ($Na^+$, $K^+$)<br>Sulfate<br>Phosphate | Amino acids<br>Proteins<br>Urea<br>Lactic acid<br>Sugars<br>Creatine<br>Choline |
| Apocrine Glands | Groin and armpits | Water (>98%)<br>Iron | Proteins<br>Carbohydrates<br>Sterols |
| Sebaceous Glands | Most of the body except on palms of hands and soles of feet. Highest concentration is on the forehead and back. | - | Glycerides (30-40%)<br>Fatty acids (15-25%)<br>Wax esters (20-25%)<br>Squalene (10-12%)<br>Sterol esters (2-3%)<br>Sterols (1-3%) |

**Table 1 - Main constituents of the secretions of the sweat glands**[82]

Many factors can have an impact on the quality of the latent fingerprint which can be developed, and hence alter the technique used to develop the prints. These can be separated into those, which are due to changes in the fingermark itself, based on variations in the fingermark components themselves, or the different surfaces on which it can be placed. The components of a fingermark can change as a result of several factors, including a person's metabolism, their diet, or the climate, all affecting how much sweat is produced[80] and hence its interactions with the surface it is placed on. The surface itself is also a deciding factor in this process.

### 1.5.2 Trace metal detection

When a person has direct contact with a metal there is inevitably going to be trace levels of that metal left in contact with the skin, glove or clothing. This has previously been looked into with analysing trace iron[83] as a result of its uses in firearm or knife attacks. As a result of its high use in such items, iron has received particular attention in comparison to other metals. However work on other metals, and the complexes they form when in contact with the skin has been studied. This has emphasised the potential of such methods being used to detect those whom have been in contact with stolen metal.

One of the earliest forms of trace metal detection was that of 0.2% 8-hydroxyquinoline solution in isopropanol, followed by viewing under UV light[84]. However the need for a UV light source, and the specialised photographic techniques[85] required mean that alternative approaches were desired. One such example was the use of 2-Nitroso-1-Napthol. This negated the need for a UV light source or special photographic equipment[86] and could work with several metals with no alteration to the reagent itself, giving a characteristic colour for each metal. Whilst this is obviously very helpful, given its potential for firearm use, as well as metal theft, there were still clear issues at this point. The most notable is the invasiveness of the procedure, involving spraying a person's hands with the chemical itself, something that, in a practical sense would be difficult to implement on a grander scale, especially with the colour changes that occur when the reagent is initially sprayed. However the work done here clearly has much potential, and the ability to 'map' the material held based on both shape and colour clearly would have great benefit to lowering levels of metal theft if it could be done non-invasively, something this project looked at in great detail.

One of the most commonly used methods of trace metal detection is that of triazines. Some of the earliest work done on this was by Thornton et al in the mid to late 1970s. The PDT reagent reacts with the ferrous ion to form a magenta coloured complex, hence proving contact with iron, and more specifically, a firearm[87]. Interestingly this reagent also reacts with copper and cobalt ions, but its high sensitivity to iron, meant that the ferrous ion was the subject of greater focus. This study then progressed to different triazine reagents in the years following, working towards being dissolved in alternative solvents with a degree of success[88]. Such trace metal detection techniques clearly have great use in proving contact with a firearm and have been used to prove a suicide based on the position that the firearm has been in contact with a deceased persons hand[89]. Olejniczak et al advanced the work done on this area. This aimed to analyse the application of triazines in the detection of iron traces after initial contact with stainless steel objects and of other metals left after interaction with nonferrous alloys and metals[90]. By doing so they aimed to discover which metal ions could form a chromatic complex with said triazines, and if a chromatic effect can actually be developed from the metal/materials being in direct contact with the skin. Their work concluded that triazines can create complexes with ions of iron, cobalt, copper, zinc, and nickel which can be *'released on contact with commonly used nonferrous alloys and metals*[90]*'*. From this, chromatic imprints can be developed from transfer from the skin for materials made of high-grade stainless steel, zinc, brass, and copper. Szumera et al also looked at the reaction of triazines with ferrous ions, and their potential to form coloured complexes[83]. This group looked at the development of new triazines, and their individual abilities at creating such complexes to show the presence of metal micro traces. What this group concluded was that the different triazines, perhaps as expected, perform differently when primed for the task of forming such coloured complexes.

Ferrozine is another triazine that has been used to detect trace levels of iron on the skin. Lee et al show that although ferrozine alone is not sufficient, when used in conjunction with a reducing agent like ascorbic acid, the detection of trace iron is greatly improved[91]. The reason for the reducing agent is to induce the formation of Fe(II) rather than Fe(III) due to the latter's lack of reaction with triazines. This is an important step for the reaction, as a result of Fe(III) being the main component in rust, and hence being present in many of the objects which this method aims to prove have been handled. For each of these, both the problems faced, and the variables seem to be similar. The fact that they are invasive procedures in general could be problematic, as has been noted by Lee et al *ˊA procedure is also outlined for transferring iron traces from hands onto filter paper for those persons who refuse to have their hands sprayed with chemicals like ferrozine whose toxicity is unknown'*[91]. The efforts here emphasise how important this is if a trace metal detection method is to be developed. The right to refuse chemical contact has the potential to derail possible successful procedures, so creating ways around such problems is vital. It is also useful for a method to work on certain materials as a result of the amount of crime that is committed whilst wearing gloves. If a method was only to work on skin, the flaws in the procedure, and the ways around a criminal being identified this way are increased. The variables in these methods seem to be reasonably consistent, and arguably, what would be expected for such a procedure. Szumera et al report that the concentration of iron traces left on skin/clothing is dependent on: *'Chemical properties of iron of which item is made, time of contact with an iron item, time elapsed after the contact, temperature, sweat presence on skin and clothing, sweat composition, washing of skin or clothing etc*[83]*.'* Similar to a more generalised fingerprinting method, the sweat composition seems to have an effect on what level of metal traces are left, or detected. It is thought this is a result of a reaction between the metal ions and the content of sweat present on the fingers of a given person. Olejniczak et al report similarities in what is required for microtraces to remain in a good concentration on the skin. They state the most crucial factors as being: *'The contact time with the object, the time elapsed between the contact with the object and the test, the grip strength, the moisture on the hand, the sweat composition, the temperature, the effect of washing the hands, and the chemical properties of the surface of the object material.'*[90] The similarities here are evident. Both of these methods mainly focus on trace levels of iron, due to its use in weapons like firearms and knives. It is noted by Lee et al that the presence of copper, zinc, lead, and various other metals can act as an 'interference' for the detection of iron levels that it is aimed for[91]. The fact that such metals are being detected in this manner shows that potential for research in this area is vast. As can be seen, a large amount of the current literature focuses on iron because of its use with firearms. However high levels of metal theft with copper and lead particularly under threat, suggest alternate methods focusing on metals other than iron is required, and that the current work being done on this can be improved upon. With trace metal detection techniques for copper, there is always the potential for such processes having equal use with regard to its alloys bronze and brass. The desire for such techniques to be suitably developed is understandable when considering the abundance of these metals found in sites that frequently house decorative items, but also in other circumstances, brass gun cartridges offering a prime example.

### 1.5.3 Interaction between fingermarks and metals

Metals are unlike many other non-porous substrates concerning their interaction with fingermarks. Materials such as plastics are chemically inert, and so have little to no impact on the development process. Some of the constituents of a mark, mainly the salts, often corrode metals and this chemical etching of the surface is of great importance when it comes to developing the print. Another important factor can be the formation of inorganic reaction products on the surface of the metal where a fingermark has been placed. These can hinder the development process if done so weeks after deposition[92]. The requirement to develop fingerprints from metals is of great importance, with said surfaces being used for ammunition, jewellery, coins, and much more. As has already been discussed, metal theft is of great concern not only to Historic England as a form of 'heritage crime' but also as a more widespread issue. With regard to ammunition, obtaining high quality fingerprints is important as this can be used as evidence at the scene of crimes such as homicide, so the challenges are widespread and the range of work in the area emphasises this.

The study of developing fingerprints from brass cartridges has also been extensive; however, there is certainly still room for improvement in this regard. The main issue is the heat that is generated when a gun is fired, the resulting 'blast' subjecting the cartridge to a great deal of heat and pressure, often destroying the cartridge case itself, as well as, importantly, the fingerprint[93]. Some of the earliest work on this issue was completed by Given in 1976 which investigated the effects of detonation on the ability of the cartridges to retain latent prints[94]. This again highlighted the negative effect that the heat and pressure generated can have on developing high quality prints, with the 'hot gaseous blowback' being referenced as the greatest effect of detonation, more so than time. More work analysing *why* cartridges are so difficult in successfully lifting fingerprints from has been completed more recently by Girelli et al, who showed that there are clearly other factors beyond the temperature and friction causing problems regarding development[95]. This group pointed towards three possible areas adding to the difficulties. Blowback of hot gases, expansion of the cartridge as a result in internal pressure, and the influence of propellant by-products brought by the blowback of gases. They also note that obtaining evidence from the cartridges is not only dependant on the technique, but also on several other factors based on how and where the fingerprint is placed initially. This is just one insight into why developing high quality fingerprints from such surfaces is so difficult, and as a result the subject of a great deal of research within this, and other projects.

Positive progress has been made however. Early signs of encouragement were obtained by Migron et al where, under laboratory conditions they were able to examine sebaceous fingerprints off of a range of fired cartridge cases[96]. Whilst there were clearly limitations with such work, such as the challenge of replicating laboratory conditions in a more practical environment, the difficulty of developing high quality fingerprints from such surfaces mean as much work as possible is required. The journal Forensic Science Chemistry and Industry, showed the potential of their technique which involved passing an electrical current through the cartridge, combined with a fine conducting powder. Here, fingerprints of reasonable detail can be developed, even up to 30 years after the original placing of the fingermark[97]. Whilst this progress is commendable and clearly shows excellent progress on what is a difficult subject area, there is still work to be done, and areas which can be improved. As is the case with many detective methods, the desire to find a technique that works well non-invasively is great. This is for a few reasons, but these differ depending on the circumstance. For most, it is simply a case of not destroying any evidence that can be analysed in other ways. This is particularly true of bullet casings for example. However, for items with cultural significance, like those that will be a victim of heritage crime, non-invasive detection procedures are paramount, as chemical treatment will hinder an items conservation and protection. There is also a lessened chance of contaminating evidence if investigations become non-invasive.

There is obviously also a necessity for the analysis of fingermark deposits on metals that are not used in bullet casings, for numerous reasons. These range from the aforementioned high levels of metal theft, to the fact that in situations where arson has occurred, metals are some of the only pieces of evidence left to analyse, and are often damaged. The range of metal found in such situations is vast and as a result, the scope for research in this area is wide. As has been noted, the two most commonly stolen metals are copper and lead, and this is reflected in a notable amount of the work in this area analysing the way fingermarks interact with said metals.

Much work has gone into the visualisation of latent fingerprints on metal, and a large portion of this has been done by taking advantage of the electrochemical interactions between these fingerprints and the metal surfaces. The method of doing so has ranged from using a Kelvin microprobe[98] to X-ray photoelectron spectroscopy, optical profiling[99] and localised changes to the electrical properties of the metal in question[100]. Both of which analyse the effect that the sweat present in fingerprints has on the metals in question, generally this is copper or brass due to their common usage in practical materials such as piping or cabling. Multiple factors seem to be behind why visualising fingerprints in this manner is possible, with the amount of copper oxide formed as a corrosion product seemingly key, and identifiable as a result of its characteristics as a p-type semiconductor[101]. Bond et al have also gone on to discuss the importance of zinc oxide in relation to copper oxide, with the results dependant on whether the charge ran through it is positive or negative[102]. This group have also shown how levels of sodium chloride found in eccrine sweat can corrode brass and hence be visualised[99] and these chloride ions present are vital in much of the visualisation methods currently used in such work. This appears to be because of these chloride ions accelerating the dezincification of brass, but more study would be required for this to be fully confirmed[102]. What is more certain however is the fact that variations in the components of sweat between different donors mean the corrosion process is different for each person. What this group also conclude is that the concentration of sodium chloride has a clear impact on the amount of corrosion, and this coupled with contact time has a notable effect on the amount of corrosion occurring at the place of contact[99]. More work is still required in the efforts towards fully understanding the electrochemical behaviour of a fingerprint, with the effect of other components within a fingermark deposit not yet fully understood, in both eccrine and sebaceous deposits.

The fingerprint visualisation manual identifies the techniques that are commonly used to develop fingermarks on a metal[92]. If at all possible remaining non-invasive is desirable, and so optical processes are preferred, such as fluorescence examination[103]. If this is possible, the evidence can be analysed further if necessary, or protected with regard to historic items and heritage crime. Such optical processes are also desirable as other techniques can be used following an initial attempt. The most highly recommended 'destructive' technique for developing fingerprints from metals is that of Vacuum Metal Deposition (VMD)[92] according to the Fingerprint Visualisation Manual[92]. This physical process uses vacuum coating to evaporate metals (usually gold/zinc or silver) and disperse them in a thin film onto the surface of materials. This then detects the fats in fingermark deposits on smooth surfaces. The differential growth that arises because of the disturbances in the physical and chemical nature of the surface due to a fingermark can be seen. This works well on surfaces that are smooth, and that have been subjected to high levels of heat, hence why it is so effective on metals. Powders can also be used *after* this should it not work. Whilst clearly being a useable technique for successful fingerprint development on the surface of metals, this method is not always applicable due to the thin film spread over said surface. In some circumstances, this method would not be suitable, and as a result developing novel methods that are non-destructive and non-invasive are of paramount importance.

### 1.5.4 Interaction between fingermarks and stone or brick

Stone is a material that has become progressively under threat in recent years. When coupling this information with the regularity with which brick or stone will be handled at a crime scene, the development of a successful fingermark detection technique from that material is becoming increasingly desirable. There has been a steady influx of work, which has focused on this issue, with only a reasonable degree of success, and there is still clear room for improvement concerning the successful development of fingerprints from such surfaces.

For some time, it was generally regarded that bricks or stone were a completely unsuitable material with regards to fingermark recovery. Despite this, there has since been development in this field which suggest this is not necessarily the case, and successful recovery is in fact possible. In 1996 Donche and Loyan[78] attempted to develop prints from a range of stones using cyanoacrylate, or colloidal gold and physical developer. Despite stones in certain conditions (generally dry and kept indoors) yielding a degree of success, it was generally concluded that stone was a particularly difficult material to develop fingerprints from, and there was still a large amount of work to complete on this topic.

Flynn et al[104] showed the spray reagent iodine-benzoflavone as having reasonable success when compared to the more commonly used practice of powdering. This yielded results with excellent detail even after 5 days of ageing had occurred. When compared to the lack of detail that is obtained with the powdering method, this highlighted a significant level of progression in terms of developing high quality fingerprints from these surfaces. Despite this, there are still clear issues surrounding the use of such reagents. Both significant cost and health and safety concerns would limit the use of such a technique to the most serious of cases.

What appears to be a consistent trend noted by those attempting to develop fingermarks from brick and stone, is, perhaps as should be expected, that both the type of stone, and the conditions they are kept in before analysis are vital in terms of potential success when attempting to develop. Hefetz et al[105] discuss the differing permeability of a range of stones, and how this must be considered before determining the most appropriate means of detection. What this group also note as imperative is attempting to develop a fingermark as soon after deposition as is possible. This is potentially a severe limitation as immediate analysis is not always possible. The development of fingermarks from rough, textured surfaces was again deemed impossible with the techniques used by this group. This has been a common issue when endeavouring to develop fingermarks from brick. There have been significant strides in recent years, with Hefetz et also work in 2015[105] noting how simple techniques can still yield identifiable fingerprints, and attributing the stall in this area to previous misconceptions about the field itself. Using black magnetic powder, high quality fingerprints could be developed in actual case studies. Davis et al[63] have also shown significant strides with their work using fluorescent fingerprint powder yielding positive results.

Despite evident improvements, there are still palpable improvements to be made in terms of detecting criminals from their contact with brick or stone, with all current methods being limited to stone and brick that are fairly smooth and in dry conditions.

### 1.5.5 Rubeanic acid

Developing fingerprints from surfaces is, in essence exploiting properties of the fingermark and the surface, in order to result in a change of this fingermark allowing it to be visualised. Three processes, optical, chemical, and physical, can do this. One such chemical process that has been looked at during the course of this research is using dithiooxamide, or as it is also known, rubeanic acid, to react with the constituents of a fingermark and the resulting reaction be visualised in the form of successful fingerprint development.

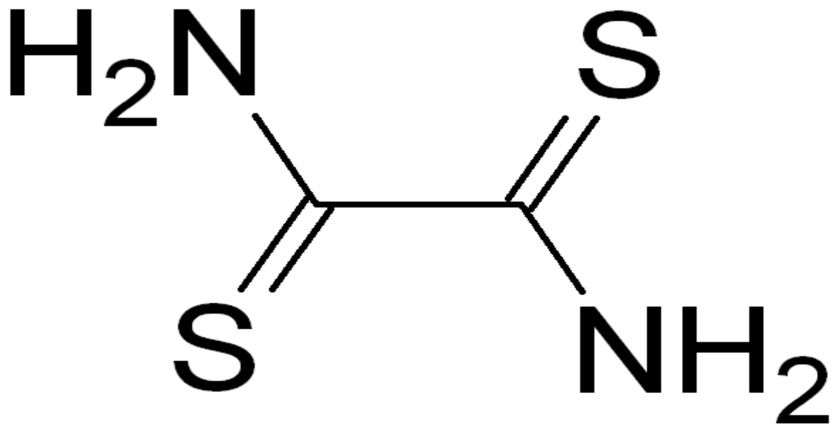
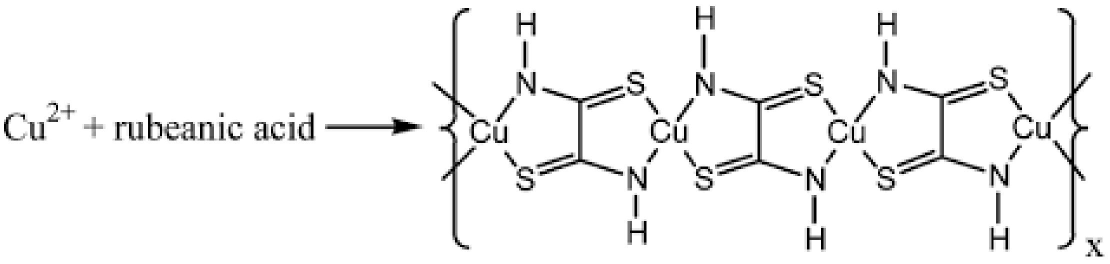


**Figure 4 – Rubeanic acid structure**

Rubeanic acid has not historically been used forensically, however has been used for detection. Specifically, this is for transition metals, due to its ability to polymerise readily with them, forming complexes with characteristic colours and insoluble reaction products[106].



**Scheme 1 – The reaction between copper and rubeanic acid forms the blue/black polymeric structure of copper rubeanate**

Rubeanic acid itself is prepared by passing dry cyanogen gas into an alcoholic solution of KSH in cold conditions. This solution is then acidified with hydrochloric acid, when rubeanic acid is precipitated in the form of a red/brown solid product. This sulphur analog of oxamide can act as a chelating agent to determine the presence of copper in trace levels. Its high sensitivity to copper has been taken advantage of in order to confirm the presence this metal, as a result of its abilities to do so even at traces as low as 1ppm[106].

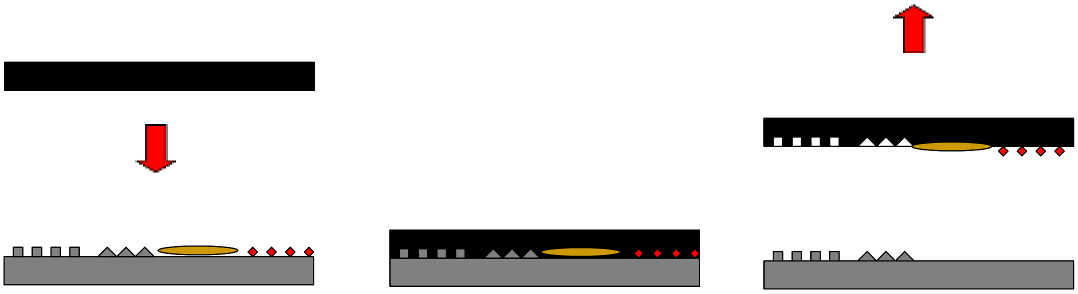
The first noted example of studying rubeanic acid was by Wohler in 1825 who commented on rubeanic acid observing that it precipitated copper, silver, mercury, and lead[107]. Although this was the first report discussing its abilities, its chemistry was not taken much further until 1926 by Ray and Ray, who showed that rubeanic acid could be used to actually detect the presence of copper, by using it in a spot test[108]. Although these were the first examples of rubeanic acid being used as a method of copper detection, the compound historically has a wide variety of uses that have been discussed by chemists. The compound can also be used to alert the presence of several other metal ions, including cobalt, nickel, and iron. Unlike copper however, additional reactants are needed in order to form a visible reaction product. Cobalt and nickel for example require the neutralisation with a small amount of ammonia or sodium acetate[109]. This group also report that the presence of each ion is made apparent by the different colouring of the precipitates, a black blue colour for copper rubeanate, a blue violet colour for nickel rubeanate and a reddish brown for cobalt rubeanate. For cobalt and copper rubeanate, the structure of the resulting complex seems fairly simple and well established, with the metallic atom forming the centre of a cyclic co-ordination complex. Nickel is also thought to complex this way, however some results suggest that it could also potentially be square planar, which would put the structure under a lot of strain, thus meaning it is relatively unstable[110], and could potentially break down to a different structure, more similar to that with copper over time[109]. This instability is also true of rubeanic acid and its reactions with several other metals, meaning the structure of the coloured reaction products formed is often difficult to confirm. Examples include palladium and gold. One area of work that has a great deal of potential is analysing the rubeanic acid derivatives to see if these could potentially form a stable complex with such ions. These have already shown positive characteristics, and could possibly be a new pathway for further work in this area[109].

As well as those already discussed, in 1939 Nilsson pointed out that when reacting with ferro-aquo ions rubeanic acid gave a blue colour.[111] Nilsson also points out that to get a dark precipitate, the rubeanic acid is better when in an alcoholic solution, something that is still commonly taken advantage of today (and within the course of this research). Another example of such was the work completed by Bhowal et al in 1974 where they proposed rubeanic acid as *'a sensitive reagent for the photometric determination of osmium(VIII) at pH 6-7.'*[112] In order for this reaction to proceed as desired the osmium was converted to osmium(VI) by using ethanol as the solvent for the reaction process. Alcohols appear to be the best solvent to use when dissolving rubeanic acid for use in such reactions; however more work could potentially be done to see if any other solvent could be used, due to the negative connotations of using such a flammable compound such as ethanol. Obviously, water would be ideal, however rubeanic acid is only partially soluble in this so would be unsuitable. Work could go into finding any other potential solvents for rubeanic acid use. As has been noted, rubeanic acids main use, and that it is most well-known for is the detection of copper. This ranges from detection when at trace levels in the environment, to trace levels in alloys of other metals. This was evident from the work completed by Willard et al in 1949 discussing the copper levels present in magnesium and magnesium alloys[113]. The advantages of using rubeanic acid as a method of detection in itself is noted, including the fact that it is *'rapid, accurate, and direct.'* Rubeanic acids abilities to detect very low amounts of copper, in magnesium and its alloys were proven using this method. Our understanding of rubeanic acids reactions with copper has now reached the point where the reaction itself is being taken advantage of, and the reaction product (copper rubeanate) being used. This is apparent by the work completed in 2008 by Kanaizuka et al, stating *'Can we make a crystalline material from components of a material that is amorphous and very difficult to crystallize? This question originates from our work on copper(II) rubeanate*[114]*'.* This work focuses on using the characteristics of copper rubeanate to construct crystalline surface coordination polymers, comprising of the copper rubeanate complex. This takes advantage of the fact that copper rubeanate is a *'high-proton conductor'* and could potentially be used to fabricate superconductors, fuel cells, or catalytic devices. Put together, this information all shows the historical significance of rubeanic acid, and how over time its uses have developed further and further, thus suggesting that much more work could still potentially be done in order to fully explore rubeanic acids future uses.

### 1.5.6 Gelatine lifters

At a crime scene, there are often marks, left from shoes, fingers, or other surfaces that need to be developed by a given technique. A common method used is to 'lift' these and analyse them on a different surface to what they were originally placed on. The method of lifting shoeprints for such lifters has been known for many years, and is very effective as a result of the low tack adhesive layer present on the gel. The original concept of gelatine lifting being used to recover fingerprints was discussed in 1913 for the lifting of marks powdered with lead acetate, before then treating with hydrogen sulphide. The lifting medium was a paper coated with a gelatine/glycerol mix[115]. By the 1970s this had progressed to using rubber based lifters, and they were commercially available, and hence their use in crime scene investigation could develop also. The basis of how the gels themselves work is highlighted by Wiesner et al, noting the need for adhesive forces which 'lift' the dust placed on a surface from a shoeprint[116]. This group comment that *'The efficiency of lifting dust shoeprints is derived directly from the adhesion of the dust to the lifting substrate.'* The appeal of the gel lifter as a method of lifting is the simplicity of its use. Simply placing it over the substrate that is being 'lifted' requires no training, and the expense is low, further strengthening its claims for usage. It is notable that as a result of the tackiness of the gel lifter, a great deal of material must be being lifted off whatever surface is required. As of yet, we know this can go as far as dust particles placed by shoeprints, but there is surely potential that other useful materials could be picked up by such a lifter, including the research completed during this project which suggests it can even reach a bacteriological level. There are issues with this however. One such example is the excess, unwanted materials that can be lifted as well as that which is desired. Some work has gone into tackling this, with work done by Shor et al suggesting that another adhesive tape can be used and placed over the gel to clean it of this unwanted material whilst maintaining the information that is desired, generally a finger or shoeprint[117]. This proved to be effective and enables longer storage of results obtained this way, without the worry of them being tarnished, as the fix appears to be simple and easy to complete.

Because of such studies, gelatine lifters are now marketed and used for lifting footwear marks, paint traces, blood traces, and recording patterns around bullet holes. The lifters themselves are available in black, white, and clear forms with each being used in different scenarios depending on the contrast desired. The practicality of the gels is highlighted in figure 5:



Surface with relief features, grease and loose particles (e.g. dust, fingerprint powder).

Apply gel lift and smooth down.

On removal of gel lift, loose particles/grease adhere to the surface and relief features leave indentions.

**Figure 5 – Schematic diagram to show how gelatine lifts can lift and reproduce surface features**[115]

There will be variables that are required to be analysed before this process can be fully understood however. It is already established that gel lifters can work in conditions that are not ideal for other lifting methods like electrostatic lifting, such as on a wet surface[116]. However in any instance where the actual placement of the material is done by hand, the variables increase, as does the potential for human error. One problem could be the attempts to ensure the gel is flat and picks up all detail, rather than air bubbles forming. This could possibly solved by using a fingerprint roller, but adds to the equipment needed on site, arguably taking away the positive benefits of such a method. The research completed thus far on gelatine lifters suggests a clear use in a forensic environment, and this has been taken advantage of to a reasonable degree. However early results in this project, coupled with the notable qualities of such a material could imply that its benefits could reach beyond that into other aspects of scientific detection. This is especially true within the work discussed here. Whilst the gelatine lifters do produce an extremely high level of adhesion, this does not cause anything that could be regarded as damaging. What is lifted is limited to dust and other debris in terms of visual evidence, and trace amounts of material invisible to the naked eye without chemical treatment of the gel. Materials which are inherent to the value of an item such as paint or other decorative features remain intact when treated with the gelatine lifters. This is why they have been such a valuable tool during the course of this work.

## 1.6 Analytical techniques

Throughout the course of this research, some analytical techniques have been used in order to gain a better understanding of what is forming in the reaction between lead and rubeanic acid, and to analyse small amounts of stone samples. This section briefly discusses the basic techniques involved in each of these processes.

### 1.6.1 Elemental microanalysis[118]

The sample that is analysed is placed in an aluminium capsule, and then injected into a high temperature furnace before being combusted in pure oxygen in static conditions. After this period of combustion, there is a further burst of oxygen to ensure all substances have undergone total combustion.

These products then pass through reagents to produce carbon dioxide, water, and nitrogen and nitrogen oxides from the elemental carbon, hydrogen, and nitrogen. This step also removes other interferences such as halogens. The gases are then passed over copper wiring to remove this excess oxygen and hence reduce the nitrogen oxides to elemental nitrogen. After this point, the gases enter a mixing chamber to ensure the mixture is as homogenous as possible, with a constant temperature and pressure.

This mixture passes through a set of high precision thermal conductivity detectors, which contain two thermal conductivity cells. Between the first pair is a water trap. The differing signal between these is proportional to the concentration of the water, which is dependent on the amount of hydrogen in the sample. Between the next pair is a carbon dioxide trap, which measures the amount of carbon in the sample. The nitrogen is measured against a helium reference.

The oxygen is finally measured as carbon dioxide, as well as by pyrolysis using the platinized carbon.

The data collected in this thesis was obtained from an Exeter Analytical CE-440 elemental analyser, with a combustion temperature of 97.5$^{o}$C and a reduction temperature of 620$^{o}$C.

### 1.6.2 X-Ray diffraction[119]

This is a tool for determining both the atomic and the molecular structure of a crystal. It is done by taking advantage of the crystalline atoms ability to cause a beam of X-rays to diffract in a range of directions dependant on the structure of the crystal itself. The angles and intensities of these diffracted beams can then be interpreted to produce a 3D picture of the electrons within these crystals. Once this picture of the electron density has been confirmed, and the mean positions of the atoms within the crystal determined, their chemical bonds can be as well (alongside as various other information). The most common form of identification process used here, is sample identification based on database matching. This involves matching experimental XRD data with those already stored in a digital library, thus allowing the structure of a crystalline material to be confirmed. However due to this, identifying novel compounds is more problematic as they are not present within this database. If this is the case it may be that XRD will be used in conjunction with another technique to identify a compound, such as elemental analysis, mass spectroscopy, or NMR.

Generally, powder XRD has been used to characterise solid state materials, particularly in cases where the material is insoluble and microporous. This is dependent on the materials ability to have a reasonable level of sample crystallinity, be that after grinding the crystals to a powder, or in their natural state. The sample preparation involved is very simple, the main cause of concern being ensuring the sample height is flat, and level with the top of the sample holder. Typically this is no less than 100mg. Another requirement is that the diffractometer is aligned such that the midpoint of the sample holder is the central point for the x-ray beam that will hit the sample.

### 1.6.3 Laser induced breakdown spectroscopy (LIBS)[120][121]

This is a type of atomic emission spectroscopy that uses a highly powered laser pulse as an excitation source. When this laser pulse impacts upon the surface of a given material, the irradiation at the point of contact leads to the ablation and hence removal of a small amount of material. As this happens a range of processes occur, including melting and intense evaporation. This evaporated material (plume) expands above the analyte surface and forms a plasma. The light emission of this plasma is what is analysed by LIBS. Because all elements emit light of certain characteristics when heated to such a level, theoretically any element can be analysed in this manner. As well as this benefit, because of the very small amounts destroyed by said process, it can essentially be classified as non-invasive, something of particular interest with the work completed during the course of this project. This is also beneficial in many other scenarios, as it can be used in conjunction with other techniques to gain a full picture of the analyte in question. Sample preparation is also simplified as the process can be used for an analyte in any state. Despite this there are limitations. A range of variables can cause problems with reproducibility as variations in laser spark, and the plume formed can affect results obtained via this technique. Also, whilst the process does work with each element, the detection limits of each vary.

### 1.6.4 Infra-red spectroscopy[122]

Infrared, or IR spectroscopy deals with the spectroscopy occurring in the infrared section of the electromagnetic spectrum. This technique takes advantage of the fact that molecules will absorb certain frequencies depending on their structure and functional group. These absorptions or resonant frequencies, will differ, depending on specific features of a compound, for example the mass of atoms, and the strength of the bonds these are connected to. The ways in which these compounds vibrate depends on their changes in dipole moments, and require more than one to be seen in the IR spectrum. Bonds that are more complex will have many different bonds, which vibrate in several different ways. As a result their IR spectra are complex.

Generally this technique will be used for fairly simple spectra where there are few IR active bonds in order to confirm the presence of a specific functional group.

### 1.6.5 Fingerprint grading system

In order for consistency throughout the course of this research with regard to each fingerprint analysed, a standard fingerprint grading system was used. This was the same system as that devised by the Home Office Scientific Development Branch (HOSDB), and is called the Bandey Scale.

| Grade | Comments |
|---|---|
| 0 | No Development |
| 1 | Signs of contact but < 1/3rd of mark continuous ridges |
| 2 | 1/3 - 2/3 of mark continuous ridges |
| 3 | > 2/3rd of mark continuous ridges, but not quite a perfect mark |
| 4 | Full development - whole mark clear with continuous ridges |

**Table 2 – Grading system used to determine quality of fingerprint ridge detail**[123]

What is most evident from this chapter is the range of problems that plague the protection of heritage sites nationwide. With this comes the need to improve the methods which are available to tackle this issue. Whilst, as outlined, there are numerous techniques which are used to detect criminals, it is also apparent that many of these are not suitable for the unique requirements that come with items of an historic nature. With this, it is without doubt that there a gap in the current detective measures which this research has addressed. To obtain more information regarding this gap, a survey was developed in order to garner more information, and further justify the work completed. This is discussed in the following chapter.

# Chapter 2 – Survey

For full survey results see Appendices.

## 2.1 Aims

The survey had a reasonably simple set of goals it set out to achieve. Metal theft was firmly expected to be reported as the greatest threat facing heritage sites, however confirmation of this would firmly justify research into this particular area. Additionally, broadening the research to incorporate other forms of heritage crime, necessitated the discovery of which other materials were deemed to be both under threat and difficult to protect. What the survey also hoped to achieve was obtaining vital information regarding both the location of materials that may be of interest, and of individuals who could be contacted for further information. Another key aim was the procurement of data which could be used alongside research, highlighting its importance. By having statistics discussing the exact amounts of crime at specific locations, this could clearly help support the statement that this research was imperative.

## 2.2 Results of the survey

To validate the importance of this strand of research, and ensure the work remains relevant to the aims of 'lowering levels of heritage crime' a survey was conducted from 24th January 2014 and ran until 19th February 2014 in order to establish the greatest threats facing heritage sites according to those who interact with them most. Generally these were contacted via email and were distributed to the following:

- Police
- Academics relevant to heritage protection efforts
- Volunteers at heritage sites
- Tenants in listed buildings
- People who own listed buildings
- Representatives of heritage sites
- People who work at heritage sites

These were largely sent to sites in England, Wales and Scotland. Despite heritage crime being a global problem, the efforts during the course of this project will generally focus on what is relevant on a nationwide scale. The ease of contact with potential respondents was also taken into account with this decision. The survey itself was distributed to 173 separate heritage sites countrywide, yielding 78 responses (45% response rate). The survey was sent to a variety of sites, ranging from large and well-known locations such as Warwick Castle, to small local churches. The majority of the responses were from smaller sites, which, whilst narrowing the information gleaned to those sites that will have limited security in general, it is also far more representative of the sites that will be relevant to the research conducted. Because of the sites which did respond, the survey will most certainly be a useful insight into levels of crime at heritage sites which are perhaps not as well known for their cultural significance. This also creates excellent localized data which whilst within a small data set, more than fits the requirements which were set for the needs of this research, merely aiming to obtain exploratory data and enable both the justification of work on metal and yield an insight as to what the primary problems facing small, at risk, heritage sites are. With an extremely large data set (over 1000), which would usually be the target of such a survey, analysing each individual answer would have been overly time consuming and unnecessary. Instead, by obtaining such localized data each answer can be analysed individually and links can therefore be made throughout.

There were various pieces of information that the survey sought to ascertain. Determining the nature of the threats to sites of historical significance was the primary goal here, but what was also imperative was investigating branches of crime that had perhaps not been reported as extensively as others such as metal theft. Determining if such a survey could help uncover any ‘lesser-known’ forms of criminal activity and research a method of detection for such a crime was a key intention.

The survey was targeted at groups and individuals interested in lowering levels of heritage crime. A further aim was to gain a better understanding from those who are practically trying to tackle the issue and seeing the problems first hand. It provided a springboard for further analysis. Indeed, some of the contacts generated proved invaluable. For instance, from the survey emerged discussions with *The Churches Conservation Trust* which helped gain an insight into how invasive a procedure was possible when attempting to analyse stone samples.

From a more practical viewpoint the survey was also beneficial in confirming the whereabouts of certain materials, should the research need to either a) ask for information about these materials, or b) request permission to use them within this research.

Prior to the survey going live, it was sent to three respondents who were aware of the work being completed. This test was done to confirm any errors were corrected and the survey was at the highest standard possible before being sent to a larger audience. Completing a small-scale test allowed a simple examination of the feasibility of the questions posed and ensured the results obtained were consistent and easy to understand. Once the results of this pilot study had been processed, and amendments made, the survey was rolled out to a larger audience allowing the full set of results to be processed. The use of a pilot study was an example of good practice outlined in literature[124]. Developing an understanding of good practice when developing a survey/questionnaire was imperative. The use of such literature, coupled with the pilot study, was invaluable in ensuring the survey was of a good standard. It was imperative to safeguard against use of leading questions and ensure the information of interest was obtained rather than a broad spectrum of information that could have been garnered my other means.

Once this pilot study had been completed and assessed, the survey went live using Bristol Online Surveys. Respondents were asked to answer questions based on the heritage site most relevant to them. This was generally the closest site, or the one they worked/volunteered/lived at. Some issues were highlighted during the analysis of the results obtained via this survey, one such example being that the questions did not necessarily relate to every site questioned, as it focused more on detection of crime (generally theft) as opposed to prevention of crime that is more of a social management issue. Despite this, the number who did complete this gave results that suggested the study was an accurate representation of the current levels of heritage crime across England. This conclusion was drawn as the results either confirmed information that we expected (as was the case with metal theft levels) or emphasised a point which Historic England themselves stated was problematic (stone theft). As has been noted earlier in this chapter, the aims of the survey meant a small sample set was suitable and actually enabled greater levels of in depth analysis as opposed to a more generalized sweeping set of data.

Prior to developing the survey, the firm expectation was that metal theft would be the ‘most common’ form of heritage crime, and hence it was important to probe for more information to ensure the course of the research was not dominated by this theme, and instead approached various forms of heritage crime. It was also vital to develop the questions asked over time, to safeguard against ‘leading’ questions, *i.e.* pushing a potential answer to or away from what was expected and prevent any bias in the results procured.

Working towards asking questions that gave unbiased, clear data was vital, and so several drafts of the survey were completed before the final version was made available to the public.

The questions asked were separated into three different sections, each asking a different form of question, with different aims within them. Section A was *‘The Background Section’.* Whilst this was partly a case of understanding who was answering the survey, and what their personal relevance to heritage crime, it could also help provide context for how respondents from differing backgrounds respond. For example the attitudes of a tenant living in a listed building could differ hugely from an owner, who would in theory have a greater concern regarding theft at that particular site.

This section asked about the background of each person completing the survey, or the organization they were representing. This included how they interacted with the historic environment, and what relevant organizations they were part of.

What the responses for this section showed was a huge amount of variation between those who responded to the survey. This was useful as it gave opinions between people interacting with heritage sites in a diverse way. As was discussed above, this is useful as it could help gain an insight into how those who interact with heritage sites in different ways respond. This will help minimize the possibility of bias by having an entire survey answered by one type of respondent. The police for example will answer that the greatest theft is the type of crime that is reported the most, whereas a tenant or owner may suggest forms of crime which, whilst problematic, are not reported to the police as often.

Of the individuals who answered ‘other’, the responses were hugely varied, but the main answers here were either students of heritage, police officers, or heritage advisors.

Of all those asked, only one person was not a member of any organization. This highlights that those who responded are generally interested in this area as opposed to members of the public with little to no understanding of heritage sites, and in turn heritage crime. Not only does this emphasise the need for protection of such sites, it also suggested that the respondents would have a good idea regarding the wellbeing of the heritage site in question, hence improving the quality of results obtained.

Section B posed questions based on heritage crime experiences that those answering the survey had been aware of at the heritage site relevant to them.

The first question in this section, and question 4 overall asked:

*Thinking about the heritage site you interact with most, was there any heritage crime at this site in the last 12 months?*

The aim of this question was merely to confirm that heritage crime was an issue, and the extent of this. It was clearly shown to be a problem worthy of research, as over 50% of those asked confirmed they had experienced it within the last year alone. This was before even accounting for longer periods of time, or a situation where a person was unaware of crime that had occurred (10.7% stating that they did not know if crime had occurred). What was perhaps of greater concern was the result suggesting that of the crimes that had been committed, 55% had been repeated, with one example citing 10+ criminal offences at the same site. Repeat victimization is particularly problematic at churches with lead theft being noted as especially prone to this[22]. The site which answered this also stated that theft of general metal was the most common form of crime they suffered, which backs this theory further. The reasons for this could also partially be explained with a quote from this survey respondent when asked if there are other problems worthy of discussion (question 12), who responded; *‘The insistence of the replacement of stolen lead, and other metal, with the same product. This in turn can be stolen once again’.* If the same materials are constantly being replaced with minimal improvements in security, something that is a common problem at heritage sites due to lack of funding, it is unsurprising that a criminal will repeat the offence where they have been successful beforehand. What these results do suggest, (with the majority of those areas suffering crime, doing so on multiple occasions) is that improvements in security measures are without doubt necessary. The likelihood is that those sites with better security are those suffering less crime. This falls in line with the work done elsewhere by Grove et al and Garrett et al who have discussed in length the issue of repeat victimization[125][126] with the former stating how the perception of known 'risk and reward' meaning a site can often be targeted on multiple occasions. Whilst it is not unexpected to see repeat victimization here, as it happens in all forms of crime, it does mean that if criminal activity can be stopped at a specific site suffering a great deal from this issue then it can disproportionally reduce the total amount of crime[125]. The question of protection was posed later in the survey. Another possibility is that those suffering less crime are the sites that are more publicly known to be culturally significant. As has been discussed beforehand the ignorance regarding the importance of certain sites is a large scale problem facing heritage assets, and improving this knowledge is key to raising awareness, and lowering these levels of crime long term. It is the hope that this research helps this process, and further reiterates the importance of this project.

Question 5 asked what form of crime was prevalent at the applicable heritage site. More detail on this answer was also requested by querying which form of crime transpired the most frequently, and which caused the most concern or damage (fig 6).

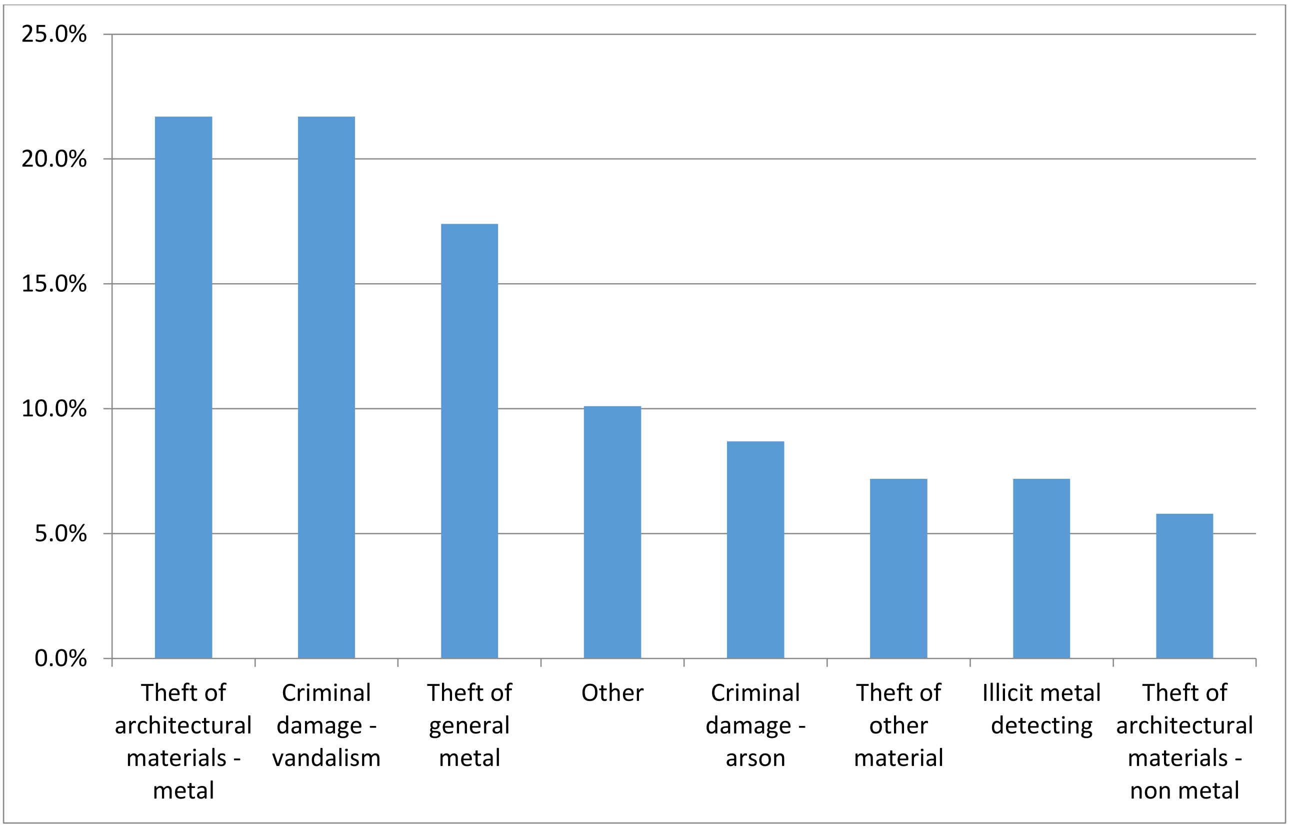


**Figure 6 - What type of crime(s) was experienced at this site?**

These questions were quite clearly an attempt at developing a clear picture heading forward as to what the main problems facing heritage sites was. The firm expectation was that some form of metal theft would be the most common form of offence, and this proved the case as can be seen in figure 6. The only other form of crime that occurred at a similar rate was criminal damage through vandalism. With regards to this research, this is difficult to tackle, and lowering levels is more of a social aim of prevention as opposed to detection. Arson also appeared a notable amount of times and as a result when developing a method of detection with regard to metal theft it was important to monitor the ability to detect when the sample was far from ‘perfect’. This will primarily be when washed, but could also be when heated to extreme temperatures as with an arson case. This could potentially be vital, as in a crime scene that has suffered an arson attack, materials like metal are some of the only surviving surfaces in which to analyse and detect the perpetrator. There are also additional benefits that this could have outside of a heritage crime arena, with the detection of high quality fingerprints from gun cartridges an area of great interest.

Of the 'other' category the responses included more specific answers that could really be placed in theft of non-metals, such as book theft. The most common answer in this section was unauthorised alterations. Similar to vandalism however, this is hard to tackle through chemical detection and is more of a social issue of prevention. Nonetheless, having such answers within the survey is fundamental to developing a full picture of heritage crime.

The follow up to this question asked what form of crime was the most frequent, and then went on to query what caused the **most** concern or damage.

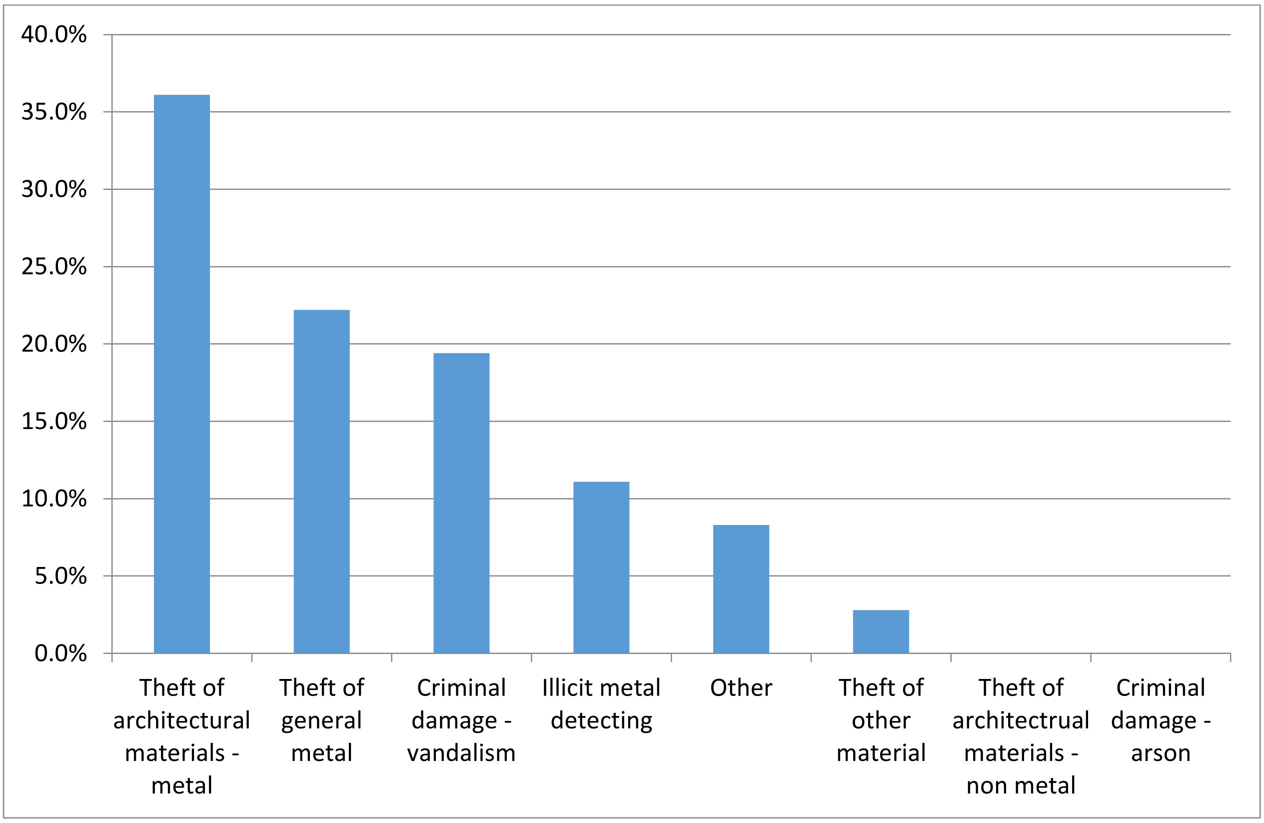


**Figure 7 - Which of these occur most frequently?**

As noted in fig 7, theft of architectural metal was the most concerning to those questioned, and theft of general metal was the next most common. This proves the great concern surrounding metal theft, and again highlights why this was the material of choice with regards to developing a method of detection. This justified much of the general thought process when the survey was originally proposed and confirmed the theory that metal theft was seen as the greatest threat conclusively. The only other offences that were happening more than theft of some form were vandalism and illicit metal detecting. However, the emphasis on improving detection methods for theft meant that vandalism and illicit metal detecting fell outside the scope of the present study, thus meaning theft, specifically metal theft, is the primary concern focus within this research. Illicit metal detecting is another branch of crime in which the detection of metal would be desirable, and is yet more evidence that targeting this was the best pathway to take in the early stages of this research. The following question emphasised this even further with the top 3 responses for 'which causes the most concern or damage' all relating to metals, be that theft or illicit detection, as can be seen in figure 8.

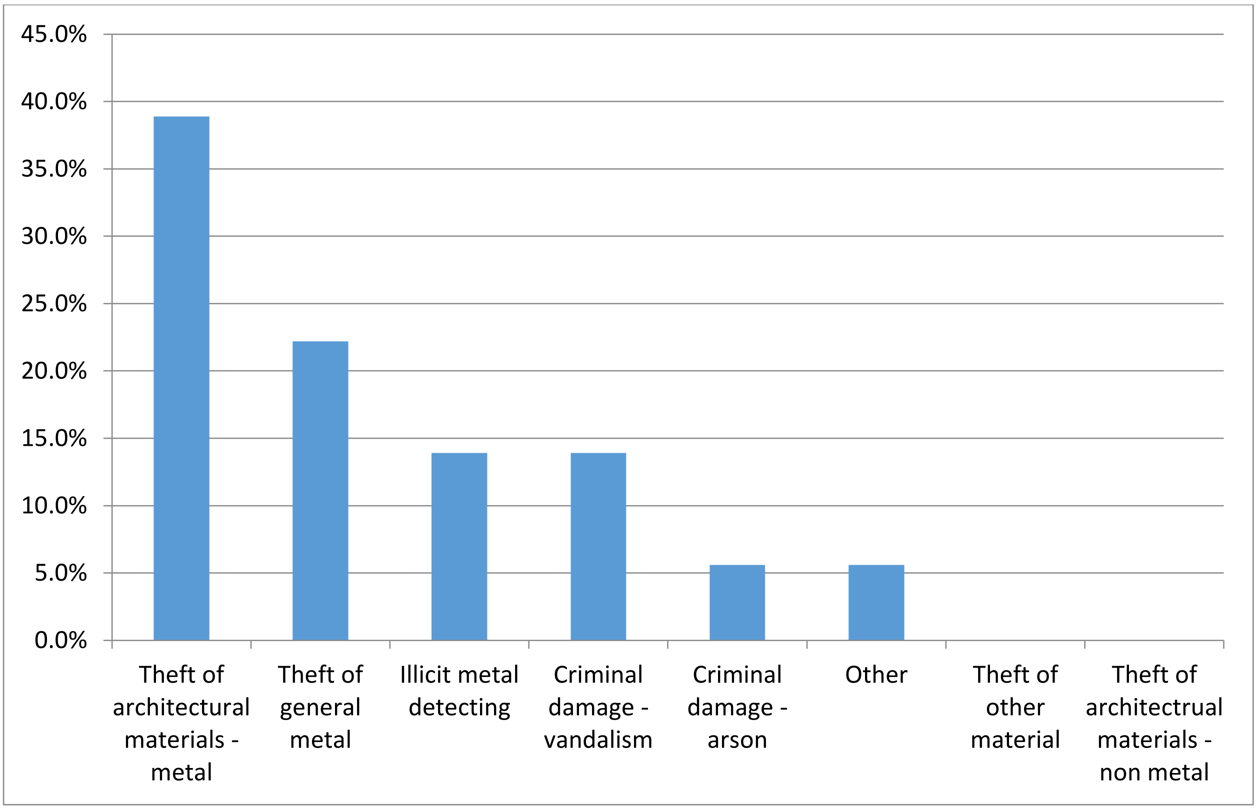


**Figure 8 - Which of these cause the most concern or damage?**

Question 6 was tasked with identifying who those asked thought were responsible for lowering the current levels of heritage crime (fig 9). This then probed further by querying who was the most responsible.

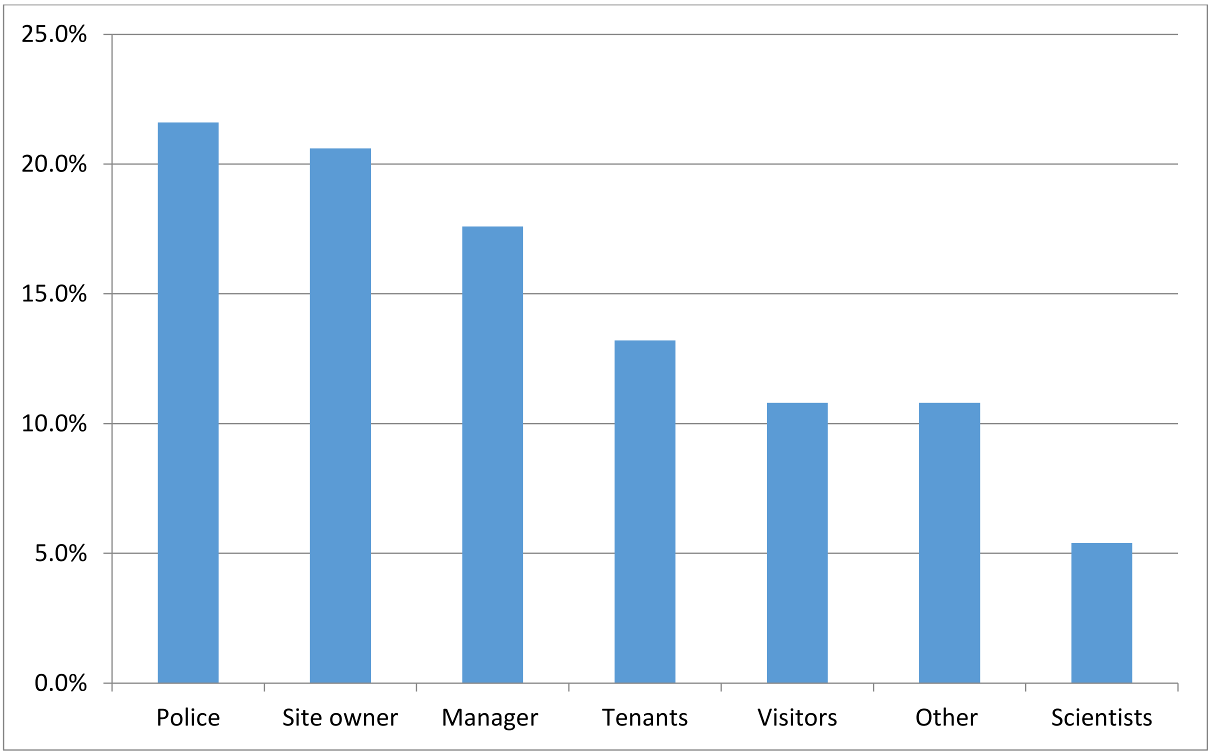


**Figure 9 - Of the following, who do you think should take responsibility for tackling heritage crime?**

By discovering who the community deemed most responsible for helping to tackle this form of crime, an idea could be gleaned as to where to the main responsibility lay, as well as perhaps noting possible areas of concern. For example if the police were the only group who were discussed here, then the idea of a 'community' helping to tackle heritage crime would seem a long way off. As it was however, the responses, whilst putting the police as the primary force tasked with lowering heritage crime, also included owners, managers, visitors, and the local authorities amongst others. The idea of communities and organisations linking together alongside police forces in order to tackle crime is not a new one. Over the past decade there appears to have been a great shift in crime prevention, with much being done to tackle crime in partnerships as opposed to single entities[125]. This desire for collaboration was clear from some responses who stated that they thought as many people as possible should be making a collaborative effort to lower levels of heritage crime, as opposed to each facing up to the task from a different standpoint, with different motives and aims. A small portion (5.4%) suggested that scientists should take responsibility. Whilst responsibility is not placed with scientists it is without doubt that they can have a role to play in developing clear methods of lowering this form of crime. This has become even more apparent as the connection between the police and scientific researchers has been consolidated under the evidence-based policing approach which is now commonly used.

Another example of this link is the scientists who helped develop forensic markers like SmartWater, a collaboration underlined by their partnership with the War Memorials Trust[74]. The small responsibility given to scientist here (5.4%) does perhaps accentuate a lack of understanding as to the potential work a scientist could bring, and the vast range of collaborative efforts that is possible here. These partnerships and collaborative efforts are vital in helping to tackle heritage crime long term, as those in the 'field' can discuss with scientists what is needed, something which this survey aimed to help this research do far more easily than would have been possible otherwise. The work together can also help in other ways. Scientists can discuss what is possible, and what research is currently being completed, allowing someone working 'in the field' to use this information as they see fit. It is without doubt a necessity for as many different groups to come together and collaborate to help lower levels of heritage crime, a sentiment that was echoed by this survey. One of the answer that was placed in the 'other' category stated the same *'I do not think it is possible for one group to take most responsibility. It needs to be a joint effort to be successful'.*

The following question (7) had two main focuses as to why it was posed. The first is simply a record for the research being conducted. So if a question needed to be asked regarding a certain material, there was a quick an easy way of knowing where that could be found. The second was establishing what materials were most common at heritage sites. For example, could this help explain why metal was stolen so much, if it was much more present than other materials?

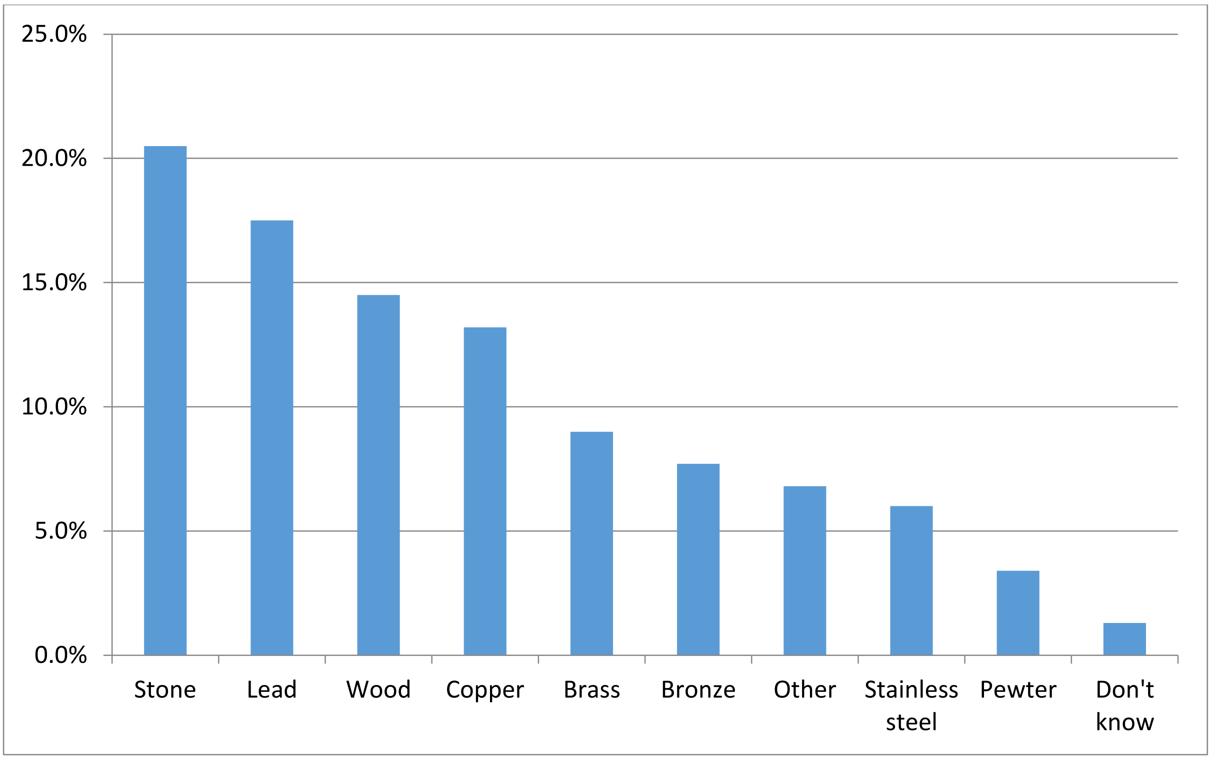


**Figure 10 - Which materials are present at the Heritage Site you interact with most? Please include materials which are inherent to the structure.**

Whilst copper and lead were found at many heritage sites (13.2% and 17.5% respectively) the most common was stone, found at 20.5% of sites. There could be an argument made, that this is the reason stone theft is increasing at such a concerning rate[127], and was ranked 3$^{rd}$ in this survey as the most 'at risk' materials. However, wood was present at 14.5% of sites and theft of this was ranked much lower in this survey regarding its 'at risk' status (fig 11), hence suggesting that there are other reasons behind the current trend of stone theft. These have already been discussed in Chapter 1, but the arguments could be that as metals become better protected with forensic markers, and the efforts of specific enforcement groups, materials like stone which are less protected become more threatened. There is also the possibility that a 'snowball effect' is occurring as potential thieves are becoming more aware of the value that stone can have when sold, whereas in the past this has been very much an untapped resource for a criminal. This also ties in with the earlier point regarding repeat victimization, originally put forward by Farrell et al[126] stating that once a site is recognised as having a ‘risk reward’ factor favouring a potential thief, there is an increased likelihood of theft.

What was also important within this survey was to note which materials were at risk of theft at a given heritage site. As has already been noted, metal theft was expected to be the form of crime that was most common. However it was important to both confirm this, and to investigate any other materials under threat that may have not been considered to the same extent. Which materials were deemed ‘at risk’ is outlined in fig 11. The follow up question then discussed which was the most under threat.

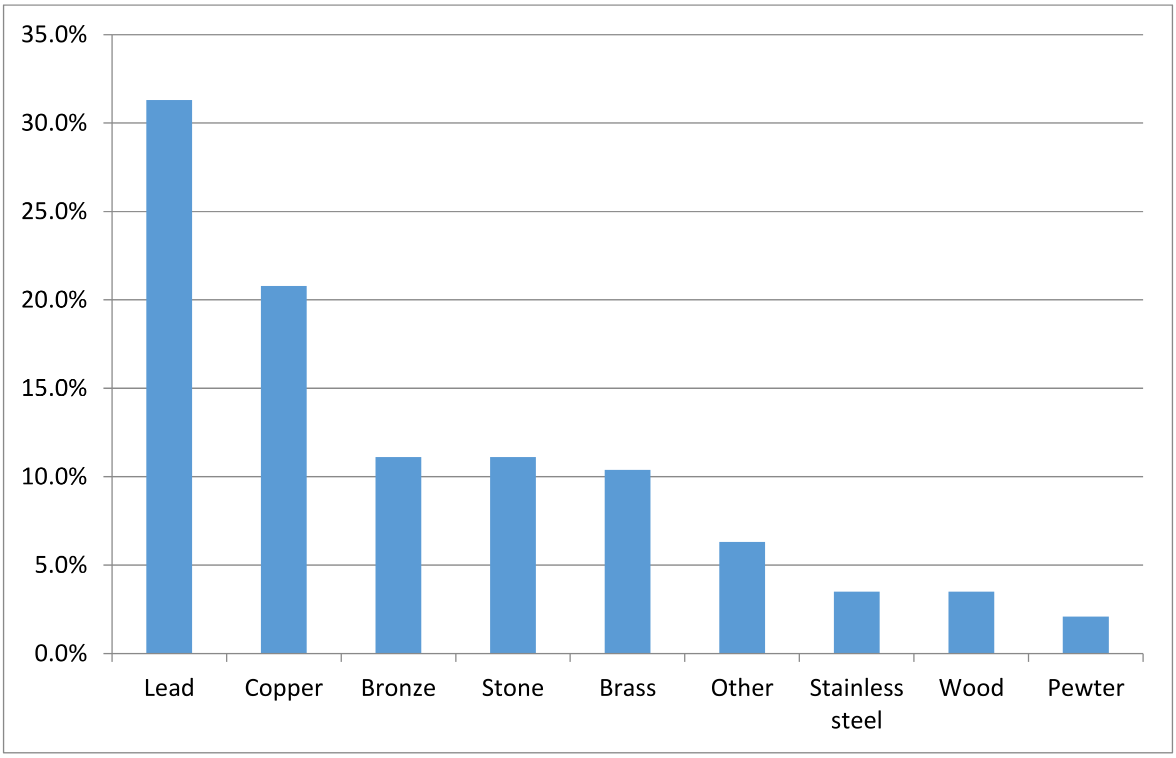


**Figure 11 - Of the following, which materials do you think are at risk of being stolen at the Heritage site you interact with most?**

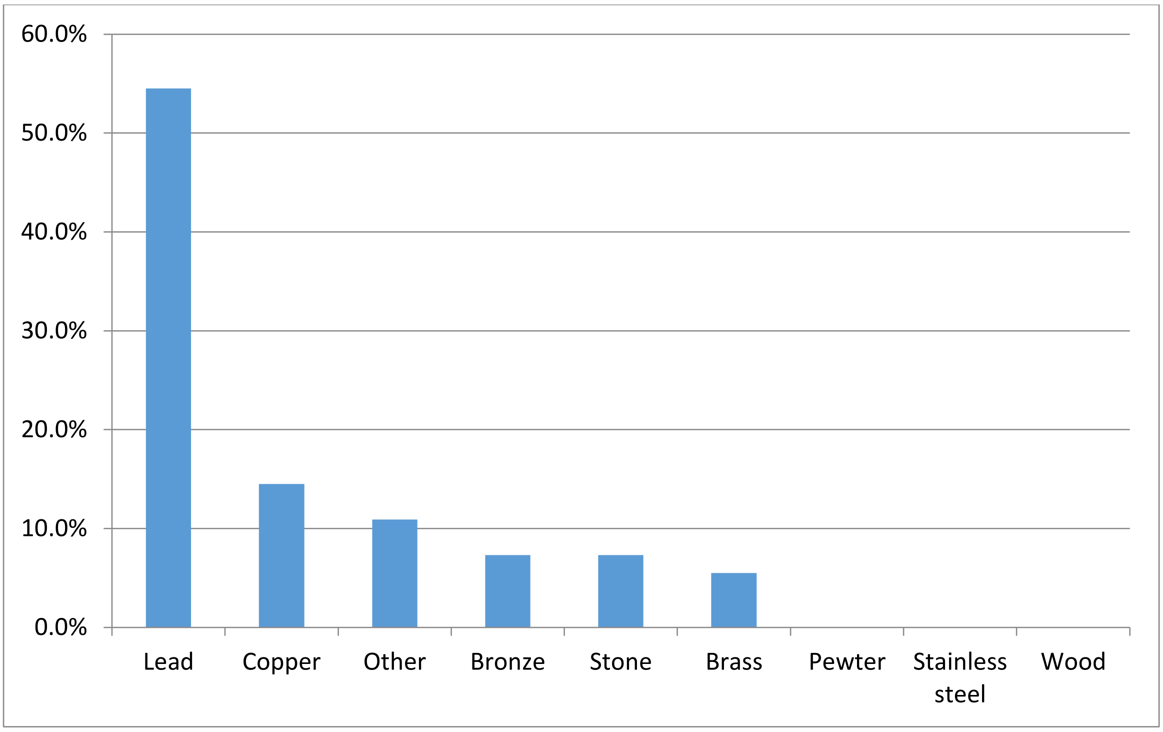


**Figure 12 - Which do you think is most at risk?**

What the results demonstrated in figure 12 show, is that, as expected, metal theft was undoubtedly the area of greatest concern. Lead in particular was seen as under threat with over half of those answering stating it as the material of greatest concern. Copper and its alloy bronze were next in the order of concern, which, as with lead is unsurprising and again fits in with what was expected at the beginning of the project. Both lead and copper have a practical function as well as decorative, so thieves will be both selling metal on for scrap, or as a piece of art. The information gathered here was not hugely surprising and justified the work being focused on finding a novel method of lowering metal theft as the most suitable way in keeping with the task of lowering heritage crime.

This survey was very interesting with regards to stone being the material that is classified as tied 3rd most at risk. Upon first inspection this was very surprising. Because of stones value being known less than that of copper, or lead for example, its presence in this survey was somewhat of a shock. However discussions with those at Historic England did not have this level of reaction and instead stated the theory of displacement already touched on. This is the belief that as stealing metal becomes more difficult, thieves will move onto another material, in this case stone. Preventing this diversification is most problematic and developing as many forms of tackling heritage crime as possible is of great importance if this is to be prevented in any way.  This survey concluded in 2014, and since then instances of stone theft have continued to occur[128].  Considering this, and the problems that are well known within the forensic community regarding developing fingerprints from the surface of bricks and stones[92] and it is easy to understand the decision to focus a significant amount of time during the course of this research on developing a novel method of detection of stone.

Aside from stone, almost every other material reported as under threat was a metal, alloys with copper present such as pewter, bronze, and brass all appeared on the survey, and hence a detective method for copper was deemed very important as there was the potential for several metals of interest to be included with one technique.

Another material mentioned briefly on this question included coins, which are generally made of one of the materials listed, so is another justification to focus on these particular metals.

Section C of the survey was entitled *'Lowering heritage crime levels'* and aimed at gaining a better understanding of the current techniques used by those tackling heritage crime, and the obstacles faced by those committing offences.

The first question in this section inquired about what security measures were currently present at a given heritage site.  The answers received here gave information about how much money was available at a given site, and how well protected they are.  This is very important, as it could perhaps give an insight into how well protected they are.  If the levels of this are extremely low, then it may explain why crime levels are so high.  The answers would help show if there were high levels of expensive security being used, or if it was simply a case of keeping metals that could be stolen out of sight.

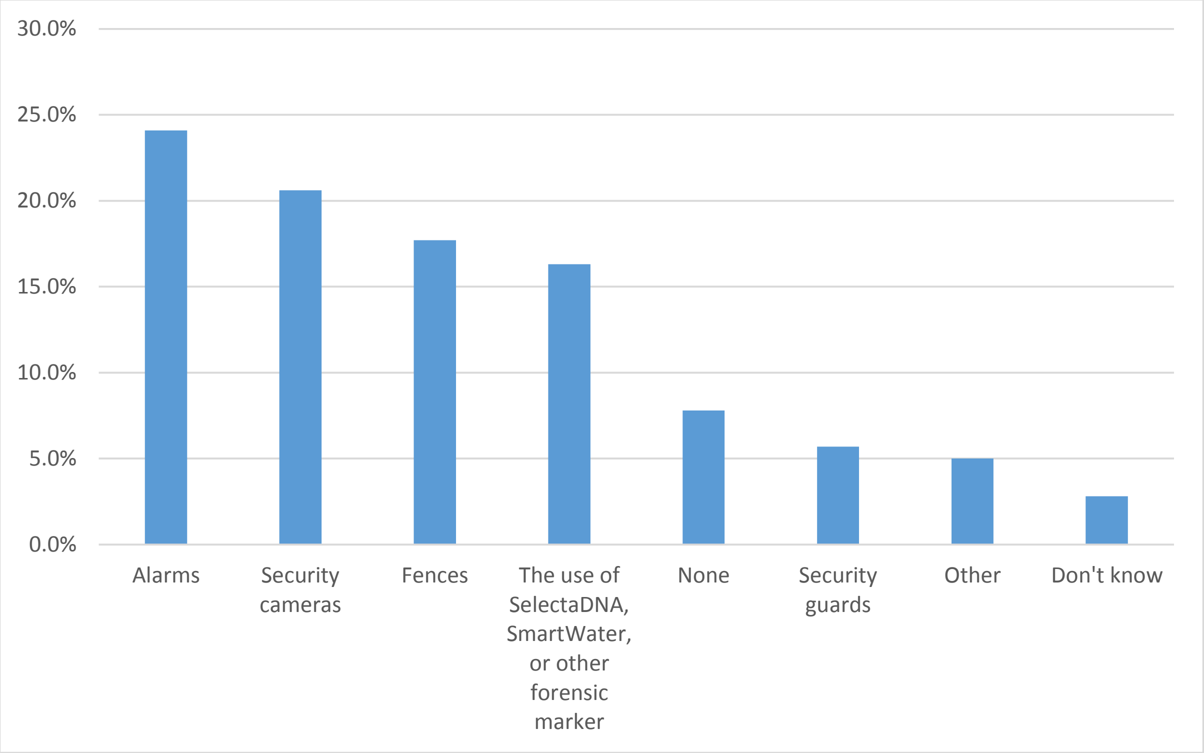


**Figure 13 - Which of the following security measures are present at the heritage site most relevant to you?**

As is shown in figure 13, the most common form of security measure is alarms (24.1%). Whilst being the most common, it is perhaps surprising that only about 1 in 4 heritage sites have this form of commonplace protection. The fact only 17.7% has fences to protect what are fairly expensive materials to sell on once stolen, is a perfect example as to why heritage sites are being targeted by thieves, and why crime levels are so high with regards to metal theft. This provides further emphasis for the necessity of the current research. By developing a cheap and non-invasive method of detection there is the potential for a means of protection to be used more widespread than any of the options listed here. Forensic markers were found at only 16.3% of the sites questioned within this survey, accentuating how useful such compounds can be, but also calling into question whether their expense means their use is limited to those sites which can afford it. These are clear links between chemistry and preventing heritage crime however, again highlighting how scientists or more specifically chemists can help in the current attempts at lowering levels of heritage crime.

The lack of finance available to many of these sites, and hence the lack of protection is also clearly problematic. 7.8% of respondents stated that they had no protective measures in place, whilst several of the ‘other’ category answers noted that tenants and volunteers checking up on the site were their only form of protection. When such simple measures are the only ones being enforced, it is easy to see why such a problem exists when coupled with the high sell on value of copper and lead, amongst other materials commonly stolen.

One of the largest factors as to why metal theft is so problematic is the ‘domino effect’ that can occur when metal is stolen. This is particularly true of lead theft. As has been discussed earlier in this report, when lead roofing is stolen, rainwater can then flood through a now unprotected roof and cause thousands of pounds worth of damage inside before the crime itself has even been detected. When added to the cost of replacing the stolen lead itself this can be more than many sites can afford. This difficulty in discovering a crime occurring is why question 10 was asked in the survey. ‘If the following crimes were committed, which, in your opinion, would pose particular problems upon attempting to discover that a crime had occurred?’ (Figure 14).

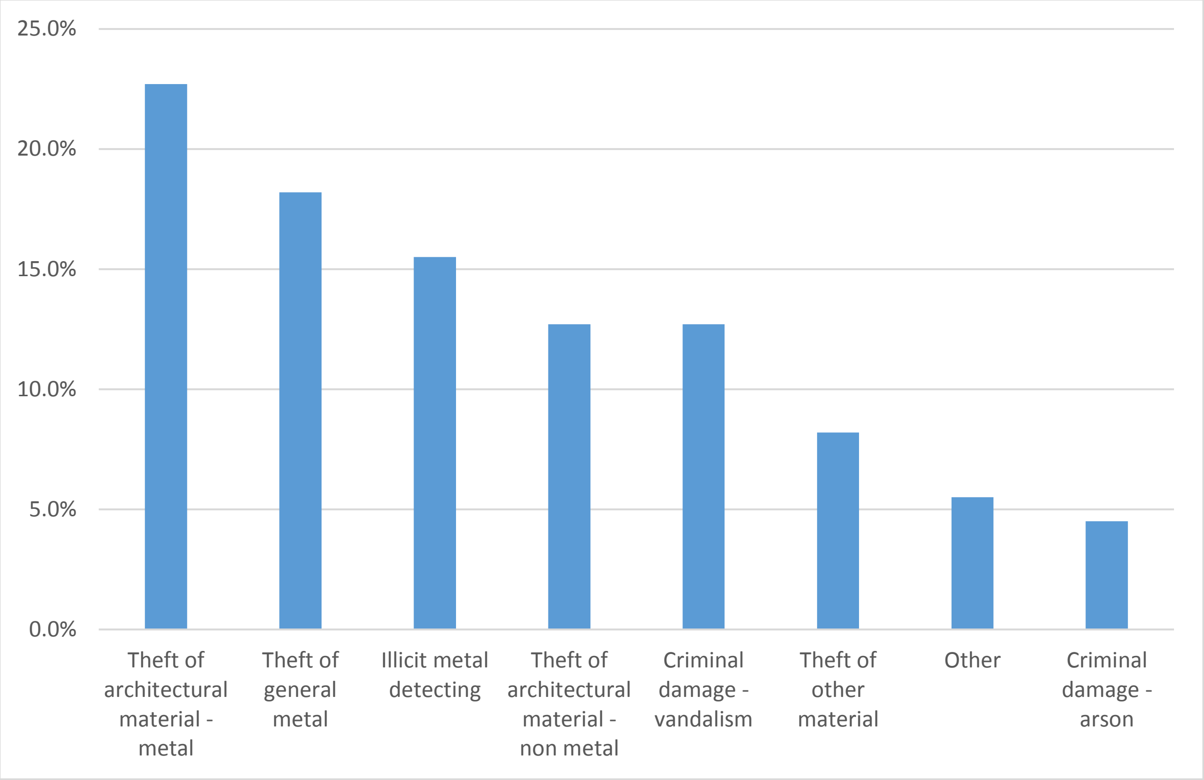


**Figure 14 - If the following crimes were committed, which, in your opinion, would pose particular problems upon attempting to discover that a crime has occurred?**

Theft of architectural metal was top with theft of general metal second, again suggesting why it is an area worthy of research. The fact that architectural material is top of the list may be slightly surprising, as if a significant artefact was stolen it should in theory be noticed immediately. However this does not take into account two large factors. The first is in situations where a site is understaffed and unprotected, hence discovering that a crime has been committed will take time, something which makes detection yet more problematic. This was mentioned by a respondent in the 'other' category whom stated *Archaeological sites (not standing structures) are often vulnerable as they can be in isolated areas and it can take a long time to discover a crime has occurred'.* The other is the vast amount of artefacts that may be present at a given site. What this emphasises is, yet again, why heritage sites are being targeted. With a large volume of valuable materials that are easily accessed but have a reasonably low level of security, it is easy to see why the problem is occurring and why it is such a challenging area to try and address. Another issue here is the demand for specific features of materials found at heritage sites. With the organised crime that can target such sites, some materials can be stolen to order and is another problem facing heritage assets.

The next question (fig 15) attempted to glean further information about which materials need to be protected from theft most urgently. To do so, the question aimed to discover which material is most difficult to replace when it is stolen. Upon writing this question, it was fully expected that lead and copper would be the top two answers, based purely on the expense and hassle involved in replacing these materials.

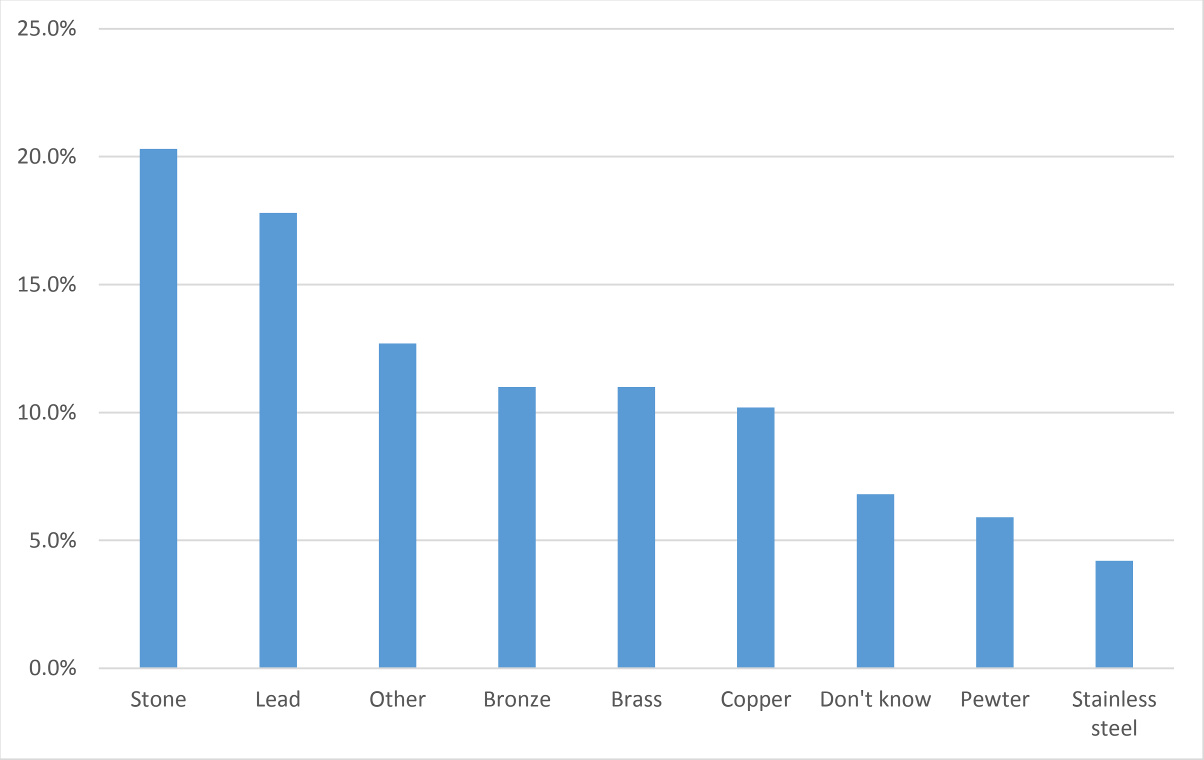


**Figure 15 - In your opinion, which of the following materials would be difficult to replace, if damaged or stolen?**

However it was found that based on this survey that stone is in fact the most difficult to replace when stolen or damaged. As has already been discussed in detail within this report, the levels of stone theft are also high[57]. Whilst lead and copper being stolen is clearly problematic, (lead was second in this particular question) there are always alternatives that can be used for their practical purposes. Lead roofing for example can be replaced by steel. Whilst this is not at all desirable as it can take away the historic nature of many sites, if it is cheaper and prevents repeat offending (something which this survey suggests is very problematic for some sites) then it is understandably taken advantage of by some places of cultural and physical significance. There is also the fact that, whilst expensive, materials used practically like copper are easily accessed with many sellers being able to easily replace the metal (copper piping for example). This is not always the case with stone, as it may have a much more specific function to the site it is stolen for (or from). It is also possible that stone which is stolen at heritage sites will generally be decorative and historic, with each stone being very specific to a given geographical location and hence difficult to replace if stolen. It can also have a very detrimental affect on a piece at a site. There is arguably still a slight ignorance as to the value of stone in comparison to metals, and their level of protection could theoretically be lower than their metal counterparts at heritage sites, despite them being harder to replace when they are stolen. There is also a more simplistic argument here, regarding the issue of damage. If stone is damaged it will generally be a whole paving slab or entire piece of work. This cannot be 'fixed' and will instead need to be replaced. Whereas small amounts of copper and lead can be replaced if damaged as opposed to a large area needing to be replaced.

The rest of the materials discussed in the answers to this question are metals. The problems that will arise in terms of replacing stolen or damaged metal will generally be as a result of the costs involved with this. Another reason was discussed in several of the responses listed as 'other' here whom said any artefact regardless of what it is made of is impossible to replace once stolen or damaged. This is a key point to take forward when underlining the importance of this research. A quote from a survey respondent sums this up nicely; *'Heritage crime is an intellectual crime in that it destroys knowledge and educational material – in a similar way to book burning'.* Once an artefact found at a heritage site is destroyed, it is a slice of an area and its history that is destroyed, and can never be rediscovered. It is, as is the very definition of heritage crime, harming both this and future generations.

The next question asking for information about heritage crime was simply inquiring about whether there was any subject matter that the respondent felt had not been discussed in great detail and was, in their opinion, a clear problem facing heritage assets. Whilst not all answers given are necessary to discuss at length here, there were a few that appeared more than once and suggested problems facing historic attractions. One trend that appeared here and was mentioned on several occasions in differing contexts was a lack of money that is required to protect such sites. The responses ranged from noting how a small budget will affect what security measures are possible. *'Most heritage sites suffer from a serious lack of a security budget. Many obvious security steps are considered too expensive.'* Others discussed how financial means, and specifically who will fund these replacements is the primary concern. Another respondent pointed out how 'like for like' replacements such as lead roofing, are desired and frequently necessary but the funding opportunities are rare. The numerous instances where a lack of funding was mentioned throughout the course of this survey suggest a cheap alternative method of detection would be greatly beneficial to a large number of heritage sites countrywide (and beyond). Another individual noted that a lack of security and the fact that structures are often in 'isolated areas' helped to create an ideal environment for a potential criminal. What is vital to help stop this is to take steps towards creating a deterrent which would mean the lack of security is less problematic. This is an area this research focuses on.

Another issue highlighted, which has been a theme throughout conversations with those relevant to the efforts tackling heritage crime, is a lack of understanding and awareness. This can be towards both identifying what a heritage site is, and what constitutes a crime. Illicit metal detecting and unauthorised alterations are two examples of criminal offences that are often committed as a result of ignorance of the law as opposed to a blatant disregard for it as is the case with theft or vandalism[129]. The other factor is that those committing crimes do not understand the long term effects of their actions. A poor awareness as to what a heritage site is means crimes can occur against them which would not happen as regularly if people understood the consequences. These are issues which large scale, long term projects like this one can help to develop.

One interesting answer in this section discussed the problems facing the current forensic detection techniques used. Again this mentioned a lack of funding, however this time with regards to the police force, something which was quoted by a survey respondent.

*'Forensic solutions only work if there is investment in tracing the stolen items. Currently that process is very poor and given the funding for policing really unlikely to change. No real point in marking materials if they aren't going to be checked.'*

What this suggests is that developing a technique which would help narrow down and cheapen this procedure would be very desirable. One such option discussed in the early stages of this research was to analyse the criminal themselves as opposed to the stolen material. By establishing a new means of detection which is both simple and cost effective there is the potential for several of the issues discussed here to be addressed, and in turn, levels of heritage crime to be lowered.

The final questions asked in the survey were simply asking if a person was willing to be contacted in order to help gain a better understanding of heritage crime at their relevant site beyond the answers given in the survey. This was important as it could enable an insight into the responses given if that was necessary. It was taken advantage of during separate discussions with two different individuals. These discussions focused on stone theft at churches and metal theft at railway stations respectively and will be discussed in greater detail later in this report.

By completing a survey, the research that was to be completed within a chemistry environment now had a clear pathway to focus on. Resultantly, with several indisputable obstacles facing heritage sites and their attempts to lower levels of crime, there is clearly a market for the research that was completed during the course of this project to assist in lowering these levels. What was important was ensuring that only problems relevant to chemistry were concentrated upon. Whilst it is tempting to try and lower all levels of heritage crime, the work here is not infinite, and so narrowing this down to those issues which can be tackled realistically within the limited timeframe was important.

Based on this attitude and the results gathered during this survey, it was decided that there would be two main areas of focus during the course of this research. Unsurprisingly when looking at the answers given these were lowering levels of stone theft and metal theft, with a particular focus on copper and lead. Whilst there will also be some efforts towards lowering other forms of crime, the main target will be the two most common forms of theft at heritage sites.

From the knowledge developed in the lead up to this survey, as well as that which was obtained from the answers given it was clear that there is a market for a form of detection despite the current options available such as SmartWater and SelectaDNA. Although well-known forensic markers like these (and others) are readily available, the expense involved often means they are not a realistic option at many heritage sites. Resultantly a cheaper form of detection is vital for the long term progression regarding the lowering of heritage crime levels, specifically the rates of theft.

Ideally a technique that is transferable between metal and stone could be refined, however this would be difficult or near impossible and so separate techniques were looked at for each material, with different metals grouped together more closely than with stone.

In order to establish a clearer understanding about what those tasked with lowering levels of heritage crime required, some contacts obtained through their contribution to the survey were contacted and asked for more information. The people questioned were chosen based on their answers given, and the heritage site or company they represented. It was hoped that via consultations with such groups, this research could emphasize participation by as many groups as possible. This is an example of participatory action research[130] and could in theory ensure a larger group are working towards an end goal of lowering levels of heritage crime. Coproduction between researchers and the end users, in this case those tasked with lowering levels of such crime is very important from both sides. The research is remaining relevant and as a result those working in practical situation will hopefully be receiving very useful developments that can be used in a real life scenario.

The first of those who was consulted was a member of the Church Conservation Trust. This was regarding the high level of stone theft, and damage dealt to stones (particularly gravestones) reported at various churches countrywide. The information gathered aimed to develop a better understanding of both what is needed at heritage sites, and what would be useable. From the brief conversation held, the following points were gleaned:

- Damage to, and theft of stone, is one of the greatest threats facing churches countrywide.
- There is little finance to help protect the assets held at these sites.
- Any form of detective procedure must be non-invasive in order to be used wide scale.
- A ‘database’ of stone, or an indication of the unique chemical fingerprint each stone has would be most useful, if possible.

- The method should be as simple to apply as possible for a larger number of sites to take advantage of such a development.

This information was taken into account when attempting to develop a novel method of stone detection later on in the project.

Conversations were also held with a member of the British Transport Police, who dealt with heritage railway lines and listed stations. These discussions were more focused on metal theft. This will clearly be an issue at railway lines at stations just because of the amount of metal found at such sites. The following information was obtained through this exchange:

- Metal theft is a huge problem.
- This is a mix between large scale, planned operations and spur of the moment opportunistic theft on a smaller scale but each is equally disruptive and harmful.
- There was a clear mismatch between amount of security needed and the amount of security actually present.
- There were hopes that the Scrap Metal Dealers Act 2013 would help lower the levels of metal theft long term as opposed to offering a short term solution.
- Any form of detection would be hugely beneficial.
- Non-invasive detective methods would have a more widespread influence.

It seems apparent that any metal which is used practically can be forensically analysed by any means necessary, whereas those that have historical significance will require a more non-invasive focus. Despite this the emphasis during the course of this research is on that of non-invasive detection, and hence protection. There are already several invasive techniques that can be used with reasonable success to analyse fingerprints from the surface of a metal, in particular copper and brass[92][131][132]. Another factor behind this is ensuring that there is a clear focus throughout on lowering levels of *heritage* crime as opposed to a more general attitude of lowering levels of metal theft. By working towards developing a novel method of non-invasive detection, coupled with the same attempts with stone it was hoped that upon completion of this project there would be a distinct improvement on the current techniques available to those attempting to lower the levels of heritage crime.

The following chapter details the initial efforts that were made into developing a novel technique which could enable this non-invasive detection of the material deemed most under threat, which was metal.

# Chapter 3 – Trace Metal Detection

Within the past few years, the general levels of crime (including acquisitive crime) appear to have dropped (although there are those who argue that this is a case of crime being displaced)[133]. Despite this, the regularity at which metal theft is occurring has risen[4][39][42]. The primary cause of this is difficult to determine, however there are several possibilities. One option could potentially be the increase in metal prices that has arrived as a result of global demand beginning greatly to exceed supply[30]. This, coinciding with a decline in the economic situation that many find themselves in, appears to have played a large role in the increased levels of metal theft. This is most certainly a fast growing genre of crime[134] and there is evidence that the same is true in the USA[135]. The amount of metal theft occurring was further highlighted by the statistics released in 2007 by the UK Ecclesiastical Insurance office who stated that the cost of metal theft was over £30 million that year[136]. The cost to the UK alone was around £360 million and there are suggestions that the actual figure is almost double this. Whilst the economic issues are vast, metal theft can have huge social consequence as well. This can include national infrastructure, with one huge example being that from rail companies. Another, which this research shall focus on, is that of national heritage. In this regard, the damage to historical monuments and listed buildings affects not only this but future generations, further emphasising the long term social repercussions of such types of theft. Additionally, the theft of metal can have what is referred to as a 'domino effect' on many listed buildings, especially true for churches. This is where the theft of metal used practically, generally lead roofing, causes knock on effects resulting in further damage to the site in question. An example this is when rainwater enters the building due to a lack of protection that the stolen metal would usually provide. As a consequence of such statistics the Scrap Metal Dealers Act of 2013[137] was introduced in an attempt to tackle these increasing levels of crime. There is some evidence which suggests that this has had a degree of success[46] however this form if illegal activity is still rife, and with it is the need for work to lower such criminal levels. Whilst there have been attempts elsewhere to develop techniques and markers (such as SmartWater) which can be used by police forces around the country, these often have little use with regard to metal stolen which has historic significance. This is because of the high costs which are often involved. As a result of the importance of many such items, the need for a technique which can detect a thief non-invasively has proven to be greatly desired by those tasked with lowering levels of metal theft. Resultantly this formed a large part of the focus during the early stages of this research, once it was confirmed that metal theft was the area of greatest concern facing our heritage sites countrywide.

Whilst there are several examples of work being done towards tackling this issue, almost all of it focuses on directly analysing the metal in question. Bond et al for example have noted that forensic analysis has advanced to a point where the methods in which stolen metal is handled and analysed could be greatly improved[138]. This work looks at how unique lead samples on a church roof are, and would help contribute knowledge regarding the origin of any recovered metal as to its original location.

What has not been investigated however is the notion of directly analysing the skin of a person who is suspected of recently handling said metal, and in turn identifying them as a potential suspect in an occurrence of metal theft. Monitoring the surface of the skin is not unique, with kits being available to test for both gunshot residues[139] and certain forms of narcotic drugs from a person's hands (or clothing)[140]. However this often has several limitations, one such example being the need for a swab of some kind to be used to collect the information that is tested. This sires a lack of accuracy when attempts are then made to 'map out' the distribution of the materials being tested for. A method which more accurately maps out the contact a person has had with a metal could add important strands to forensic evidence which in turn could be used by those tasked with lowering levels of metal theft. This has particular promise with regard to metal found at heritage sites, as a patterned or specifically shaped piece of metal could be mapped out and identified from the contact a person has had with said metal. Ferrotrace is another example of a detective method that analyses the skin[141][142]. This is a non-toxic spray that, when applied to the skin acts as a presumptive test for the detection of iron residues that are present as a result of recent contact with an iron item. Lukaszewicz et al have progressed from this with their development of several 1,2,4-triazine chromogenic reagents that detect both ferrous and nonferrous metal traces on a person's skin[90]. These both have the distinct disadvantage however of being invasive procedures and evidence that can be long lasting (photographs) must be taken at the time of testing. Szumera et al noted an awareness of this limitation and thus made efforts in enabling this process to be non-invasive. This was done by using a triazine soaked cotton pad, hence reducing the chemical contact with the skin[83]. The ‘bleeding’ that occurred here however limited the practicality of such a procedure. In addition to this, there was still a degree of contact, and this stained a person’s hands which negates the attempts at it being ‘non-invasive’. The above techniques focus on iron as the metal being tested for, presumably as a result of this metals uses in firearms.

The work completed during the course of this research examined copper and lead, as a result of their high levels of theft reported both in the media and in the survey reported in chapter 2. Adhesive gelatine lifters were used to access the trace levels of metal that was present on the skin, thus negating any need for direct chemical contact. These sheets are commonly used to ‘lift’ and then store developed fingerprints, and also to retrieve evidence such as footmarks. However they have, somewhat surprisingly, rarely been used in terms of direct application to the surface of the skin. The final component of this technique is the developing agent which will be used to visualise the trace metal residues. Dithiooxamide (or rubeanic acid) $H_2NC(S)C(S)NH_2$ is a polydentate ligand which chelates to metal ions via both nitrogen and sulphur. This has historic uses in an assortment of studies, mainly focusing on its interactions with copper[143][144][145]. These interactions have been studied much less in terms of rubeanic acid and lead. There have been reports that a yellow complex initially forms, which over time decomposes to form lead sulphide[109], which was investigated during the course of this research and will be discussed in greater length later on in this thesis. With regards to this research the appearance of a characteristic colouring of leads presence when exposed to UV light, suggests a sensitivity to this UV light. However the colour that becomes apparent is an orange/brown as opposed to the black precipitate which would suggest the appearance of lead sulphide. The analysis done on this will be discussed in greater detail later.

## 3.1 Experimental procedure

Rubeanic acid (0.05g) was dissolved in ethanol (50ml) with constant stirring for 15mins.  This forms a clear orange solution.  A subjects hand is placed on the metal in question, be that copper, an alloy of copper, or lead.  After a few seconds of contact time and removal of the hand from the surface of the metal, a gelatine lift from the hand is taken and the gelatine sheet then treated with the 0.1% w/v solution of rubeanic acid in ethanol prepared above.  This can be treated by one of two methods.  The first is simply using a standard dip tray and dipping the gelatine lifter into said solution for a few seconds.  The second is to use an EcoSpray bottle and spray the lifter with a fine mist of solution.  There is little difference between the effectiveness of both these methods, however the greater consistency and longer storage time combined with the fact that the spray could potentially be used on site far more easily than the dip tray suggest this is the better option long term.  The spray also needs much less solution for each piece of analysis, meaning one stock solution can be made and used over multiple sprays, as opposed to the dip tray where a fresh solution must be made up after every sample or else run the risk of contamination from a previous sample which has been analysed.  Whilst copper and its alloys will react almost immediately, lead requires UV light, and so was placed directly under a UV light for 5 minutes after treatment with rubeanate solution.

The copper, brass, and bronze used here varies, as numerous samples were to be attempted thus confirming the process works on metals that have aged and hence oxidized differently.  The lead used was a lead block pictured below (figure 16):

**Figure 16 - Lead block**

This was the only lead sample used throughout when detecting trace metal residues on the skin.

Unless stated, in the experiments discussed, the hands were in a ‘natural state’ ie not ‘loaded’ to give sebaceous or eccrine prints.

In the case of sebaceous prints, an individual rubbed their hands across their forehead and nose briefly.

In the case of eccrine prints, an individual washed their hands thoroughly, before wearing latex or nitrile gloves for 10mins in order to develop purely eccrine material.

## 3.2 Rubeanic acids interaction with copper and its alloys

When a hand has been in contact with copper and its alloys of brass and bronze and placed on the gelatine lifter, the presence of these metals is confirmed by the appearance of a dark blue/black colouring pictured below.

**Figure 17 - Handprint lifted after contact with bronze statue**

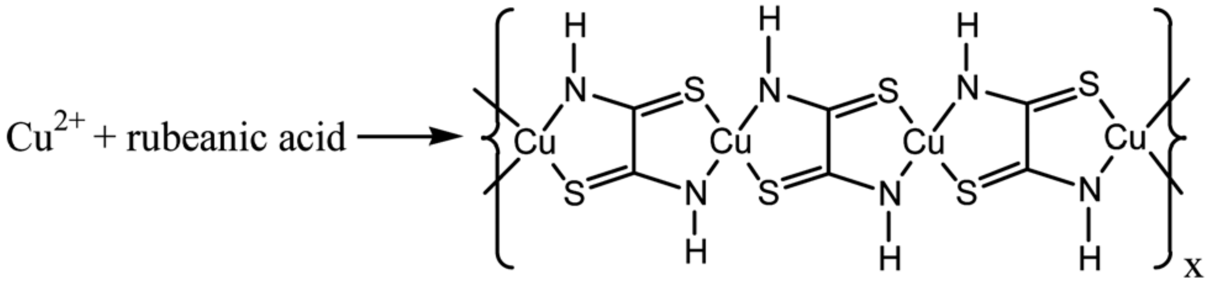
Copper was analysed here as a result of its designation as a metal under threat, confirmed by the survey results in chapter 2. This metal is used both practically (copper piping) and decoratively, so is undoubtedly one of the metals most worthy of consideration when attempting to tackle metal theft. However both brass and bronze appeared on this survey as well. Resultantly both were also analysed, along with pewter when attempts were made to detect trace levels on the surface of a person's skin.

The pewter that was analysed was a jug, and gave no indication of coppers presence with the tests conducted. This is most likely a result of a low amount of copper present within the alloys makeup, which will be instead made up with tin and other trace metals like antimony. This theory was further confirmed when tin was analysed in the same manner as copper and also produced negative results *i.e.* no characteristic colouring.

However copper, brass, and bronze all showed much greater promise, and when analysed using the rubeanate solution and gelatine lifters produced a dark blue/black colour where there had been direct contact between the metal in question and a person's skin (generally the hand). Whilst other metals to be discussed showed differing colours, an important point, all of the copper based alloys yielded the same blue/black colouration as copper itself. What this shows is that copper alone is what is reacting with the rubeanic acid at this point, and the same reaction process is occurring with each alloy. Whilst both brass and bronze comprise of a majority copper composition, this appears to be enough copper present to produce said reaction process. This, as discussed in the above section, is not the case with alloys containing a more minimal amount of copper such as pewter. At this point it appears having copper as the majority contributor to a metals makeup is vital as to having this process work successfully.

The technique has a level of sensitivity which is such that differences between the detection of copper, brass, and bronze cannot be seen. In each case, the amount of copper required to react with rubeanic acid solution (or copper itself) has been transferred to the hands.

Copper rubeanate's formation in this form of reaction has been reported before[108][109][110] so the assumption is that the blue/black precipitate forming is that of the polymeric copper rubeanate complex shown, in the following reaction scheme:



**Scheme 1 – The formation of the polymeric complex of $Cu^{2+}$ with rubeanic acid**

To confirm that the above process is most likely to be that occurring, a crystal of copper (II) sulphate was touched, before the skin was analysed using the gelatine lifter and rubeanic acid.

**Figure 18 - Copper sulphate crystal touched at 3 different points before resultant fingermark developed**

These all gave clear detail. To yield further information, the crystal was touched and then hands were rinsed in distilled water.

**Figure 19 - Hand rinsed after contact with copper sulphate (left), differed considerably to when not rinsed (right).**

As pictured, this gave no evidence of copper contact. However, when the same was attempted with a copper pipe, the following evidence was obtained:

**Figure 20 - Still clear detail even after rinsing finger in water**

This is still showing that copper has been recently contacted. As a result of this, it can be assumed that in the case of copper (II) sulphate, the copper traces transferred onto the skin are being washed off by the water, due to the solubility of $Cu^{2+}$ in water. However in the case of a copper pipe or sheets of copper, there is a mix of $Cu^{2+}$ (which is being washed off) and elemental copper, which is not and is still present to be detected by the rubeanic acid.

It was noted that there could be instances where the bulk material could be copper, however this is then covered in another substance which could then shield this from the gelatine lifter thus preventing the trace copper being transferred to the gelatine lifter surface. The most common such substance was believed to be paint. However paint itself often has metallic components so it was thought that different coloured paints could be tested to examine the potential for this to produce a reaction with rubeanate solution. A small amount of paint was placed on a sheet of paper in a range of colours and then the gelatine lifter was placed on this once the paint had dried. After gel was left in contact with this paint for 5 minutes, it was removed and treated with rubeanate solution. However in no instance did this produce any colour indicative of a reaction with the rubeanate solution. Following on from this, the next test involved placing a small amount of paint on the surface of copper and again leaving to dry overnight. This was then analysed using the same process as previously with rubeanate solution and gelatine lifter. Where the paint had been on the copper produced no reaction between copper and rubeanate solution. The paint had ‘blocked’ this reaction from occurring, as the trace amounts of copper required for the reaction to occur had not been allowed to transfer to the surface of the lifter.

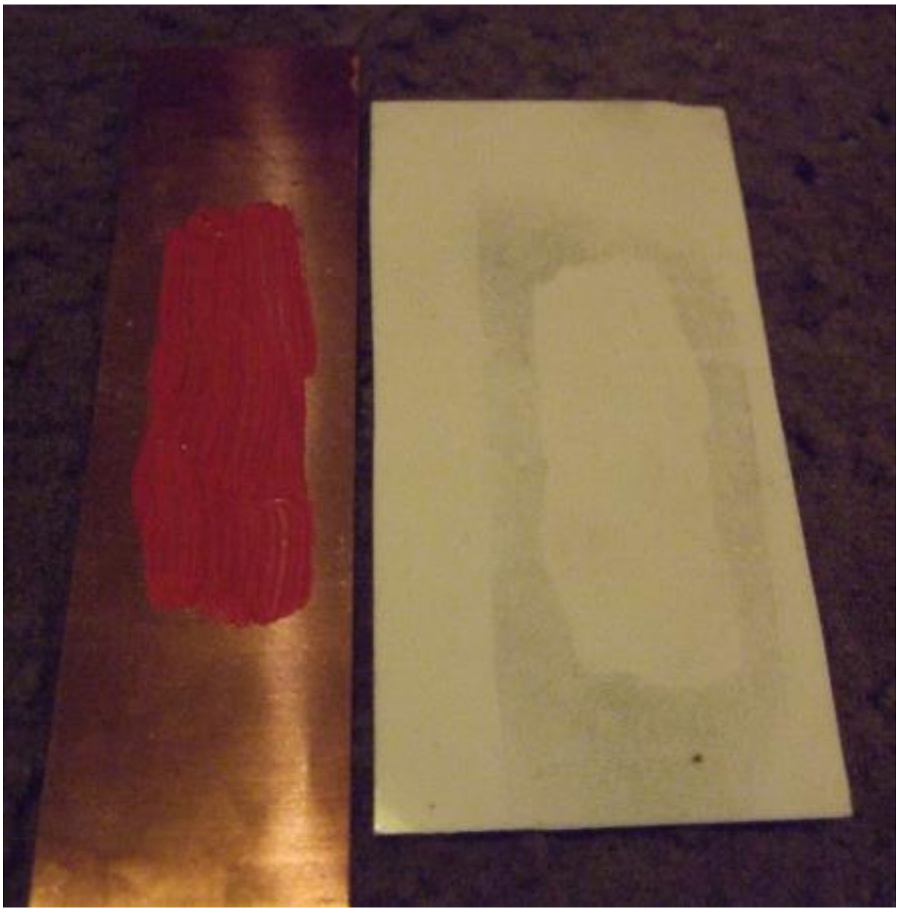


**Figure 21 – The area covered by paint on the copper (left) is then visualised in the development using rubeanate solution**

This result has both pros and cons. Whilst it could be viewed as being problematic that such a substance could block the ability to ‘lift’ this is not necessarily an area of concern. It is rare that an entire copper piece will be painted (if at all) and instead will only be partially covered. The paint will be used decoratively, and this is where the sensitivity of said procedure becomes so useful. The issue of a ‘false positive’ for copper can be removed when a specific pattern can be visualised. Coins are a prime example of this and are addressed later in this chapter. This is also the case here where the painted pattern can be visualised based on the lack of copper rubeanate against the gel, contrasting to areas where there is no paint blocking the copper and hence the blue/black colour is seen as normal. This will also be true for substances or materials other than copper which can ‘block’ the normal reaction from occurring. This could be a different metal, or plastic casing for example. Whilst this may not be particularly relevant with regards to copper used practically like piping, it is of great relevance in terms of its potential in identifying a person who has recently had direct contact with a decorative piece. The shape gives a clear indication of how a person has held the copper in question. Further information can be gleaned if the decorative piece either is comprised of multiple materials, or is covered in another substance such as paint.

### 3.2.1 Rubeanic acids interactions with lead

The same process as in the previous section was attempted with lead, another metal that is clearly under great threat at heritage sites. Whilst copper and its alloys produce the characteristic blue/black colour immediately after being treated with the rubeanic acid solution, the same cannot be said of lead. It was noted however, that having been left in the open lab for a few hours the orange/brown colour that proves lead’s presence on the skin becomes apparent. To confirm this, a sample that had been in contact with lead was placed under a UV light for 10 minutes. This produced the characteristic colour within this timeframe, and suggests the complex forming is UV sensitive. Without an intense UV light source the appearance will begin to appear at any point between 1 hour and 12 hours depending on the environment it is placed in, due to natural UV light present. Leaving a sample with zero UV light however ensures no such colour appears, further confirming the reliance on this feature. Assuming a UV light is present however, the process discussed involves minimal fuss and the detection of trace lead residues can be completed within an hour.

### 3.2.2 Leaving the gels for a period of time prior to analysis

What was also important was ensuring that such a technique has viability within a practical scenario. Such a process would best involve analysing a suspect’s skin (hands) on site. In this case, a UV light may not be at hand, so it was important to ensure that a handprint can be taken, left for a given amount of time, and then analysed with rubeanic acid solution and UV light. To ensure this a sample was left for 1 week in a lightless cupboard before being treated with rubeanic acid, and left under a UV light. Despite the additional waiting time, the characteristic colour of lead appeared within 15 minutes, and the wait had little/no negative effect on the results obtained.

Another pertinent feature of this technique is the fact that results can be obtained many hours after the original contact with the metal, in this case lead. This can extend to a 24 hour period in the absence of thoroughly washing the hands (with soap). When merely rinsing the hands with water the process described above still yields the orange/brown colour, and confirms the presence of lead on the skin. This was important information to gather, firstly to highlight the durability of the technique and the extent that it can work successfully. Secondly, it can give some hint as to the chemical nature of the metal species being detected as it confirms that at least part of that transferred is insoluble in the water being used to wash the hands. The exact identity of the lead complex responsible is difficult to confirm, and as a result a more in depth analysis of that being formed was completed via elemental analysis and IR spectroscopy.

As well as producing a characteristic colour confirming a person has had recent contact with copper or its alloy, the detail is of such quality that the specific metal distribution can be mapped out. This can clearly be seen below where the letters of the 'RSC' can be picked out in the blue/black colour, against the orange/brown backdrop that shows there has been contact with lead (figure 22).

**Figure 22 - The blue black of copper is apparent with the RSC, against a backdrop of orange/brown from the lead block.**

Figure 23 - The lead block analysed above.  The RSC is copper, against a lead block.

This ability to link precise distribution to potential artefacts that could be found at a heritage site has obvious potential.  The level of detail that can be obtained via this method even allows ridge detail of an individual's fingerprint to be seen, which whilst unnecessary when a person is discovered, does highlight the potential of lifting fingerprints from the metal as opposed to metal from the skin.  This led to further work, which is discussed later in this thesis.

### 3.2.3 Analysis of the lead complex formed

In order to gain a better insight into the orange/brown lead complex being formed, a lead complex prepared via reaction of lead acetate trihydrate (0.159g) was dissolved in 50ml of ethanol and rubeanic acid (0.0493g) with stirring.  The resulting solution was left in the presence of UV light overnight to see if this yielded the characteristic colour of the lead complex formed in the rubeanate reaction described above.  Initially there was no colour change, however the addition of UV light for a 10 minute period of time caused the formation of a clear brown/orange colour to become apparent.

2ml of this sample was then placed onto a white gelatine lifter using a Pasteur pipette. Initially this appeared as a yellow colour, however with time this darkened to an orange/brown very similar to that present when used to detect from the surface of the skin (figure 24). Due to the similarity in colour, analysis was done on the compound prepared above and compared to a known sample of lead sulphide.

**Figure 24 - The yellow colour (top) quickly broke down into the orange/brown colour (below). This is very similar to the orange/brown seen when detected from the skin.**

This experimental procedure was completed three times in order to confirm that the product forming was consistent. IR analysis of the product formed did indeed verify the consistency of the reaction occurring.

### 3.2.4 Elemental analysis

Because the actual structure was unknown, the RMM was calculated assuming the presence of 1 lead atom and 1 rubeanic acid molecule being present. As a result, the RMM of this compound noted to be 327.39656. Therefore the expected results would suggest that the contributions of the following are:

7.3% carbon

1.23% hydrogen

8.556% nitrogen

The results instead showed:

6.37% carbon

0.52% hydrogen

6.89% nitrogen

As a result it is clear that the reaction occurring is not simply the formation of 'lead rubeanate' as is the case with copper. It also shows that what is forming is not a pure lead sulphide complex either. An IR spectra was obtained for both the rubeanic acid and the lead rubeanate based complex forming to allow further information to be gleaned.

### 3.2.5 IR spectroscopy

An IR taken of both rubeanic acid and the lead based rubeanate complex formed above to analyse potential similarities between the two. If the resulting product was a simple lead rubeanate complex, there would be noticeable similarities between the two, with minimal differences. These are shown in figure 26:

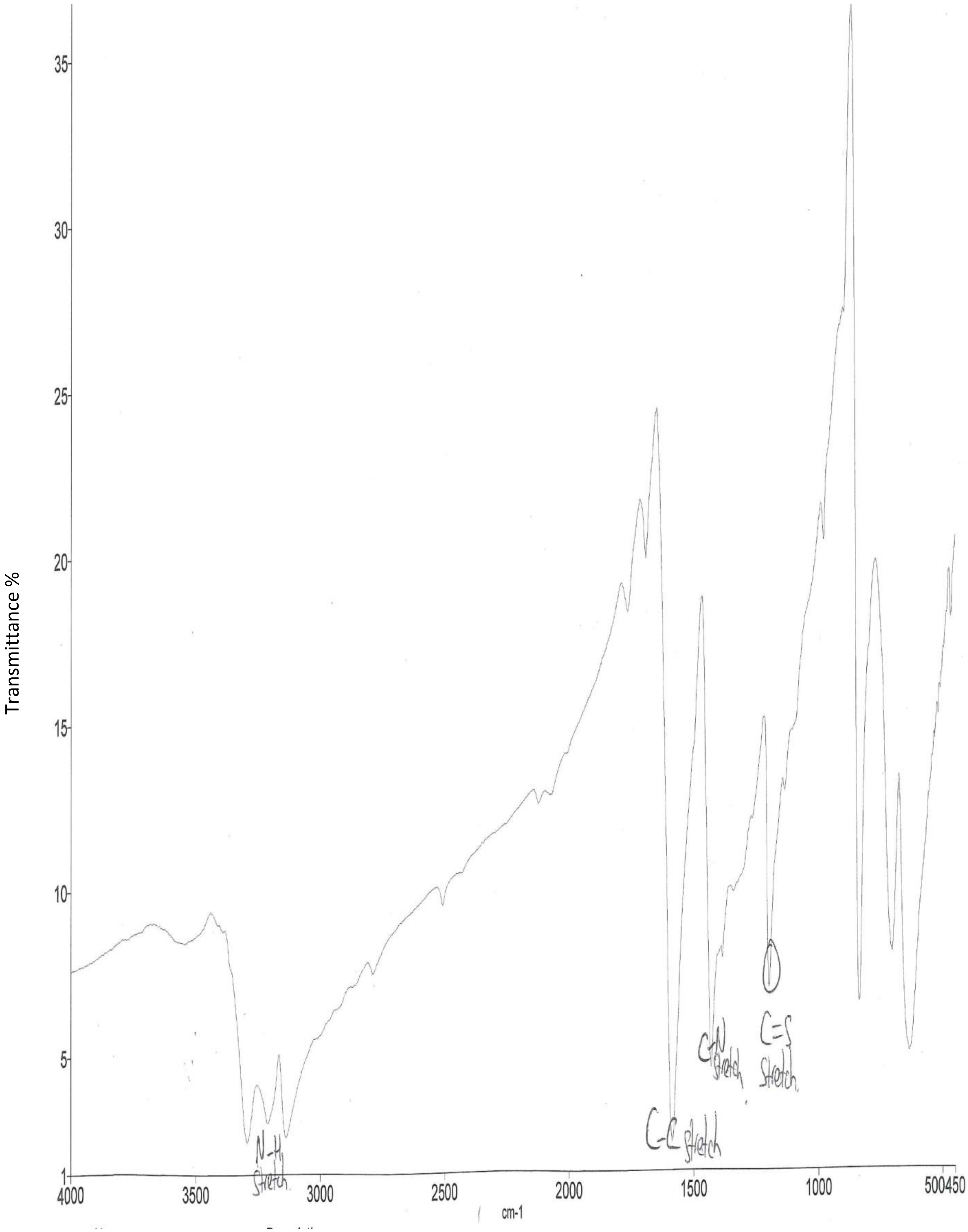


**Figure 26 - Rubeanic acid IR (with handwritten points of reference regarding the cause of certain troughs).**

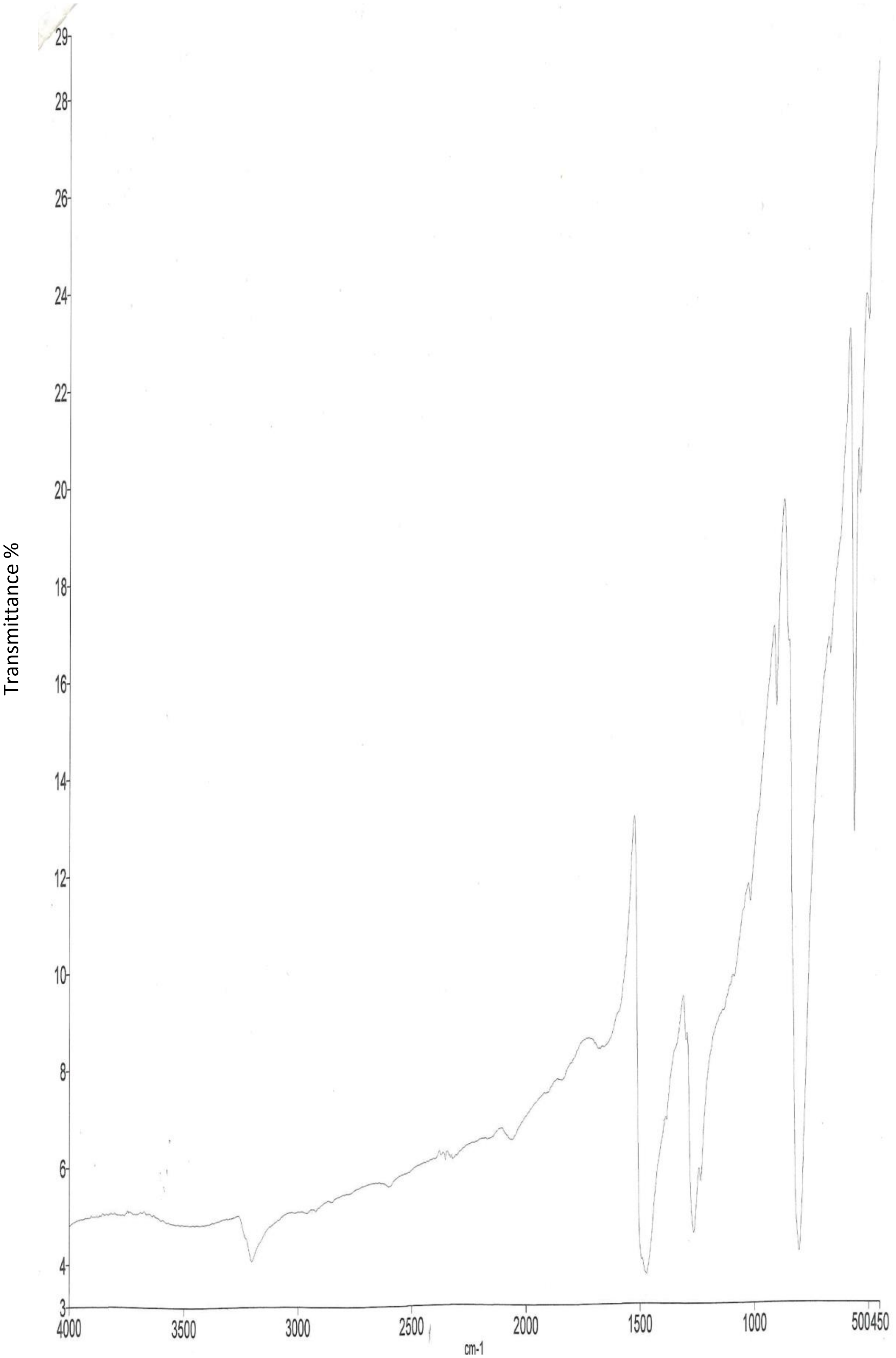


**Figure 28 - IR of lead complex formed**

Whilst limited information is garnered, there are enough similarities between the two spectra obtained. There is a slight trough at around $3250^{-1}$, indicative of an NH stretch. Clearer similarities are apparent at the lower end of the spectrum with a noticeable trough at $1400 cm^{-1}$ characteristic of a CN stretch and another at $1200^{-1}$ highlighting the presence of a C=S stretch. Coupling this information with the fact that the compound is UV active (as was shown by the colour change from yellow to orange/brown) and yields a near identical final colour, appears to give credence to the theory that the complex forming involves both lead and rubeanic acid. However this does not appear to be forming as stable a final product as was the case with copper rubeanates formation.

### 3.2.6 XRD

The yellow crystals formed in the above reaction were left for 1 week. This in theory would enable the breakdown to lead sulphide that is the suspected reaction scheme at this point. During the course of a week, the crystals changed colour from yellow to a dark brown. An XRD taken of these crystals to compare to lead sulphide.

Attempt 1 had a range of 5-90.

Both gave near identical results. Whilst there were clear matches, at 21, 43, and 70 in the 2-theta scale. There were also huge differences between the ideal match for lead sulphide, and what was obtained from the rubeanate complex. What was the most notable issue was that of the background noise which was preventing the emergence of a clear picture, and thus making a full interpretation and comparison difficult. As a result, another XRD was taken, however the step time and amount of steps were increased in order to hopefully see a cleaner XRD.

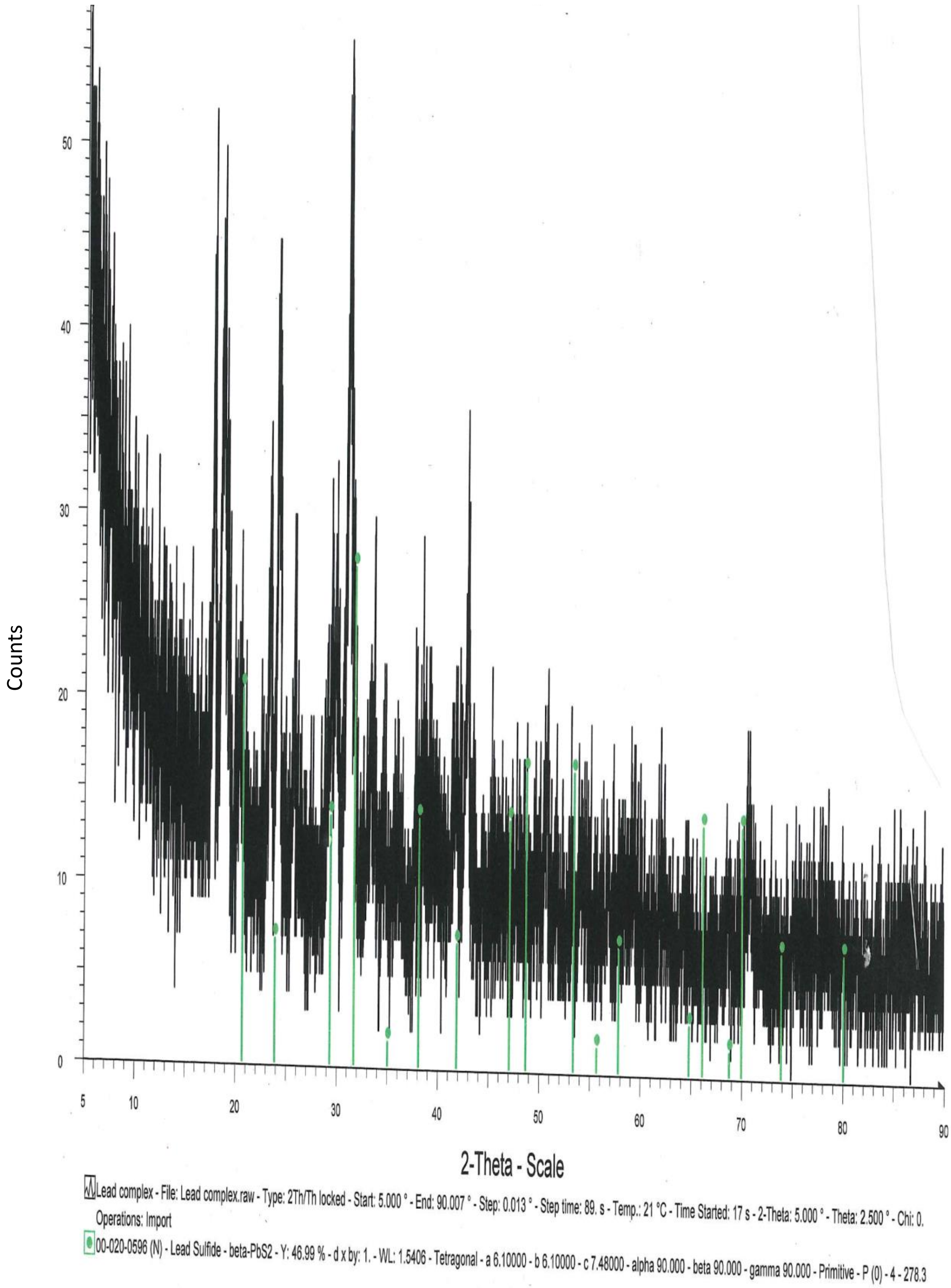


**Figure 29 - XRD. Background noise made successful visualization difficult**

The closest match for this XRD pattern was a mineral called Anglesite ($PbSO_4$). The colour for this is usually white or pale yellow, however interestingly when impure it is a dark grey. The IR does not match this theory however. After an additional 2 weeks, another XRD was completed with a reduced range of 10-80.

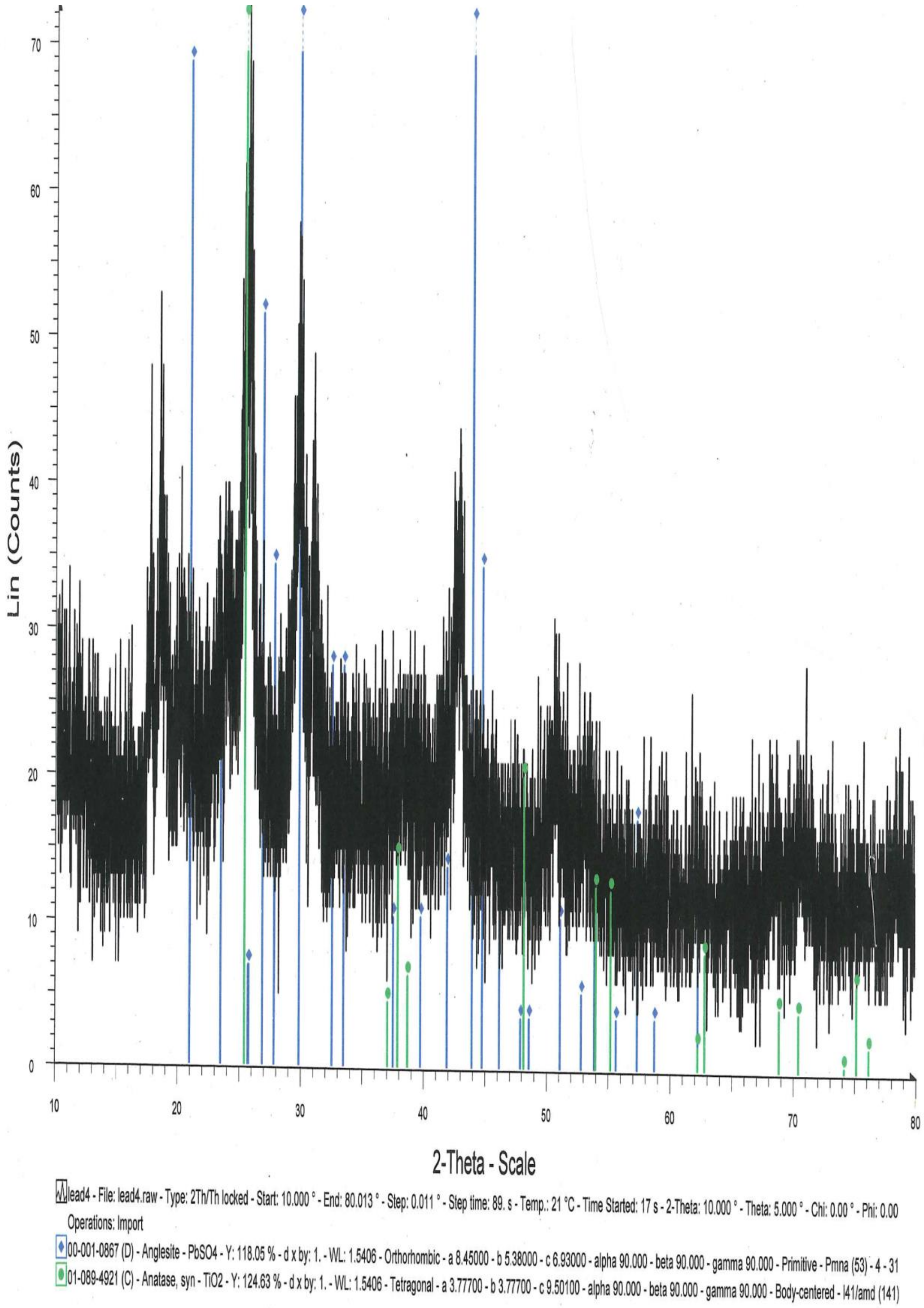


**Figure 30 – XRD after a further 2 weeks.**

From the results obtained, it is evident that the complex forming in the reaction between lead and rubeanic acid (in ethanol) is *not* forming a simple lead sulphide compound. It is also clear that the formation of a polymeric complex with the rubeanic acid (as is the case with copper and its alloys) is not happening in this instance. Based on the analytical techniques employed above it appears most likely that initially a lead rubeanate based complex is forming (which is responsible for the yellow colour formed when the reaction first occurs) and over time this breaks down towards a lead sulphide complex. This is in line with work done by *Ray et al* who stated both that $Pb^{2+}$ forms a yellow precipitate with rubeanic acid, and also that this compound is unstable, decomposing more or less into the corresponding sulphide[109].

## 3.3 Optimizing the process - Copper

The first step towards optimizing this process was confirming how long copper could be held, and still produce the characteristic blue/black colour when a handprint was treated with rubeanic acid. Hence a copper pipe was handled for times ranging from as little as 1 second to 10 seconds. Even as short a time as 1 second of direct contact produced clear elucidation of copper rubeanate.

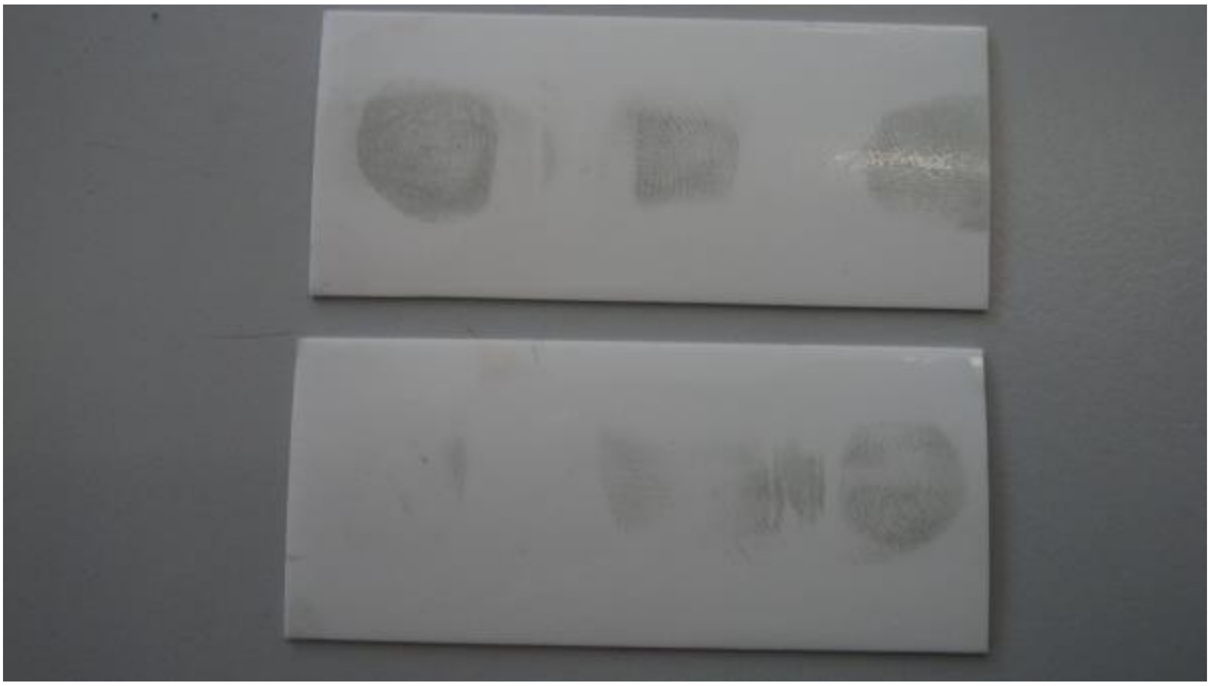


**Figure 31 - Contact with a copper pipe for 10 seconds (top) and 1 second (bottom)**

The colouring was slightly lighter at a lessened contact time, but this could be as a result of the difficulty in establishing contact throughout the metal for such a short period of time.

### 3.3.1 Optimizing the process - Lead

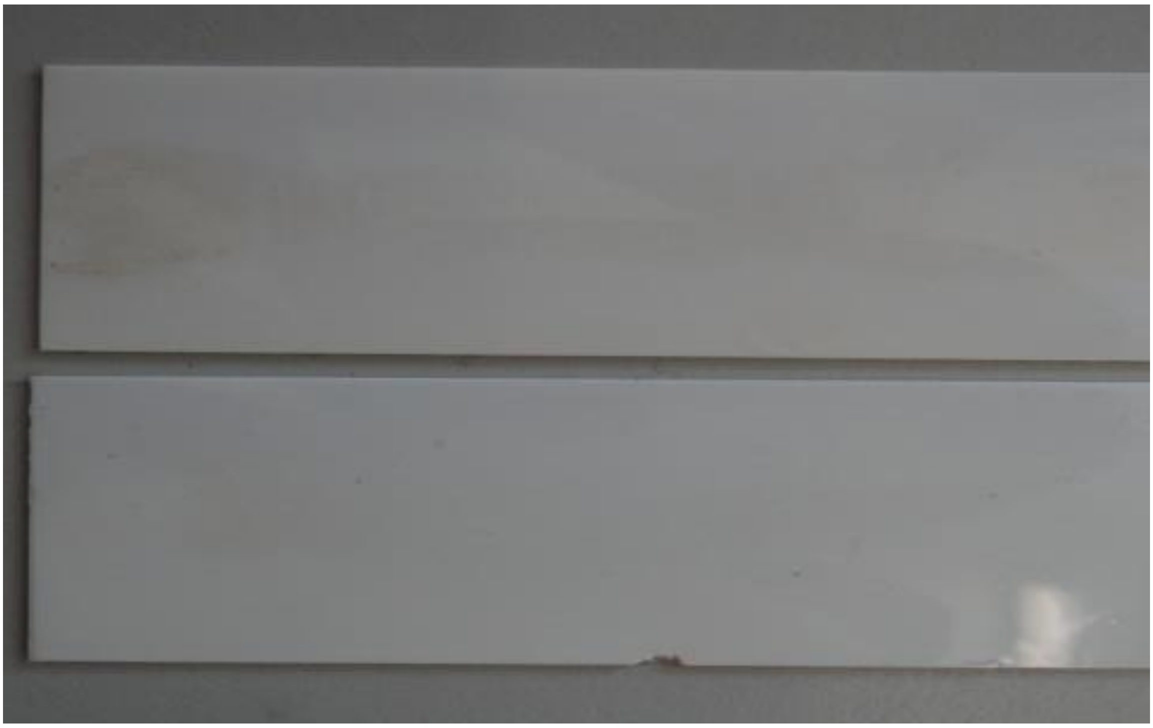


**Figure 32 – (Top) After 10 seconds of contact time with lead, there is evidence of lead rubeanate formation, however after 1 second (bottom) there is not.**

Figure 32 demonstrates that rubeanic acid seems less sensitive to lead, which is again in line with previous work completed by Ray et al[108]. Despite this there is still merely a minimum of 10 seconds contact time required before lead contact can be proven.

This technique can work effectively with both the Ecospray and when 'dipped' into the standard dip tray, the Ecospray is generally used because of its greater long term usage and ease of application. The fine mist produced by this is desirable over other, more general spray bottles as the droplets formed are consistent throughout and thus ensure consistent coverage across the gels surface.

Thus far white gelatine lifters had been used. To confirm that these were the optimum gels to use, a comparison was made with the other two available which are produced by BVDA (transparent and black). The same process and timings were maintained for each.

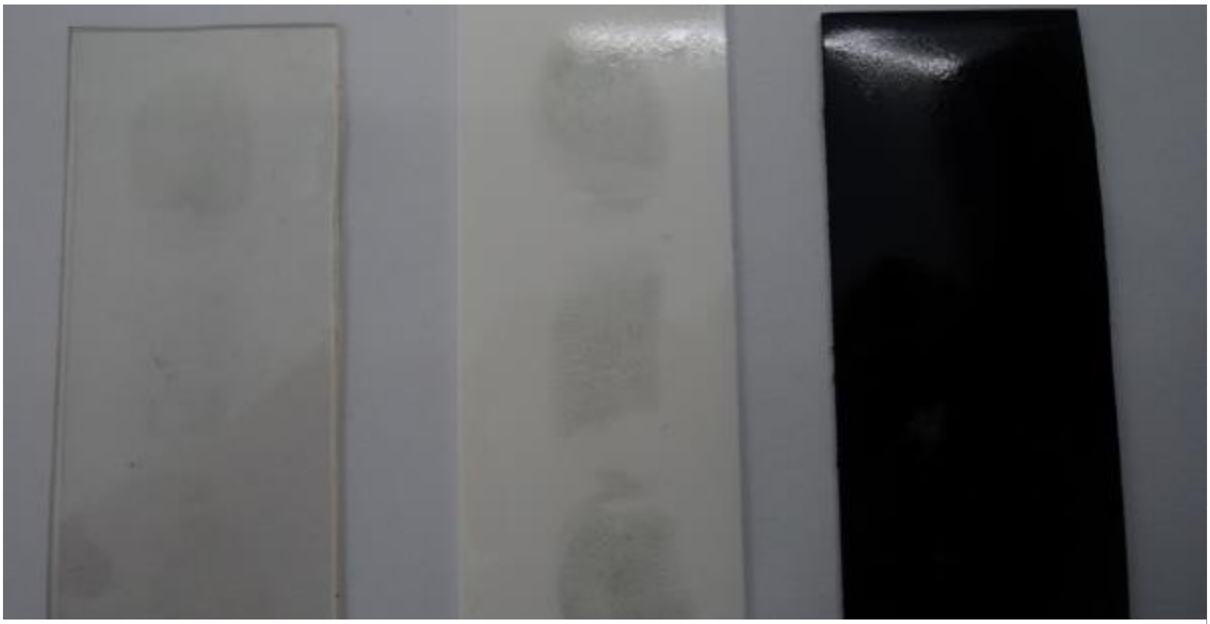


**Figure 33 - From left to right, transparent, white, and black gelatine lifters. The white give the clearest results for copper detection as shown**

What is apparent from this is the clear advantage when the white gelatine lifters are used. This is a result of the dark colours produced contrasting especially well on white gelatine lifters as opposed to the dark black gels or the clear transparent gels.

The same was then shown for detection of lead also:

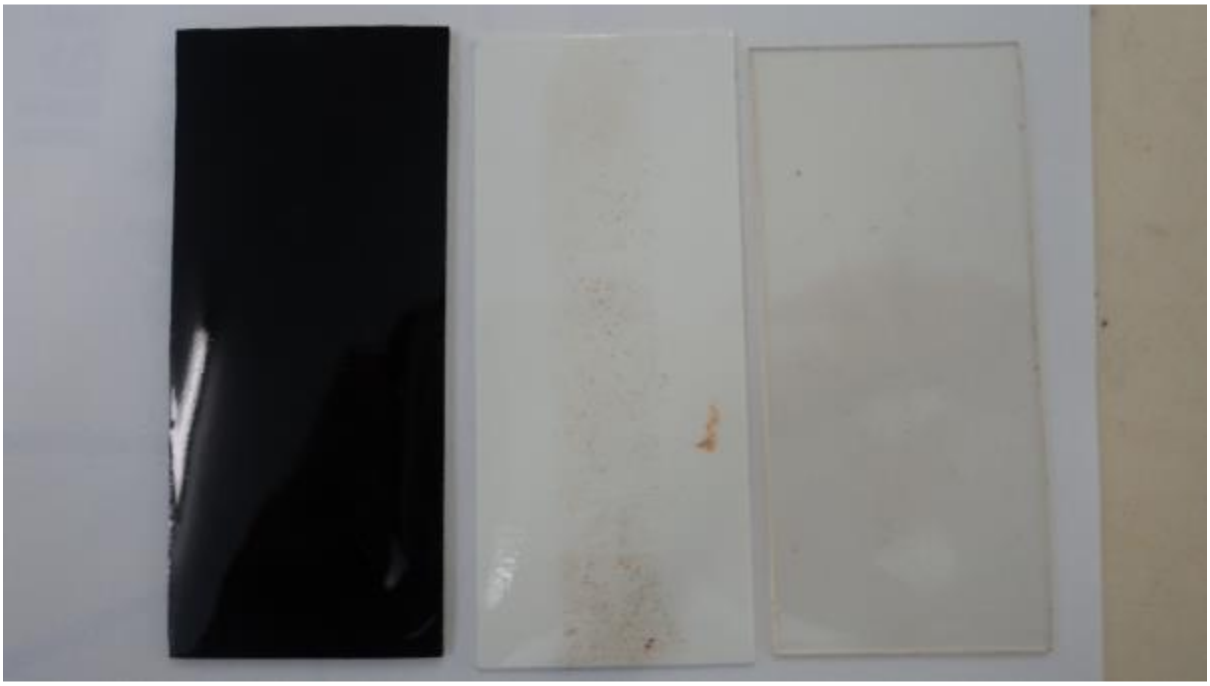


**Figure 34 - Lead is clearly the easiest to detect on white gelatine lifter**

### 3.3.2 Washing hands

It stands to reason that there will be occasions where a potential thief will wash their hands between stealing a metal and being analysed. As a result, determining if washed hands will still retain traces of copper and to what extent this happens is important. The first step of this process was rinsing the hands in water, and then then leaving various time periods between this washing and development using gelatine lifters and rubeanic acid. In this instance there is minimal differences in time periods up to 6 hours.

**Figure 35 - From left to right hands left for 1, 2, 4, and 6 hours after rinsing before development**

For longer periods of time, leading up to overnight, there have been instances of detection however this is not consistent and appears dependant on how many other materials have been handled between washing and detection.

This is also the case when hands are more thoroughly washed with soap and water. Whilst on occasion some details can be picked up this is by no means consistent, with this varying between individuals. With an increased level of washing, there is a reduced chance of detection of copper on the surface of the skin. With mere rinsing of the hands, the level of detail remains of a good standard. However when soap is introduced, this reduces, and whilst this can sometimes yield fingerprint detail of a reasonable quality, this is rare.

When a hand was not washed with water and instead wiped with a cloth, there is still clear detection of copper traces. On occasion this can be more ‘smudged’ than usual however in general will still yield the usual detail:

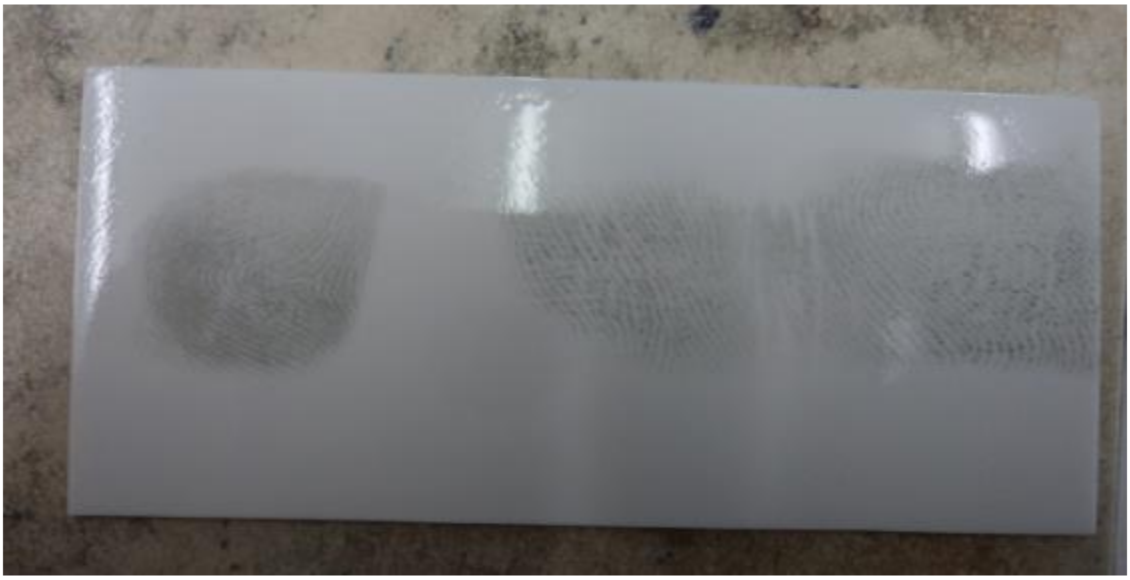


**Figure 36 - Still some good detail when hand is wiped on a cloth after contact**

These limitations are certainly worthy of analysis, however it is also clear that the technique itself appears most suitable for a potential criminal caught fairly soon after a crime has been committed and hence the likelihood of the hands being washed in the meantime is minimal regardless.

With lead, the characteristic orange/brown colour was still visible after rinsing the hands when analysed within an hour after said rinse. As time progressed from this point however, the likelihood of detecting lead on the surface of a person’s skin decreased, and there was no detection after being left overnight. The level of detail possible from this technique also decreased with the addition of washing.

When hands were washed with soapy warm water there was no detection as the lead residues appear to have been wiped off in this instance.

In the case of hands being wiped with a cloth, results similar to that with copper became apparent, with the characteristic orange/brown colour still appearing albeit with decreased detail. Instead the presence of lead on the skin was indicated by a smudged appearance of the colour in question.

### 3.3.3 Detection after a period of time

With simple washing, i.e. rinsing in water, copper traces can still be detected on the hands up to 24 hours after the initial contact. Following on from this, the research aimed to uncover if this was also the case when not washed and if there was a considerable difference.

When hands are not washed copper was clearly being detected and yielding excellent detail even 24 hours after the initial contact. Any longer than this was not attempted and appears an unrealistic timeframe in which a person would not wash the hands regardless. Handling of general materials does not seem to have a great deal of effect in terms of reducing the amount of metal that can be detected in this manner. This is likely a result of the reaction occurring between the rubeanate solution and sweat constituents, and the product of this reaction being difficult to remove via contact with general materials.

The results obtained for copper and its ability to remain on a skins surface are aligned with what was discussed earlier. When washed with just water, it appears that whilst soluble Copper (II) is washed away and therefore not detected from this point, the elemental Copper (0) remains and can still be detected up to a day later. This can be removed by more thorough washing however, ie using soap and warm water. There are two theories as to where the Copper (II) is from that is detected. Either it is oxidized copper present on the surface of the metal itself, or some of the elemental copper transferred to the hand when contacted, which is then oxidized by some of the fingermark residues themselves. Copper is still being detected when a hand has been immersed in water for 1 minute, so it is apparent that some of the copper is still being retained regardless, and so not all of the copper (0) is being oxidized if this is the case. This was true of copper, and also both of its alloys brass and bronze, as these yielded identical results to the copper throughout.

## 3.4 Rubeanic acid's interaction with other metals

In 1926 Ray and Ray reported that rubeanic acid formed complexes with metals other than copper, stating that complexes can form in the presence of both nickel and cobalt[108]. This was expanded on further in 1961 by Ray and Xavier who discussed rubeanic acid's interaction with several other metals[109]. As a result of this, the technique described at the beginning of this chapter was investigated with metals other than copper alloys and lead. Some of these were analysed due to their threat of theft, such as silver, whilst others could help develop a fuller picture of the sensitivity of the reaction. The process itself was identical to that with lead detection unless stated.

### 3.4.1 Silver

A silver ring was handled for 1 minute, before analysis. This yielded no markings upon treatment with rubeanic acid, even after exposure to UV light.

### 3.4.2 Nickel

A nickel based spatula was handled for 1 minute, before analysing with rubeanic acid and UV exposure. This gave no markings. However previous work done by Ray and Ray, had noted nickel rubeanate required a strong ammonniacal solution to yield a characteristic pink/red colour. As a result, after being treated with rubeanic acid solution, and left exposed to UV light the gel was then dipped in a solution of concentrated ammonia. This immediately gave a pink marking (figure 37), which then began to turn darker as time passed. A blank was completed with no metal contact, to confirm this was not merely a reaction between nickel, ammonia, and rubeanic acid, which yielded no formation of colour. Whilst nickel is not a hugely common material in a heritage crime context, it is nonetheless important to understand the capabilities of such a process, and shows its potential for uses even outside of heritage crime. Coins can be nickel plated for example. It is also present in several alloys, which could be of relevance to heritage crime, white gold for instance.

**Figure 37 - Nickel detection from the thumb**

### 3.4.3 Stainless steel

A Stainless steel plate was held for 1 minute.  Upon spraying with rubeanate solution there was slight development of a blue/black colour, similar to copper.  This was then left overnight in the presence of UV light to see if this darkened further.  There was slight colouration, but this was not as dark as with copper.  Iron was then analysed in the same way to determine if what was being detected by the rubeanic acid was the iron in stainless steel, or another component such as chromium.

### 3.4.4 Iron

Iron fillings were touched for 1 minute.  Upon treatment with rubeanic acid, there was no formation of any characteristic colour.  This suggests that what is forming above is not the iron present in steel, but instead another metal that will be present in more trace amounts, such as chromium, aluminium, or titanium.

### 3.4.5 Tin

This metal was chosen for analysis as a result of its presence in the bronze alloy.  It aimed to confirm that copper alone was that being detected when the alloy was being analysed on the surface of the skin.  A piece of tin wire was handled for 1 minute before analysis.  This gave no development under any conditions, even after treatment with both UV and ammonia.  Therefore it can be concluded that in copper alloys, it is copper alone which is contributing to the formation of the characteristic blue/black colour.

### 3.4.6 Aluminium

This was analysed as it is an abundant metal, both individually and as part of an alloy.  Hence, this has the potential to have been contacted by countless potential thieves.  This gave no development however, and can thus be discounted as a possible contributor to formation of a precipitate on the gelatine lifter.

### 3.4.7 Gold

Due to its relevance to a heritage crime scenario a gold ring was analysed.  This gave no results on a ‘natural’ fingermark, however when a fingermark was loaded with sebaceous material and exposed to UV light there was slight detection and the appearance of a blue/black colouration similar to that of copper.

**Figure 38 - Slight appearance of colour when detecting gold on the surface of the skin**

Based on the work outlined above, it appears that rubeanic acid is most sensitive using this technique to copper and its alloys, lead, and nickel. Copper presents itself as particularly sensitive, a view which was also backed up by Ray and Xavier, who discussed the comparative levels of sensitivity and concluded copper to be able to be detected to levels of 0.0190ppm[109].

## 3.5 Detection limits and false positives

As criminals become more adjusted to improved forensic methods, there is the need to test the limitations of developed methods, and resultantly tackle these issues by progressing the work further.  One such issue which was raised was the potential for a criminal to be wearing gloves when stealing metal, which is a common tactic employed by thieves.  Whilst the work done thus far would still have great use with regard to opportunistic crime, ie stolen with little to no plan ahead of time, a more organised group are far more likely to take action to avoid leaving fingerprints at the scene of a crime by covering them.  As a result of this, the research aimed to see if a copper and lead traces could be transferred to gloves (and other surfaces) in a similar manner to that in the case of the skin.

A copper pipe held for 1 minute whilst wearing woollen gloves.

Figure 39 - Gloved hand holding copper pipe, prior to deposition

Then the outside of the glove was pressed against the surface of the gelatine lifter before being sprayed with rubeanate solution. This gave the clear blue/black markings characteristic of coppers presence.

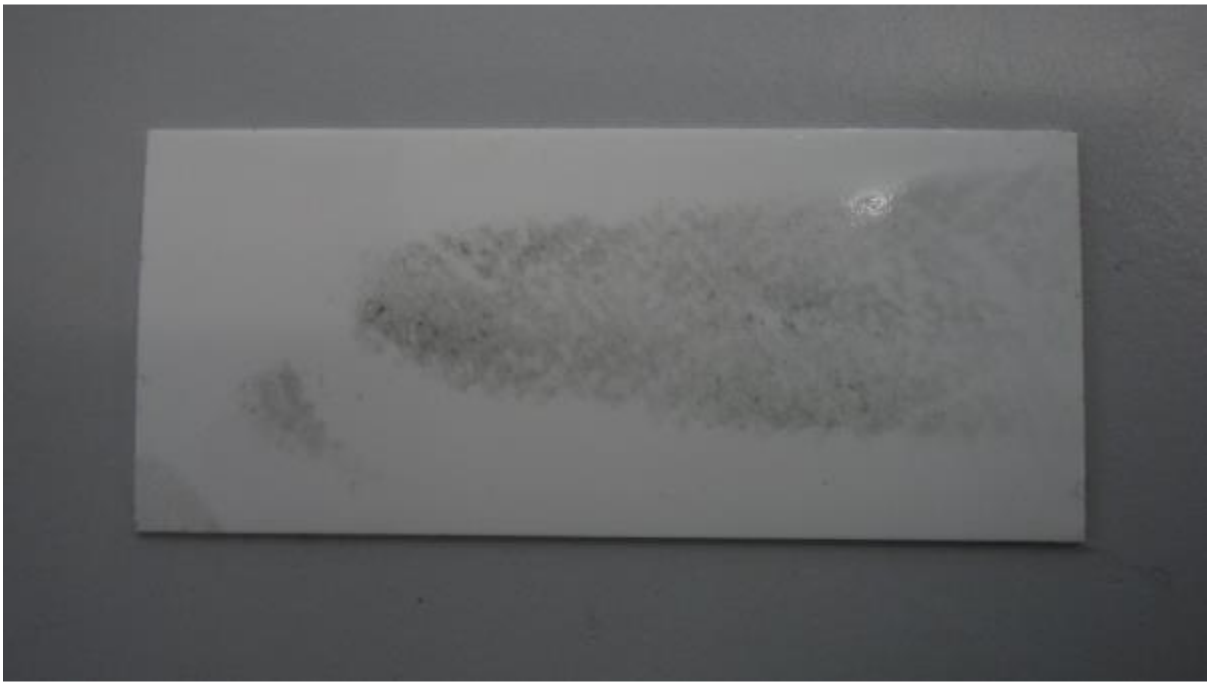


Figure 40 - Copper detected on surface of a woollen glove used to handle copper

The same was true for both brass and bronze. Whilst there is no great detail as is with the case when lifted from the surface of the skin, the technique can still confirm that a material has had recent contact with copper or one of its alloys.

This process was then attempted with lead.

**Figure 41 - Lead detected from surface of a glove when lead handled**

This was harder to ‘map out’ than copper and the appearance of the orange/brown colour was not as consistent, albeit still proved contact had occurred.

Metals that were more difficult to detect and appeared less sensitive to rubeanic acid such as nickel, or gold were not detected in any circumstances using this method, most likely as a result of this reduced sensitivity.

The same was attempted with other materials, such as a lab coat, a pair of leather gloves and a silk scarf. This consistently gave results matching that of the woollen glove. It was shown that trace copper residues can be transferred and developed with reasonable efficiency from fabrics.

The same process as above then attempted with latex gloves, which yielded identical results.

Following from the above, other relevant materials were also analysed to see if they retained their traces of said metals.  In practicality, stolen metals will in all likelihood be transported in a bag, and so the copper pipe was placed on the surface of a polyester rucksack before lifting.  The results outlined below were obtained:

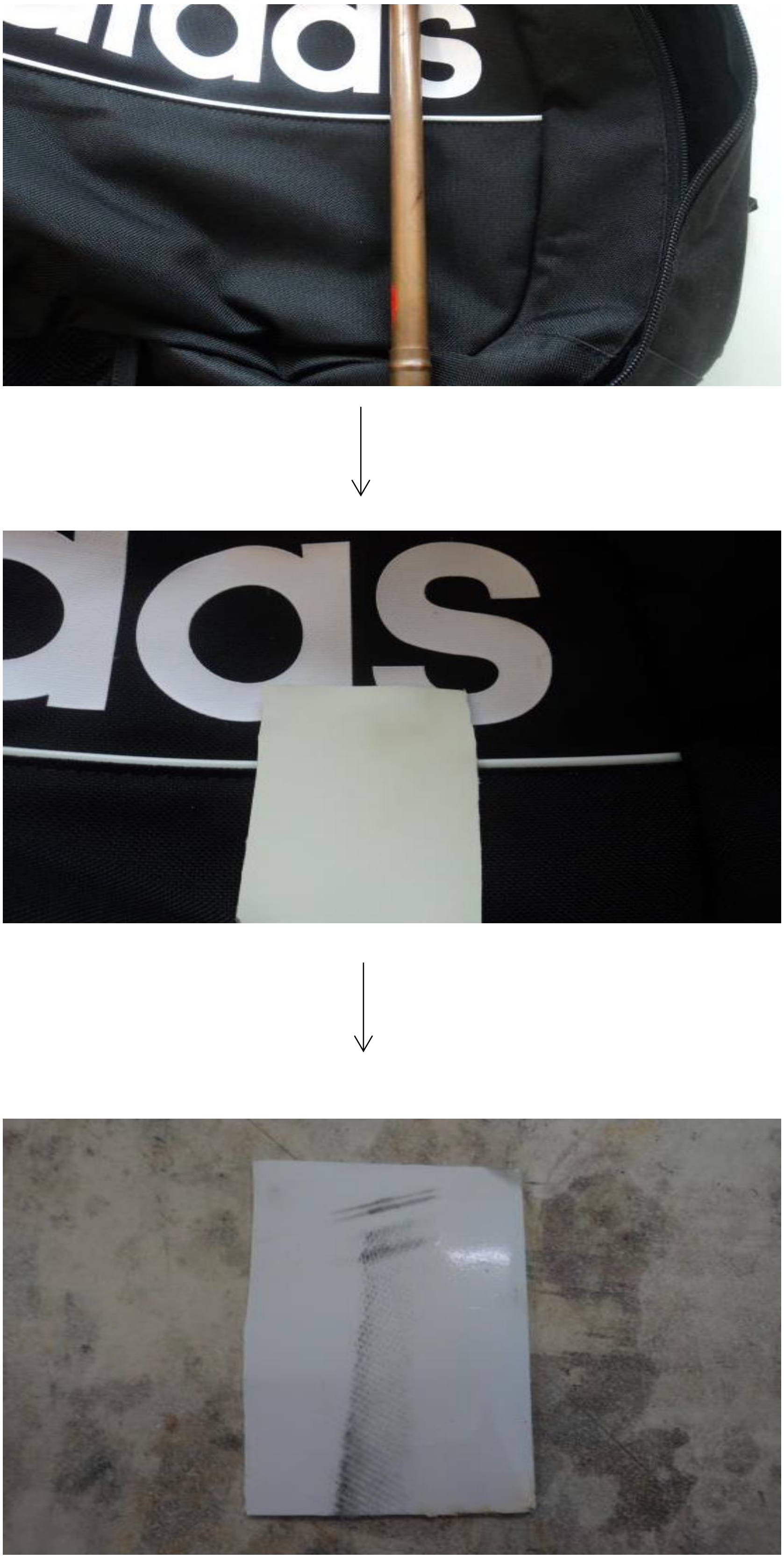


**Figure 42 - Copper traces lifted from polyester rucksack. There is slight detail of the design itself also shown**

This has practical relevance, as metals could potentially be stored inside such a surface or transported in this manner. Because of this, proving it has had contact with a metal is another potential addition to the evidence against a metal thief.

The success of these techniques was limited to copper, brass, and bronze rather than other metals, again as a result of increased sensitivity towards the rubeanate solution.

When a bulk amount of metal is stored, it will theoretically be on another surface. As a result the process was then attempted, with regards to lifting traces of copper from a laminate desk. This also gave detail in a manner similar to that with the glove, however it was more difficult to map out. When the metal was on a similarly hard surface it appears that not all will be in contact or transferred to the other material. As a result, only parts show the characteristic blue/black colour.

**Figure 43 - Gelatine lifter, post lift from laminate desk**

Another material analysed was cardboard, with the thought that this could be another material used to transport stolen copper from one site to another. This gave clear markings showing the blue/black of copper rubeanate. The rough texture of the cardboard was apparent by the way the copper was mapped out, with some areas slightly more raised, and hence more in contact with the gel as is shown.

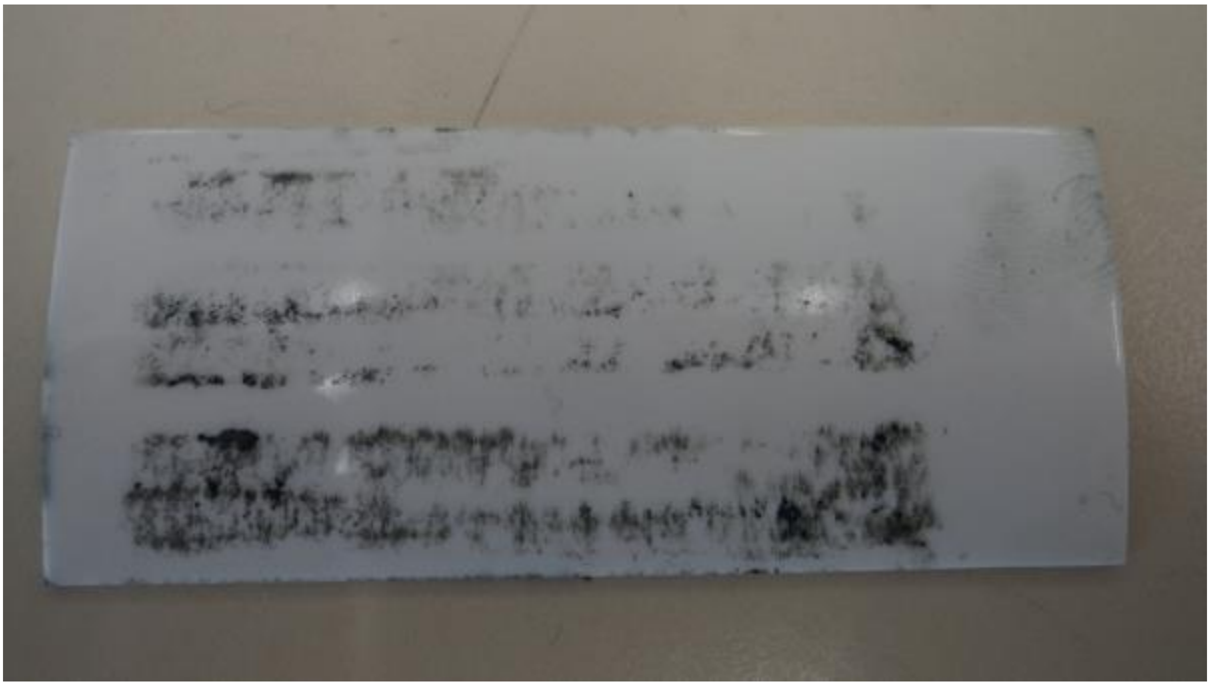


**Figure 44 - Cardboard box containing copper analysed**

The final material analysed in this manner was the bottom of shoes. It makes sense that copper would be transferred onto the clothing work by a thief, and standing on the metal itself when stealing and loading into for transport is most certainly a possibility. As a result, the sole of a shoe was analysed. Here, one of the greatest problems concerning using the gels in this manner became apparent. Because the lifters themselves are very adhesive they not only lift the material of interest ie the trace metal. They also lift dust and dirt, of which there is an abundance on the sole of a shoe.

The issue itself can be seen below:

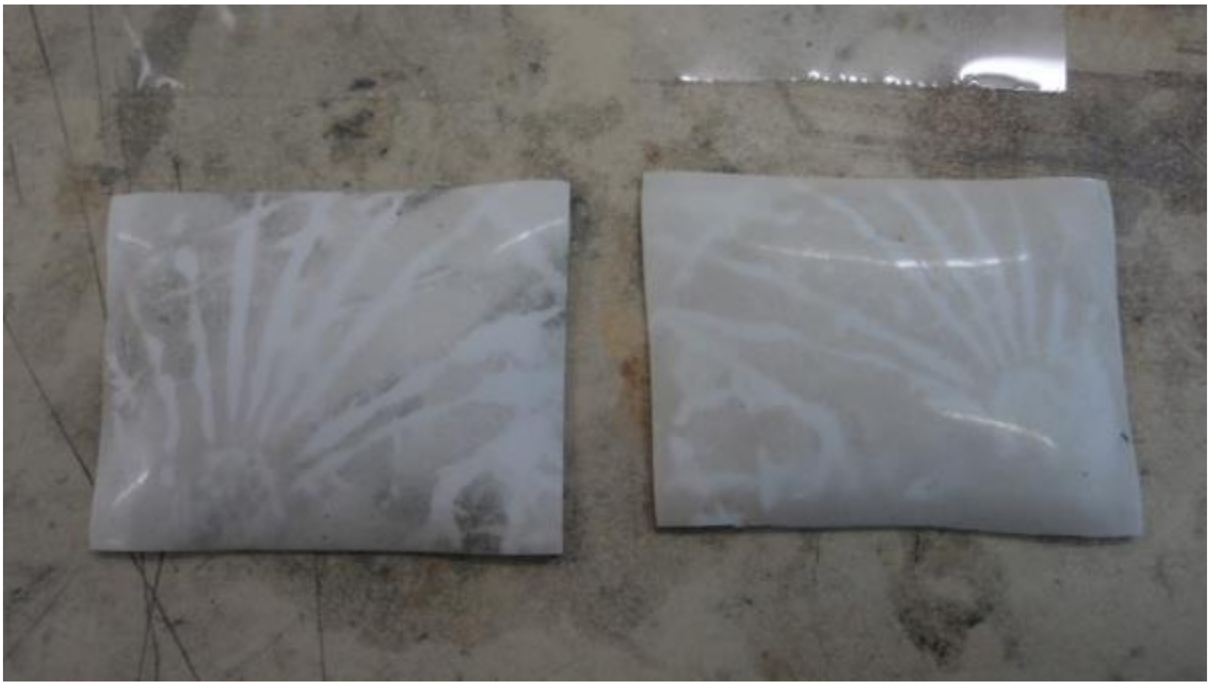


Figure 45 - Copper from sole of shoe on the left, in contrast to no copper on the right.

Whilst there are differences, with the blue/black apparent at points, these are harder to discern than on surfaces with no dust or dirt on them. Despite this, there are still differences between the two, and this could potentially be another piece of evidence that could be used to uncover a potential metal thief.

For lead, because of the process being far more difficult to 'map out' harder surface materials such as the laminate desk did not yield any results, and this suggests either less is transferred to the surface of the desk or what is transferred is not as easily detected.

The results discussed highlighting how copper traces (and lead from certain materials) give an insight into the process that is occurring. When detecting from the hands it is assumed that the fingermark residues on each individual will be having an effect on the cuprous ions transferred.

Whilst this is likely the case, the results outlined in this work have shown that this is not necessarily a mandatory feature of the technique. When copper (or its alloys) are being left in contact with materials which will not have these fingermark components, the traces of metal are still being both transferred onto the surface, and then ‘lifted’ via the gels. This in turn can be detected via the rubeanate solution. What this confirms is that elemental copper is being transferred as well as the cuprous ions, and this can still react with the solution to form the copper rubeanate which is visualised. This elemental copper has either oxidised prior to lifting when on the surface, or there is an oxidised surface layer on the copper which is transferred onto the surface being analysed and can then be lifted using the gels. It could also be a combination of both. What is imperative, regardless of which pathway has been taken by this reaction are the positive results, which this yields. When used in conjunction with the ability to detect said traces on the skin, this emphasises real possibilities for this technique to detect a metal thief non-invasively.

### 3.5.1 False positives

Because of the high sensitivity of the technique the problem regarding false positives needed to be addressed. If a person was proven to have recently handled copper using this technique, an obvious defence would be that they had simply been handling coins made of brass. Hence comparing how the rubeanate solution reacts with coins when handled, and how this differs from other materials that could be stolen was of great importance. A coin was held between the thumb and forefinger for 1 minute. When placed on a gelatine lifter and treated with rubeanate solution this gave clear detail of the coin itself, with the design on one side evident.

**Figure 46 - A 2p coin that was held, shows the clear pattern of the design**

Comparing this to when a piece of sheet metal is handled (figure 47).

**Figure 47 - Copper sheet handled for 1 minute**

The difference is notable. In the case of a flat surface, there is clear the fingerprint detail, however when the metal is patterned this is detected on the skin as well as the fingerprint itself. This has clear relevance to metal that is stolen at heritage sites, as this will commonly be patterned and hence be able to be matched in the same way the coin has been above.

The above was when a single coin had been held at a specific point, so to further confirm that false positives will be a minimal issue a large group of coins was held. Numerous 2p coins were handled and sorted for 1 minute, to prove sorting coins would not be an effective argument against this technique. Whilst not showing the same level of detail as when a lone coin was held, there were marked differences between that and when a simple pipe, or solid surface were touched.

Figure 48 - 2p coins handled before skin detected.  This gave circular markings where these coins had been handled.

This is where the ability of this technique to chemically map where a person has had contact with copper is of great importance.  Whilst proving a person has had recent contact with copper is hugely important, progressing this to giving an insight into the particular piece which has been held, or touched is highly desirable.  This ability to link precise distribution to a stolen artefact has obvious potential with regard to handling heritage items.

Historic items will have often been subjected to a range of conditions throughout their existence, and as a result will have become weathered over time.  Because of this, the surface is rarely smooth and uniform.  Taking into account the sensitivity of the rubeanate procedure, it was believed that irregularities in the surface of such pieces could be ‘mapped out’ via the formation of the precipitate on the gelatine lifters.  A bronze statue (The Watchers) was touched for 30 seconds, before the hand was analysed for copper traces.  Upon treatment, the following results could be seen when focusing on the thumb.

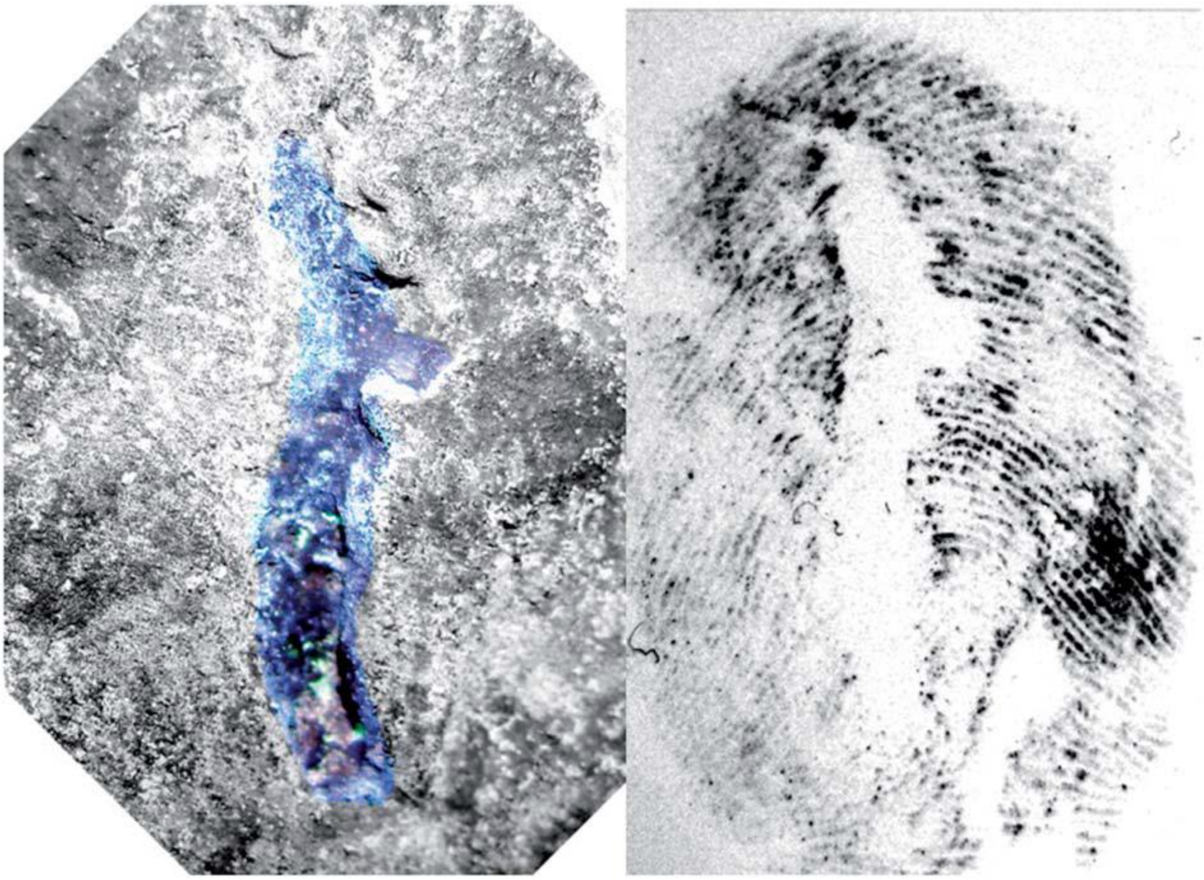


**Figure 49 – (Left) A deformation (ca 2cm in length) in the surface of a weathered bronze statue, highlighted in blue; (right) corresponding image developed from a gel lift off a thumb briefly placed over the area in question.**

It can be observed that slight surface irregularities in the weathered bronze sculpture were mirrored in the distribution of copper on the thumb that touched it, thereby linking that copper presence to contact with the item in question. This technique has particular suitability for items where obtaining fingermarks might be undesirable as a result of its historical and cultural significance. This ability also means the threat of a 'false positive' can be negated in many situations, as a piece will have a unique design, which in turn can be analysed via the process outlined.

Because of the high levels of sensitivity this process has shown, it was important to show that the issue of 'false positives' is easily overcome.

In order to confirm the lack of false positives, firstly 10 individuals hands were analysed who it was known had no copper contact within the last 1 hour. The hands were also thoroughly washed beforehand. None of these showed any signs of copper contact. In addition to this, another 10 individuals were analysed for copper contact at a random interval during the day, to see if there were signs of any residual copper contact with coins for example. None of these showed any sign of copper contact. Hence if there were clear markings from someone suspected of stealing copper or lead, it can be deemed reasonably likely that they have handled the metal in question.

The technique outlined here has obvious potential in terms of helping to examine those suspected of stealing metal. The process can link an individual to a particular metal based on the colour of the developed handprint (or fingerprint) and the pattern of the metal traces distributed across the surface of the hand (or finger). The process can be used either on site using the spray solution, or transported back to a laboratory environment and examined at a later date, due to the traces remaining on the gels surface for a significant amount of time. It can continue to work after light washing, and when the hand is analysed up to a day after initial contact. The process has worked with every donor (50) tested during the course of this research, albeit there is occasional different intensities of the markings developed. This is most likely a result of rubeanic acid interacting with fatty acids present in fingerprint residues in different ways depending on the types of these acids. Each individual will have varying amounts of each fatty acid due to differing diets or their own health, age, or gender and hence their hand or fingerprints will interact with the rubeanic acid solution differently[80].

With regards to this research, what is most promising is the level of detail that can be mapped out via said process. As a result of this detail there is great potential within heritage crime scenarios. An obvious example is the opportunistic theft of small, high value antique items. It is unknown exactly how many heritage offences such thefts account for, but those which do occur are likely to be of great value due to the very nature of the crime. What is also notable with this type of crime is the difficulty in tracing the perpetrators and eventually finding the stolen metal. It is believed that the introduction of such methods described in this chapter could potentially make this task far more likely to result in a successful outcome in terms of conviction and discovery of the stolen item.

The work outlined in this chapter involved successfully linking an individual to a specific piece of metal. However the excellent level of detail which could be seen gave credence to the additional research to be discussed in the following chapter. This focused on developing high quality fingerprints from the surface of the same metals, again taking advantage of rubeanic acid's high levels of sensitivity to the surfaces of interest, as well as the suitability the gelatine lifters have shown with regards to this type of work.

## Chapter 4 Non-invasive fingerprint development from copper and its alloys

As has already been discussed, crimes against our sites of historical and cultural significance are on the rise. With metal theft being reported as the main threat there is the requirement for as many techniques to be developed which aim to focus on the detection of the perpetrators of such criminal offences. What is unique about protecting heritage assets however is the fact that maintaining the pristine conditions of a stolen item is as vital as the recovery itself. With this, the need to develop a method of detection that is non-invasive was a key focus during the course of this research. The work in Chapter 3 discussed how the trace metals on the skin can be analysed to link a suspect to an item in question. This process utilized the sensitivity of rubeanic acid to both copper (and its alloys) and lead. The level of detail that this process enabled resulted in further work being completed on non-invasively detecting fingerprints from the metal itself. In the case of analysing the skin, the most likely scenario would involve catching a potential criminal reasonably soon after the offence had been committed. However, to further enhance the possible techniques and methods available to those tasked with lowering the levels of heritage crime, work was also completed in analysing the metal itself for fingermarks and the development of said marks. Whilst such techniques do exist already[100][131] there are none with the prerequisite aim of tackling the issue of heritage crime. Because of this, maintaining a non-invasive nature with any technique developed was a clear priority.

Because of rubeanic acid's high sensitivity to copper and lead, superb detail can be obtained when picking up traces from the surface of the skin. The actual ridges on the hand could be clearly visualised when developed on the surface of the gelatine lifter.

**Figure 50 - Excellent detail that can be obtained from the surface of the skin via rubeanic acid development from copper**

This detail, coupled with the high level of adhesion that the gelatine lifters possess (as is shown later in the thesis, they can lift to a bacteriological level) suggested that they could lift the actual fingermark detail left on said metal in the first place.  Bond et al have reported that the residues present in a fingermark will corrode it, thus oxidizing the surface[102].  As has already been discussed in chapter 3 this oxidation of copper is pushing forward the polymerization of the copper rubeanate, and hence allowing said visualization.

## 4.1 Experimental procedure

Rubeanic acid (0.05g) was dissolved in ethanol (50ml) to form the clear orange solution as before. Metal plates of copper, brass, and bronze were cut to size in order to allow deposition of a single fingermark on each. For analysis of lead, the same lead block as in previous chapters was used. These fingermarks were either natural (ungroomed), sebaceous, or eccrine. Natural prints were prepared by not washing the hands for 30 minutes prior to deposition. Sebaceous prints were prepared by rubbing the hands across the bridge of the nose and the forehead. Eccrine prints were prepared by wearing latex gloves for 10 minutes after washing hands thoroughly. One fingermark was laid on each piece of cut metal, before analysis. The fingermark was laid on the metal for times ranging from 1 second to 1 minute and then left in a set environment for times ranging between 1 minute and 10 days. After being left for this period of time, a gelatine lifter (also cut to size) was applied to the surface of the metal and rolled with a fingerprint roller in order to avoid air bubbles as much as possible. The gelatine lifters were left in contact with the metal (and fingermark) for times ranging between 30 seconds to 30 minutes. This gelatine lifter was then carefully removed before being sprayed with the rubeanic acid solution, using the Ecospray identical to that for the work completed in chapter 3. In this instance, the fine mist produced via use of this spray is desirable when comparing to the ‘dip’ method for the same reasons, and also yielding greater detail. The results with the dip tray can also be streaky, ie leave traces of the orange colour of the rubeanate solution and hence block some visualization. This is not the case with the Ecospray. Upon spraying with the rubeanic acid solution the lifted mark is able to be visualised via the formation of the polymeric copper rubeanate which shows the fingerprint ridges in the characteristic blue/black against the white of the gel.

Both male and female donors were used here, with ages ranging from 19-42.

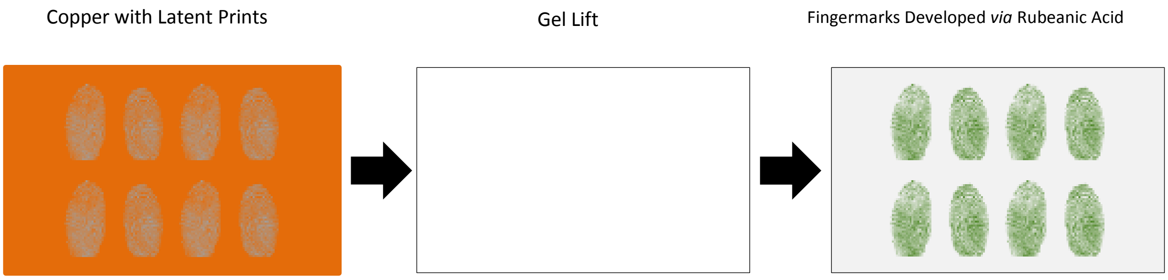


**Figure 51 – Schematic highlighting the technique discussed**

### 4.1.1 The fingermarks interaction with copper and its alloys

Residues abundant in a deposited fingermark are corroding the metal in question, in this case copper and its alloys of brass and bronze. It would be expected that if a gelatine lifter was to be placed on the copper itself, then it would detect the entire surface, and give blanket coverage across the gel in the characteristic blue/black colour. However what was noted is that whilst this does occur eventually, for it to do so the lifter must be in contact with the surface of the metal for a reasonably lengthy period of time (1+ minute generally). This is opposed to when lifting from the surface of the skin itself in the work discussed in chapter 3, where once copper is held, the gelatine need only be in contact with the hand for one second and clear ridge detail in the blue/black colour of copper rubeanate becomes apparent.

The reaction scheme for this process states that the $Cu^{2+}$ is what is reacting with the rubeanic acid and forming the blue/black polymeric product. Whilst after a period of time the lone metal can produce the colour when in contact with the gel, once there is contact with the fingermark residues this process appears to be accelerated.

As a result of this, when a fingermark is deposited onto the metal surface the reaction occurring oxidizes the copper, most likely due to a reaction with various constituents of the fingermark residues, including salts and various amino acids. Hence, when the gelatine lifter is carefully placed on the metal with a fingermark on it, the mark itself is becoming apparent before the ‘background’ of the more general copper which is also in contact with the gel.

This process is outlined below:

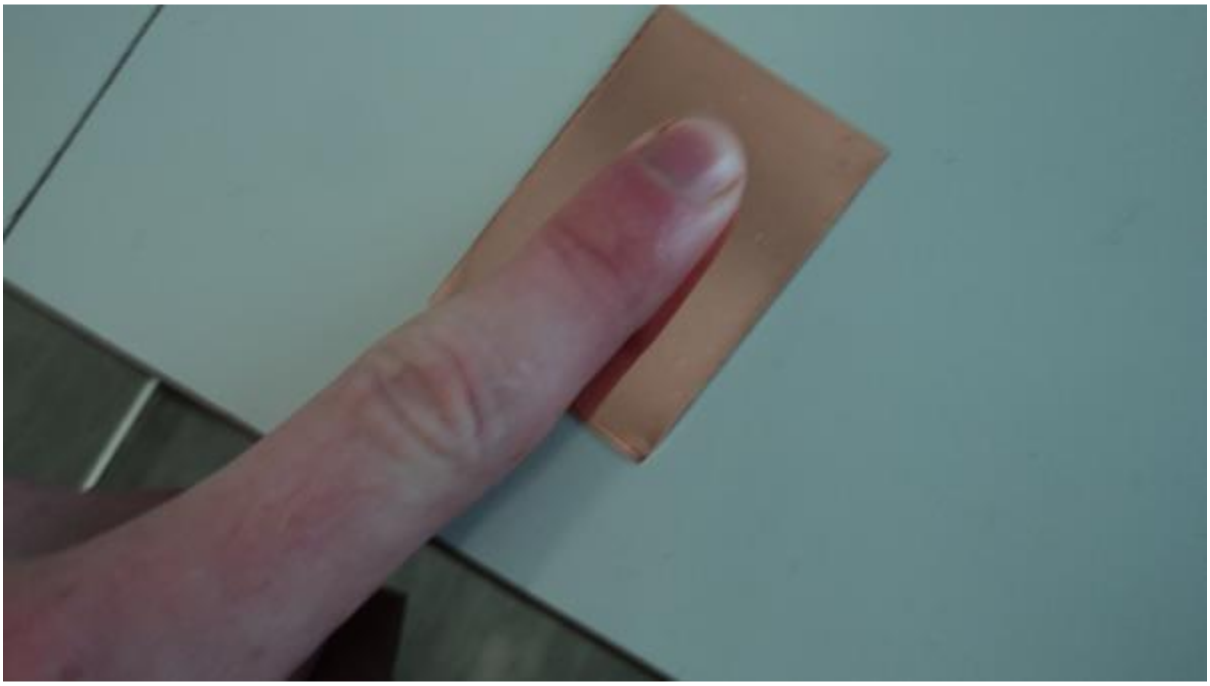


**Figure 52 - Fingermark deposited on copper plate**

**Figure 53 - Gelatine lifter placed over the fingermark on the copper**

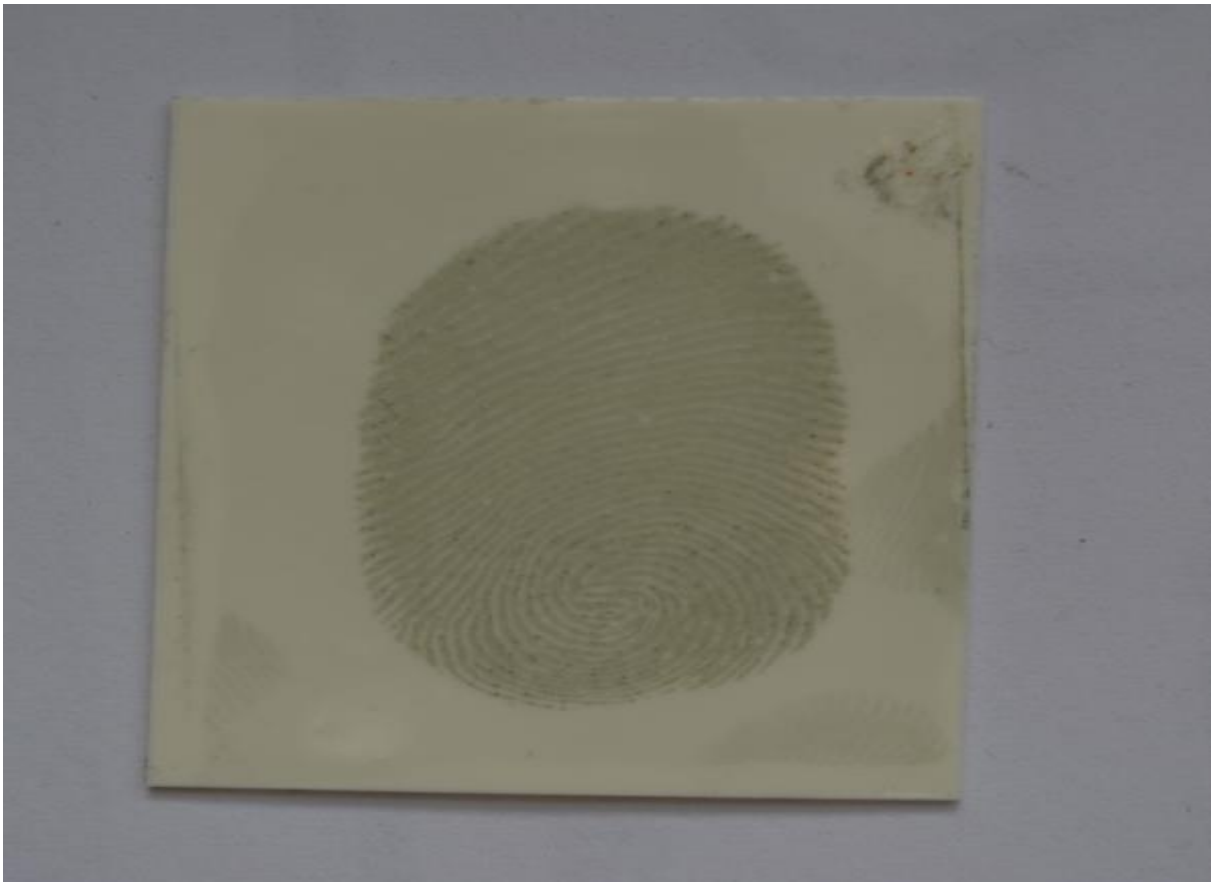


**Figure 54 - Excellent ridge detail is obtained once sprayed with rubeanic acid solution**

As with the work in chapter 3, there was little/no difference between the results obtained with copper, brass, or bronze. Unless stated otherwise, the work was completed with copper, due to greater availability and higher threat of theft at heritage sites. Each technique was attempted on both brass and bronze to ensure there was no difference between the results obtained here and with copper. There was no difference unless stated.

This research highlights great development with regards to the techniques available involving non-invasive detection of deposited fingermarks. This is of great importance to items with a significant history ie those which are commonly found (and stolen) at heritage sites. Whilst this technique shows considerable promise, there were various issues that needed to be addressed, which would help to optimize said procedure.

## 4.2 Results and discussion

One of the greatest problems facing this technique was ensuring the timings could be perfected, so that there was no ‘background’, which hindered the ease of visualization. Whilst a fingerprint can still be seen with reasonable detail when the background is apparent, the contrast against a white background is much preferred.

**Figure 55 - An example of how background can affect fingerprint visualization even when there is a good quality fingerprint**

The background becomes visible when the gel has been in contact with the metal for a prolonged period of time. In order to establish the exact point this happens, a fingermark was deposited onto the surface of copper and brass, before being left for times ranging between 30 seconds and 30 minutes. From left to right, the times the gelatine lifter was left in contact with the copper was:

- 30 seconds
- 1 minute
- 2 minutes
- 5 minutes
- 10 minutes
- 15 minutes
- 20 minutes
- 30 minutes

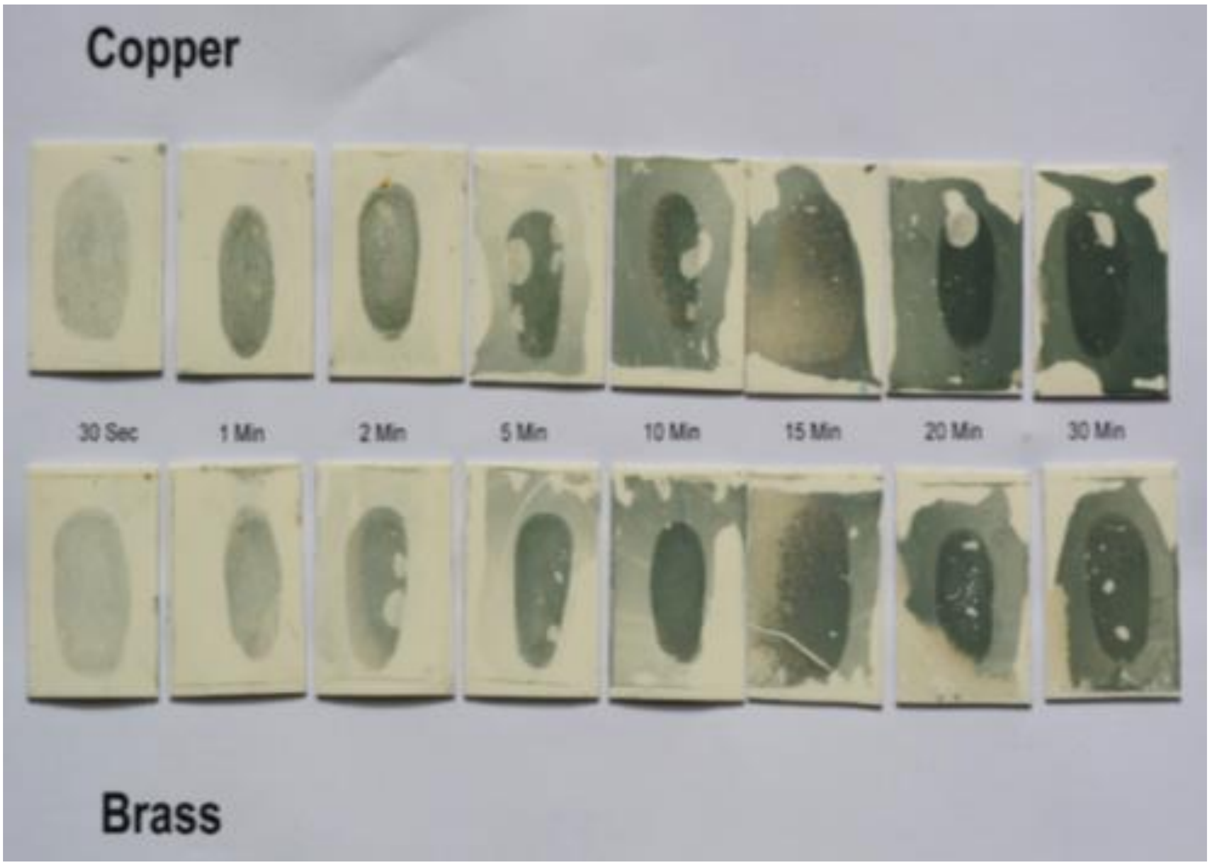


**Figure 56 - Background appearing as the gel is in contact with metal for longer. Times here range from 30 seconds (left) to 30 minutes (right)**

Background is starting to appear between 5 and 10 minutes, with some detail still apparent however. There is minimal detail still visible after 20 minutes of contact, however from 30 minutes onwards there is almost no visualization of ridge detail possible, as there is too much background being detected and hence the information of interest is being blocked. After 30 seconds of contact the fingerprint developed is slightly 'lighter' than would be preferred, and hence the optimum time of contact appears to be between 1 and 2 minutes. Two minutes was used as the 'standard' from this point when optimizing the rest of the steps within this process. This was to ensure as much detail as possible was picked up, whilst maintaining as slim a chance as possible of there being considerable background apparent.

The next variant was not so much determining an 'optimum' but instead confirming that the technique will continue to work when the deposited mark has been left on the metal for a prolonged period of time. This is vital, as the likelihood of discovering a freshly laid print is unlikely.

Times were staggered up from a very short period of time as a means of comparison. Fingermarks deposited on copper and left for:

- 30 seconds
- 1 minute
- 2 minutes
- 5 minutes
- 10 minutes

All of which gave near identical results, yielding faint, but clear fingerprint development.

**Figure 57 - An example of the reasonable detail obtained after a short period of contact**

This is interesting as it highlights that the corrosion of the metal via the fingermark residues is occurring almost instantaneously. Obviously however, the chances of discovering and being able to analyse a piece of stolen metal within this short timeframe is minimal. As a result, longer periods were allowed to elapse and the same process undertaken. These were at the following intervals:

- 20 minutes
- 30 minutes
- 1 hour
- 2 hours
- 6 hours
- 12 hours
- 1 day
- 2 days
- 1 week
- 1 month

All were left in the open laboratory environment for the given period of time. At the 20 minute mark was where the print began to appear darker, and made for a better contrast against the surface of the gel. All time periods between 20 minutes and 2 hours yielded near identical results. This was a clear dark mark contrasting against the whitened background of the gel.

**Figure 58 - Excellent levels of detail can be obtained after longer contact time**

For periods of time over this, the results were still positive; however there was a deal of inconsistency with the darkness of the print which could be developed. This appeared to vary day to day, where on some occasions the developed print was appearing as good as any other time, however on others was only yielding faint markings with less detail than when left for a shorter period. This was despite them both being left in the laboratory on the same bench. As a result of this, it was deemed that temperature or humidity is likely having an effect on how well the fingerprint is being developed. More work was done on this, and will be discussed later on in this chapter. What was also noteworthy was the appearance of the fingermark on the metal itself for those left for longer periods of time.

Some areas of dark ridges were clear, most likely a visible representation of the oxidation that is occurring on the copper surface at this point. When this had transpired the amount of material from the fingermark which could be 'lifted' was reduced, and this was when the developed print appeared lighter in colour and was hence more difficult to visualise (especially when background also made itself apparent). This is another factor which will be altered depending on the environment in which the metal is discovered. Warmer, more humid conditions for example will speed up this oxidation process on the metal, and form the precipitate on the surface of copper which proved more difficult to develop. This may just be a limitation of the technique, however work was done analysing if placing a piece of metal into a certain environment **after** it had already been exposed to said conditions could improve the potential results which the process could yield.

What is without doubt however is the potential such a technique has showed thus far. The clear ability to detect natural fingerprints with no chemical contact on the metal in question would be hugely desirable under numerous circumstances, most notably for the course of this research as part of the arsenal for those tasked with lowering levels of heritage crime.

### 4.2.1 Natural fingermarks comparison to eccrine and sebaceous

The same process as above was also completed with eccrine and sebaceous fingermarks. It is understood that rubeanic acid will interact more easily where there is a greater amount of amino acids and salts, compared to the eccrine print which has a much greater content of water, which is unreactive with the rubeanate solution here.

Fingermarks were deposited on the surface of copper which were natural/ungroomed, eccrine, and sebaceous. These were all then analysed using the rubeanic acid solution.

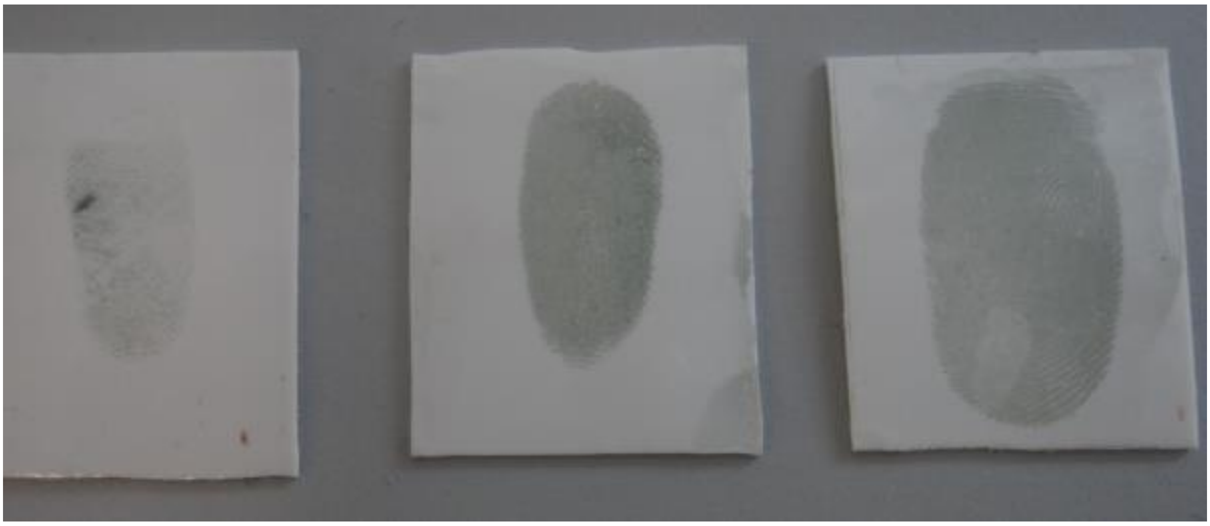
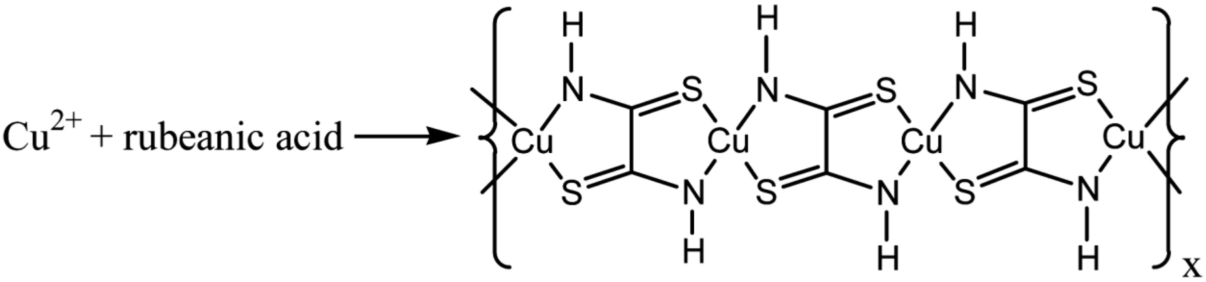


**Figure 59 - From left to right, Eccrine, natural, and sebaceous fingerprints developed**

The results here are as expected. It is known that the reaction occurring is as shown below:



**Scheme 1 – Copper(II) reacts with rubeanic acid to yield a polymeric structure**

Sebaceous and natural, ungroomed fingermark deposits are far more likely to cause the reaction in the first step of this process (oxidizing copper), thus ensuring the formation of the copper rubeanate. Eccrine markings will have less of these substituents, i.e. fatty acids and chlorides, which are appear vital with regard to the reaction occurring. What the results above suggest, is that the material in a natural fingermark is sufficient to yield almost identical detail to when ‘loaded’ sebaceously. However, this is not necessarily the case. Each individual will have a different ratio of fatty acids in their fingermarks makeup. As a result of this each person’s fingermarks may interact differently. Hence a group study was completed, comparing 10 individuals sebaceous, eccrine, and natural fingermarks in the same manner as that completed above. The results were again graded using the Bandey scale. This could be deemed a reasonably subjective method of approach and so an example of each grade is shown below as a point of comparison for future group studies discussed within this chapter.

**Figure 60 - Grade 0 (no development)**

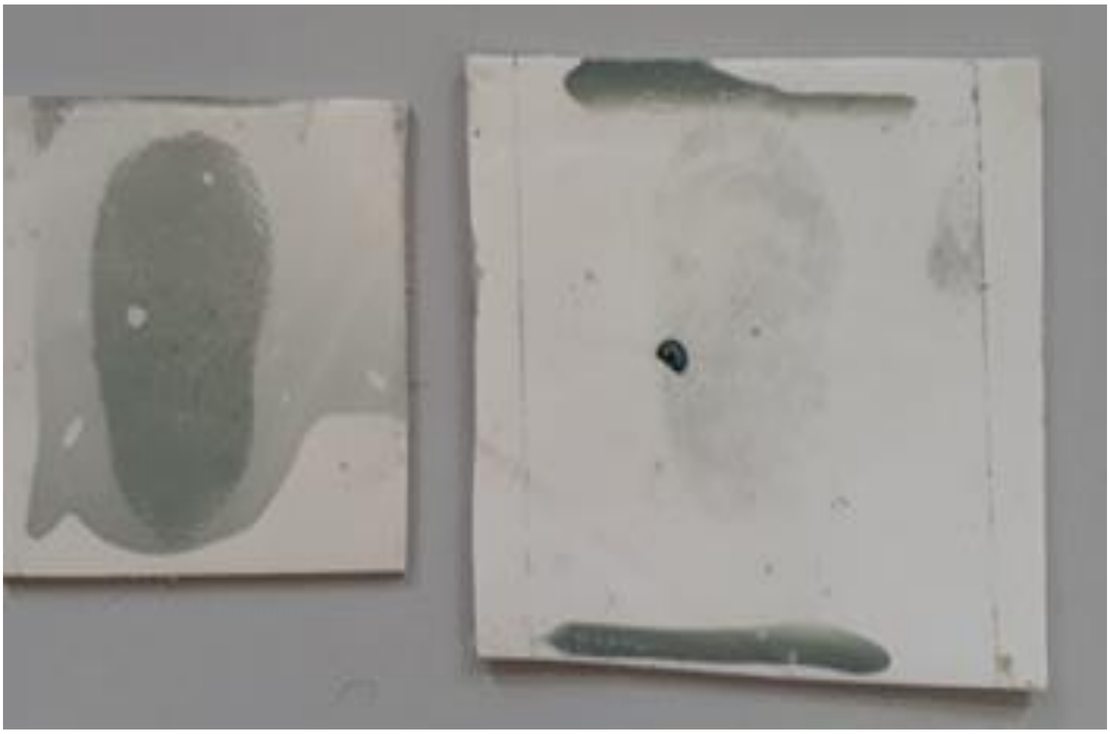


**Figure 61 -Grade 1 (signs of contact but <1/3rd of mark continuous ridges**

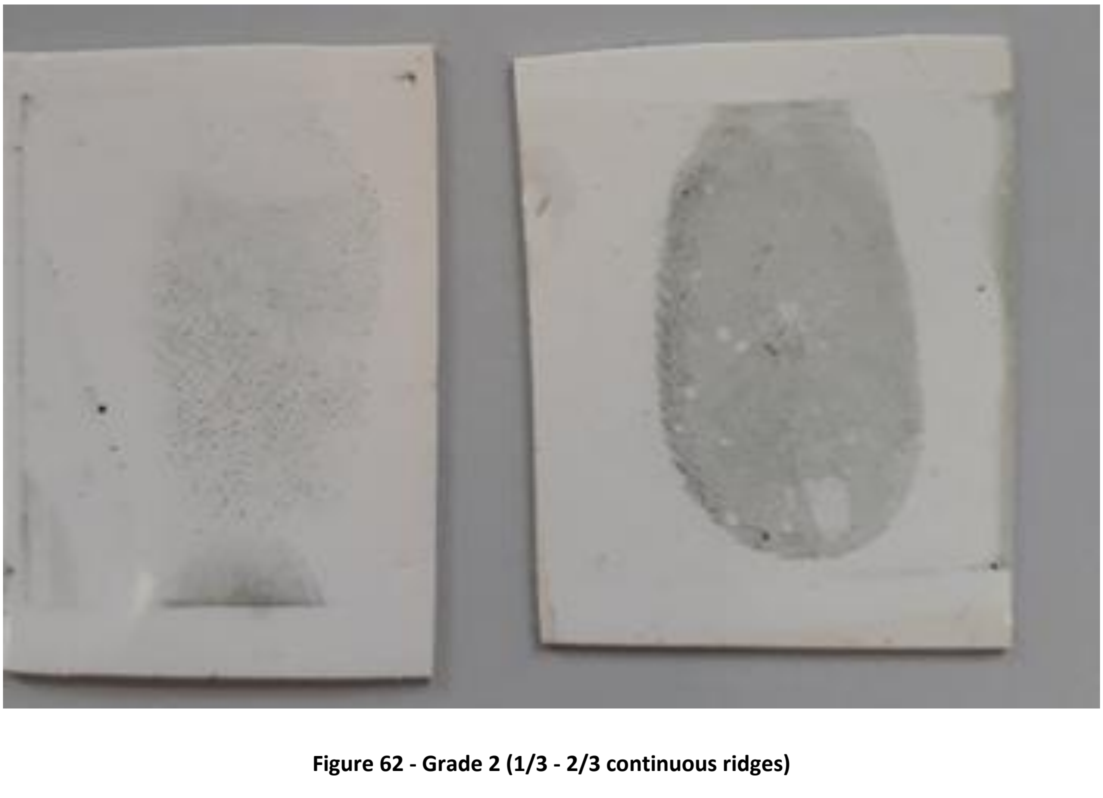


**Figure 62 - Grade 2 (1/3 - 2/3 continuous ridges)**

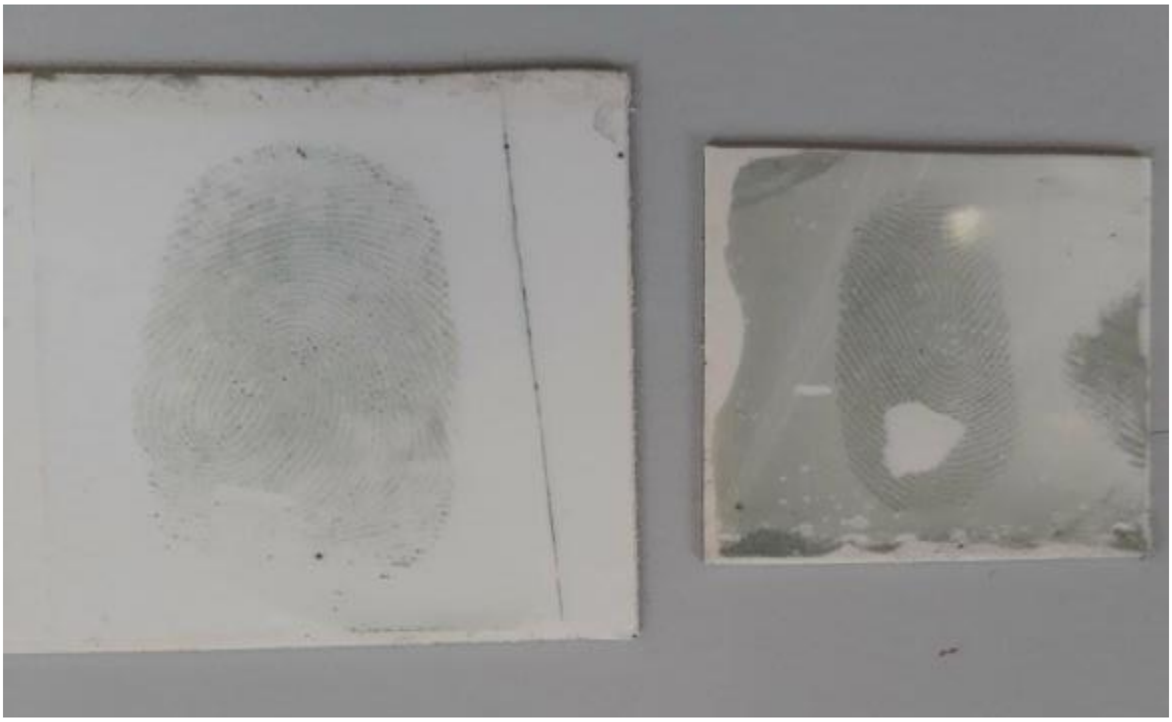


Figure 63 - Grade 3 (> 2/3rd continuous ridges, but not quite a perfect mark)

Figure 64 - Grade 4 (full development - whole mark clear with continuous ridges)

The Bandey scale itself is shown below:

| Grade | Comments |
|---|---|
| 0 | No Development |
| 1 | Signs of contact but < 1/3rd of mark continuous ridges |
| 2 | 1/3 - 2/3 of mark continuous ridges |
| 3 | > 2/3rd of mark continuous ridges, but not quite a perfect mark |
| 4 | Full development - whole mark clear with continuous ridges |

| | | Grade | |
|---|---|---|---|
| **Donor** | Eccrine | Natural | Sebaceous |
| **1** | 1 | 2 | 2 |
| **2** | 2 | 4 | 3 |
| **3** | 0 | 3 | 2 |
| **4** | 1 | 3 | 3 |
| **5** | 1 | 4 | 2 |
| **6** | 2 | 3 | 3 |
| **7** | 2 | 3 | 3 |
| **8** | 1 | 2 | 2 |
| **9** | 2 | 3 | 3 |
| **10** | 1 | 3 | 2 |

**Table 3**

Whilst there are differences the pattern is consistent throughout. This appears to confirm that this process will work excellently for non-invasively developing natural fingerprints. Whilst the technique is not as sensitive to eccrine deposits, there is still sufficient material to still yield a fingerprint of reasonable detail for certain individuals. Whilst fatty acids which are abundant in sebaceous material will initiate the oxidation at a faster rate than eccrine, components of eccrine deposits such as chlorides and even water itself will still still result in oxidation of the copper (albeit on a lesser scale than with sebaceous markings). This is believed to be decisive in determining the ability of this technique to visualise a fingerprint using rubeanate solution, and explains why the technique has success with any fingermark deposit, the levels of consistency are much greater for natural and sebaceous fingermarks.

For both natural and sebaceous deposits these was a consistent level of superb detail from a range of donors. Theoretically natural fingermarks are the most likely to be found at a crime scene, and so the positive results here are hugely promising.

### 4.2.2 Maintaining constant conditions

Whilst the technique developed has shown great potential thus far, ensuring the results that are possible are as consistent as possible is vital. Whilst the length of time the gel is in contact with the metal surface can be controlled quite easily, other factors such as temperature and humidity require closer attention. Based on the previous results obtained it was thought that these two factors, both of which fluctuate day to day, could be having a marked effect on the quality of the developed fingerprints. It was also worth studying how the latent fingermark interacts with the metal and the gelatine lifter at both elevated and diminished temperatures. Because of this, the metal was placed in both an oven at 80$^{o}$C and a fridge at 5$^{o}$C. The metal was left in these conditions for 24 hours before having the gelatine lifter placed on its surface prior to treatment with rubeanate solution.

With the metal that was left in the fridge at low temperatures, the ‘background’ detection of oxidised copper was appearing at a much quicker rate. Numerous attempts were made, with less contact time between gel and metal, and background detection was still occurring even after 10 seconds of contact time between gel and metal, much less than when left in an alternate, more natural environment. This was believed to be because of a small layer of condensation appearing on the surface of the copper. This will increase the rate in which the copper is oxidized and is simultaneously catalysing the increased reaction with rubeanate solution to yield copper rubeanate. In other circumstances this oxidation is not happening as quickly as where the fingermark is placed, hence the print can be visualised via this process. In these particular conditions however, the background is appearing at the same time as the fingerprint, ‘blocking’ the ridge detail which can be seen.

Figure 65 - Background blocking some fingerprint development

The elevated temperatures on the other hand yielded much more consistent and promising results. These appeared to highlight an increase in the consistency of the procedure, producing high quality fingerprints and also appearing to marginally delay the appearance of background, further highlighting the improvements such an additional step can add to an already promising technique. Despite these improvements, heating to such a high temperature would be undesirable in certain scenarios, especially those within a heritage context, which this research has primarily focused on. As a result, lower temperatures were attempted and at 60°C the same results were exhibited. Consequently, it was theorized that it was not in fact the elevated temperature which was producing improved results, but instead a reduced humidity. Because of this, the same experiment was completed, but the metal with latent fingermark deposited on it was placed in a desiccator for 24 hours as opposed to the oven. This produced equally positive results to when placed in an elevated temperature, and is a much more desirable technique. Whilst there is the chance an item of historical significance could not be placed into an oven being heated to such temperatures, it is difficult to foresee such issues with regard to placing the item inside a desiccator in order to enhance the chances of developing a latent fingermark. This was done numerous times, and whilst on occasion showed no improvement, it instead had no effect on overall fingerprint quality. Since there is no decrease in the potential quality of fingerprint development, this method could be used without the threat of harming the print itself. The same 10 donors as above were analysed in the same manner. However in this instance, there was a comparison between those analysed in differing humidities.

Each donor placed 3 natural/ungroomed fingermarks on the surface of copper and each was then left in the open environment for 24 hours. They were then placed in one of 3 differing environments for a further 24 hours. The 3 different environments were:

1. Open laboratory environment, (room temperature and general humidity).
2. A desiccator (low humidity).
3. A superglue cabinet with a relative humidity of 80.

These were each then removed from their specific conditions and analysed using the gelatine lifters and rubeanate identically.

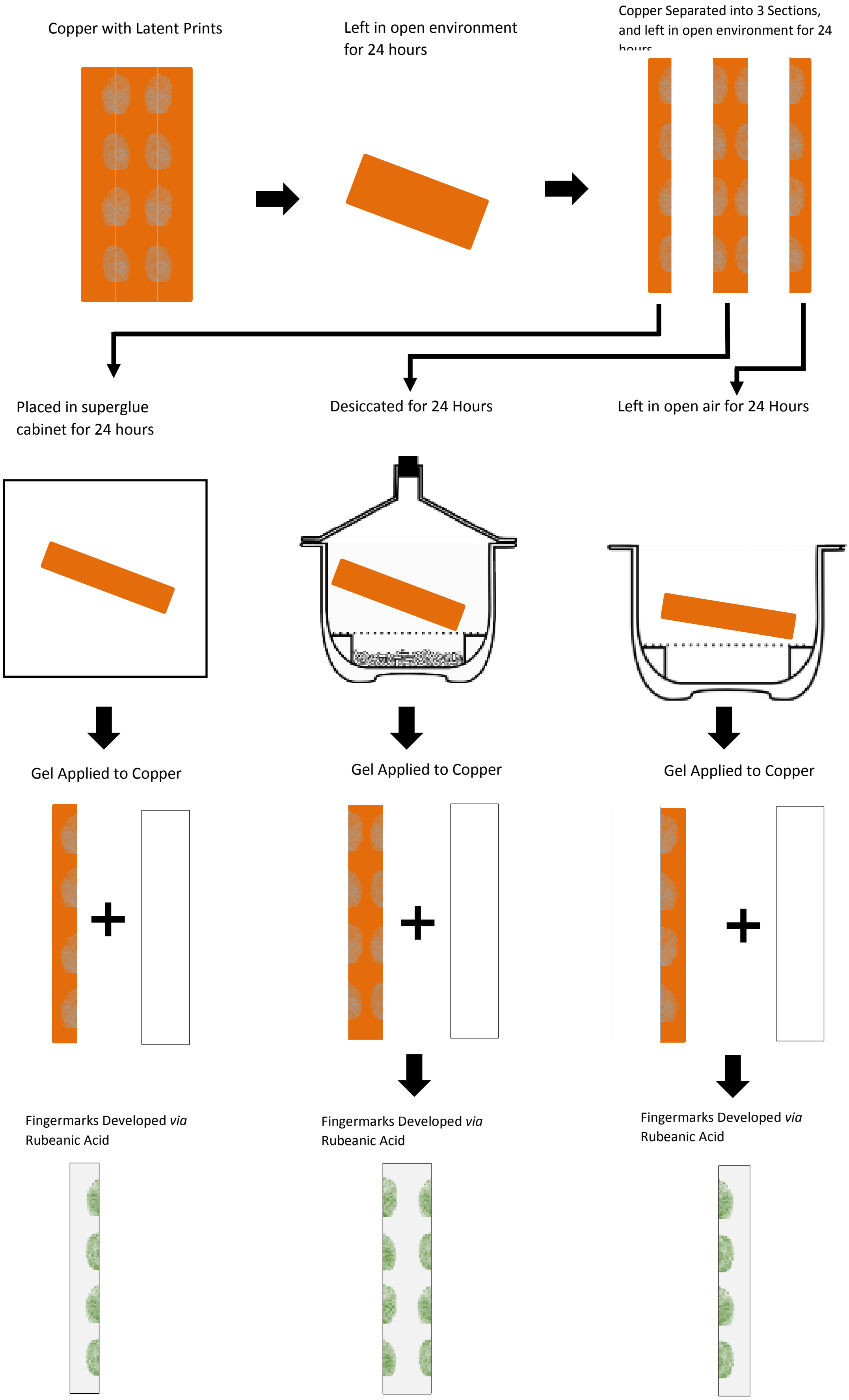


**Figure 66 – Schematic showing the process outlined.**

The results are highlighted below:

| | | Grade | |
|---|---|---|---|
| **Donor** | Open Environment | Desiccator | Cabinet |
| **1** | 4 | 4 | 2 |
| **2** | 3 | 3 | 2 |
| **3** | 2 | 3 | 2 |
| **4** | 2 | 2 | 2 |
| **5** | 2 | 3 | 1 |
| **6** | 3 | 4 | 1 |
| **7** | 2 | 3 | 2 |
| **8** | 3 | 3 | 1 |
| **9** | 4 | 4 | 2 |
| **10** | 3 | 3 | 0 |

**Table 4 – Natural fingerprint comparison**

There are several things to note from these results. The first is that those desiccated clearly show improved results. On 4/10 occasions there is improvement of 1 grade to those kept within an open environment, and improvement on 9/10 occasions compared to the superglue cabinet. The second thing worth consideration is the fact that on no occasion did placing the metal in a desiccator harm the fingermark and make the developed prints visualization more difficult. This is vital should the technique move towards widespread used, as the addition of this step can, at worst, maintain identical levels as when kept in an open environment. Finally, the increased humidity of the superglue cabinet appeared to have a harmful effect on the quality of fingerprint developed. This is often a result of an increased background occurring. As with other examples of background occurring, this makes visualization of the entire fingerprint developed more difficult, albeit not impossible. The contrast is far superior when this is reduced or minimized, and hence reducing the humidity of the environment in which the fingermark is stored when analysing using this technique is desirable.  Shown below is an example of the improvements this technique can produce.  These are from donors 1, 2, 3, and 4.

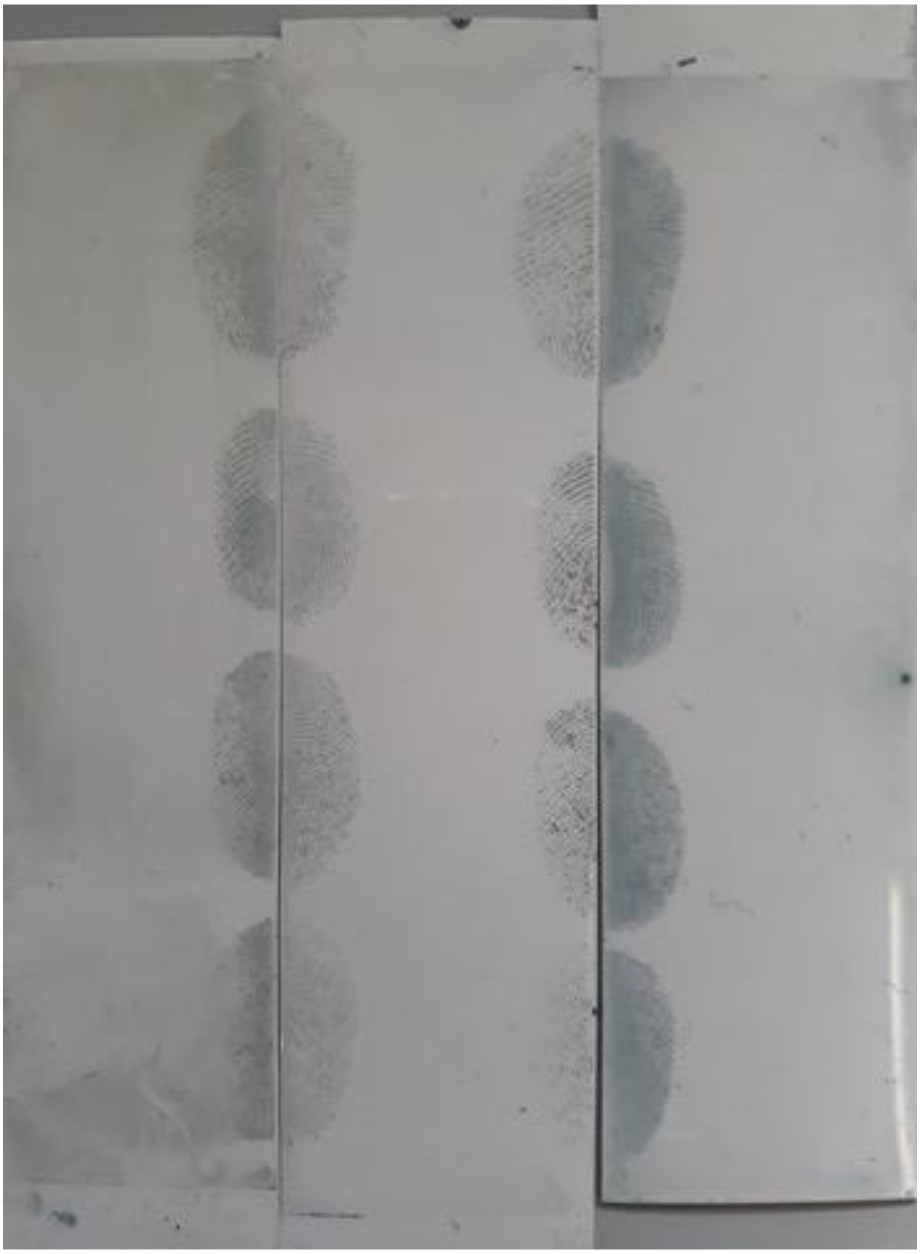


**Figure 67 - Donors 1-4, in open environment (left) desiccated (middle) superglue cabinet (right)**

The results for the above were when examining natural fingermarks.  To gain a better and well-rounded understanding of the reaction that is happening, the same was done for the analysis of eccrine and sebaceous marks. The same pattern occurred in both instances.

| | | Grade | |
|---|---|---|---|
| **Donor** | Open Environment | Desiccator | Cabinet |
| **1** | 1 | 1 | 0 |
| **2** | 1 | 2 | 0 |
| **3** | 1 | 2 | 0 |
| **4** | 2 | 2 | 0 |
| **5** | 1 | 1 | 1 |
| **6** | 2 | 2 | 1 |
| **7** | 2 | 2 | 0 |
| **8** | 2 | 2 | 1 |
| **9** | 1 | 2 | 0 |
| **10** | 0 | 1 | 0 |

**Table 5 – Eccrine print comparison**

| | | Grade | |
|---|---|---|---|
| **Donor** | Open Environment | Desiccator | Cabinet |
| **1** | 2 | 3 | 1 |
| **2** | 3 | 3 | 2 |
| **3** | 2 | 3 | 2 |
| **4** | 3 | 4 | 1 |
| **5** | 4 | 4 | 1 |
| **6** | 2 | 4 | 1 |
| **7** | 2 | 2 | 0 |
| **8** | 3 | 3 | 1 |
| **9** | 3 | 4 | 2 |
| **10** | 3 | 3 | 1 |

**Table 6 – Sebaceous print comparison**

For sebaceous markings, the only issue facing development was that of background, as the residues themselves react readily with the rubeanate solution in both the desiccator and the open environment.  Eccrine prints on the other hand show a more varied response.  This is most likely a result of the constituents present here varying with individuals.  Different individuals will each have unique residues, which are interacting with the rubeanate uniquely.  One such example is the amount of water comprising an eccrine print, which will vary between individuals.

Since the amount of fingermark residue constituents vary from donor to donor, the amount of copper oxidation will reflect this in the level of corrosion observed when developing the fingermarks left using this technique.

### 4.2.3 Attempts to optimize desiccation improvements

It is without doubt that desiccation is improving the quality of fingerprints that can be obtained via this process. However gaining a well-rounded understanding of this procedure is vital with regards to further work and ensuring this work is as accurate and reliable as possible. A step towards doing this, is to examine whether its positive effect on fingerprint development is permanent or if it can be negated by removing the metal from this desiccated environment.

A row of natural fingermarks were deposited along a piece of copper. This was then placed in a desiccator for 24 hours. Each fingermark was then ‘split’ for analysis in different environments. After this period of time, one half of the splits were developed using the gelatine lifters and rubeanate solution, whilst the other half were removed and left in the open laboratory environment for a further 24 hours. For another piece of metal, the same was completed however whilst one half was left in the desiccator for 24 hours, and then open environment for a further 24 hours, the other was left in the desiccator for the entire 48 hour period. This would ensure the results would confirm if the positive effect could be removed by either time, or by re humidifying the metal.

Whilst all gave good ridge detail there were clear differences between those which had been analysed immediately post removal from the desiccator. Far clearer detail could be visualised in this case, whereas when re humidified before analysis, there is a slight decline in the quality of fingerprint obtained. After a further 24 hour period, the metal desiccated for 48 hours was also examined. This also showed the improvements from desiccation. This highlights that said improvements are a result of this changed environment as opposed to time.

## 4.3 Washing fingermarks

As the *modus operandi* of criminals develops, and perpetrators become more aware of the risks involved with leaving latent fingermarks at a crime scene, the obstacles facing examiners increases as well. One such action they may take is washing marks from the surface of the metal. However, whilst to the naked eye the fingermark has been removed, the residues and corrosion signature of a mark is still present and because of this can still potentially be recovered. In an actual crime scene, it is unlikely and rare that the latent mark itself will remain in pristine conditions. Perhaps the most likely form of damage a fingermark may undergo is from water. This will be either when washed away by a criminal who is aware they may have left markings or when stored or thrown away in a body of water. These will obviously effect the fingermark and can make visualization difficult. Because of this, enhancing the ability to visualize these fingermarks when they have been subjected to such conditions is a key aim during the course of this research.

The first step was confirming that this process can work effectively on washed metal. This was then pursued further by examining whether the addition of desiccation enhanced this visualization. A deposit was left on a piece of cut metal and then washed in a variety of ways with differing degrees of intensity.

The act of ‘washing’ can be interpreted in numerous ways and because of this there were several forms of washing completed and studied. These were:

- Storing in a body of water at room temperature overnight (Technique A)
- Rinsing under a tap for 10 seconds (Technique B)
- Thoroughly washing with soap and water (Technique C)
- Thoroughly washing with soapy water and acetone (Technique D)

Ten donors placed 4 natural/ungroomed fingermarks on different copper plates, which were then left for 24 hours in the open laboratory environment. These were then washed in each of the ways described above before being left in an open environment again for a further 24 hours. These gave the following results:

|  |  | Grade |  |  |
|---|---|---|---|---|
| **Donor** | A | B | C | D |
| **1** | 2 | 2 | 0 | 1 |
| **2** | 2 | 3 | 1 | 2 |
| **3** | 2 | 1 | 1 | 1 |
| **4** | 2 | 2 | 1 | 1 |
| **5** | 1 | 1 | 0 | 0 |
| **6** | 1 | 2 | 1 | 0 |
| **7** | 2 | 3 | 2 | 1 |
| **8** | 2 | 3 | 1 | 0 |
| **9** | 2 | 2 | 2 | 0 |
| **10** | 1 | 1 | 0 | 1 |

**Table 7**

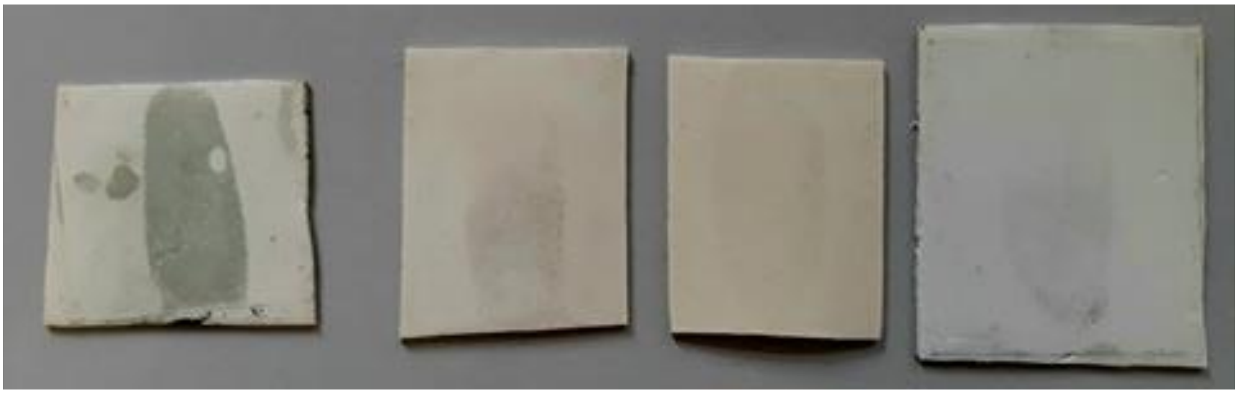


**Figure 69 -Results from donor 1**

The results obtained here show clear promise with regard to the technique and its used in regard to developing latent fingerprints from metals which have been in contact with water. There are clearly residues of the fingermark being removed upon washing as merely from a visual point of view, there is a notable difference pre and post ‘washing’. However what appears to be occurring is that in most instances there is some degree of corrosion of the metal that can still be detected via this technique despite being washed. Despite this, there are instances where there is no such development. Whilst washing in just water still consistently yields fingermarks which can be developed, when soap and acetone are introduced this process shows greater inconsistency and there is clear room for improvement. It can be hypothesised that the oily residues of a natural fingermark cannot be rinsed away, however once soap or acetone are added, these can largely be removed and the level of corrosion is decreased.

Because of the work reported earlier highlighting how a desiccator can improve the quality of a developed fingerprint, the same experiment as highlighted in table 7 was completed, however in the final step the metal plates were stored in a desiccator for 24 hours as opposed to being kept in the open laboratory environment. The initial steps were kept consistent, as was the fact natural/ungroomed fingermarks were used from identical donors. This yielded the following results:

| | | Grade | | |
|---|---|---|---|---|
| **Donor** | A | B | C | D |
| **1** | 3 | 4 | 2 | 1 |
| **2** | 3 | 3 | 1 | 2 |
| **3** | 4 | 4 | 3 | 2 |
| **4** | 3 | 4 | 2 | 3 |
| **5** | 3 | 3 | 1 | 2 |
| **6** | 3 | 2 | 2 | 1 |
| **7** | 2 | 2 | 1 | 1 |
| **8** | 4 | 4 | 3 | 1 |
| **9** | 2 | 4 | 1 | 2 |
| **10** | 3 | 3 | 1 | 1 |

**Table 8**

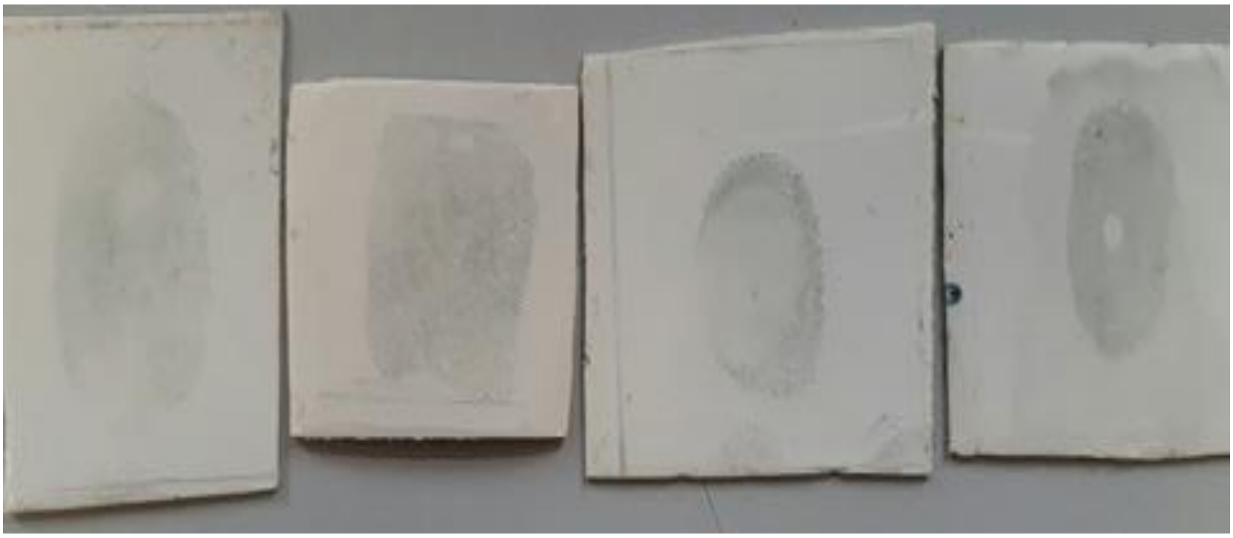


Figure 70 - Results from donor 1

As can be seen, there was clear improvement for all techniques used and for every donor. The same pattern was evident as without the desiccator, ie the quality which could be obtained remained consistently high when the metal was washed or stored in water, and this then dropped with the introduction of additional substances such as soap or acetone. What was notable for both sets of results, both inside and outside of the desiccator, was that ‘scrubbing’ the metal (techniques C and D) with a rough cloth often appeared to smudge detail.  This often caused the print to appear overloaded in areas despite a fingermark clearly being apparent.

Figure 71 - An example of the 'smudging' effect which can occur.

This was worse on certain occasions, and the desiccation certainly improved this issue. When this is not as much of a problem, the corrosion of the metal from the fingermark residues is occurring at a greater rate. This cannot be ‘scrubbed’ off and hence is still detectable. The same process was completed, but with the presence of no liquid to clean the surface, instead a microfiber cloth being used to scrub the surface alone. This gave the following:

| **Donor** | Grade |
|---|---|
| **1** | 2 |
| **2** | 3 |
| **3** | 3 |
| **4** | 2 |
| **5** | 3 |
| **6** | 3 |
| **7** | 1 |
| **8** | 4 |
| **9** | 3 |
| **10** | 3 |

**Table 9**

This gave better results than when scrubbed with the addition of liquid. They were very similar in general to when rinsed or stored in a body of water. In this scenario, there appears to be far less removal of material, instead any reduction in fingerprint quality being the 'smudging' effect that is seen. The soluble cuprous ions will not be removed without the addition of water or acetone and hence will remain here, and thus is why there is increased quality with the removal of these solvents from the washing procedure. What appears likely here is that a combination of scrubbing and the cleaning properties of soap, water, and acetone are all contributing to the removal of cuprous ions and copper itself. The more of these which are present, the less likely to detect a high quality fingerprint.

Because of the improvements highlighted by the addition of the desiccation, the belief is that this step is causing an increased corrosion of the metal, or as is more likely, is preserving this corrosion signature by maintaining an environment with a much lower humidity than in the open environment. This signature is then being detected via the addition of the gelatine lifter and rubeanate solution. There have been no previous reports discussing the effects of a desiccator on a fingermarks interactions with metal, in this case copper and its alloys. A possible suggestion as to how and why this is happening is a relatively straightforward mechanism, in that the desiccation is preserving the corrosion signature and thus allowing for improved future analysis. This is compared to when a metal with fingermark deposited on its surface is left in the open environment before analysis, where the signature is being hindered by the presence of water and other inorganic constituents which are not being detected by the rubeanate solution. Because the desiccation removes these constituents, the developed fingerprint is more susceptible to visualization. The other theory put forth is the formation of a passivation layer over time, which is preventing the mobility of $Cu^{2+}$ ions. Because of this reduction in mobility, the cuprous ions will not adhere to the gelatine lifters, hence preventing detection via the rubeanate solution. It is theorized that the addition of a desiccation step delays the formation of this passivation layer.

In order to further establish the level of improvement possible via this method, the same process was completed but with alterations to a range of variables, most notably time both pre desiccation and within the desiccator itself.

In order to test this, a number of copper plates with fingermarks deposited on their surface naturally were left in the open environment for a range of timeframes after being washed thoroughly with acetone and soapy water. These were each then left in a desiccator for a further 24 hours in order to see if the desiccation still yields the same positive effect when the metal has been left in the open environment for alternate periods of time. This was then compared to if the metal was then left in the open environment for a further 24 hours to ensure the same positive outcome was occurring in this case. The results are shown below:

| | Desiccated | |
|---|---|---|
| | Yes | No |
| **Time spent in open environment** | Grade | |
| **2mins** | 1 | 0 |
| **5mins** | 1 | 0 |
| **10mins** | 1 | 1 |
| **30mins** | 2 | 1 |
| **1 hour** | 1 | 1 |
| **2 hours** | 2 | 1 |
| **6 hours** | 2 | 2 |
| **12 hours** | 2 | 1 |
| **24 hours** | 3 | 1 |
| **48 hours** | 2 | 2 |
| **5 days** | 2 | 1 |
| **1 week** | 1 | 0 |

**Table 10**

A clear pattern is emerging, highlighting the notable improvement placing the metal inside a desiccated atmosphere can provide with regard to developing higher quality fingerprints. What is also noteworthy is the trend occurring which suggests an optimum timeframe for detection. If the metal is treated between 30mins and 5 days after the metal has been washed there is an increased chance of developing higher quality fingerprints.

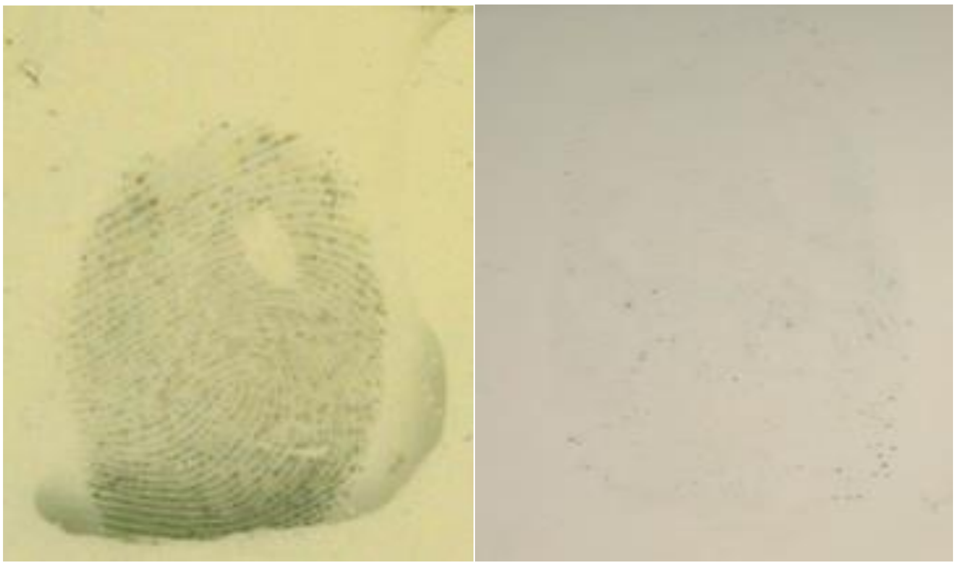


**Figure 72 - Comparison of desiccated print (left) and non-desiccated print (right) after 24 hours in open environment**

Outside of this timeframe, even with the addition of desiccation the quality of fingerprint which can be developed is limited.

The same process was then attempted again, however on this occasion leaving for 2-4 weeks outside in the open environment before desiccation. This also showed a similar pattern with the quality of print developed being minimal (1 on the Bandey Scale). This method appears to work most effectively when the metal can be analysed within 1 week of the metal (and fingermark) being washed, if done so thoroughly. This quality can extend to lengthier periods of time if the level of washing is decreased. When the metal itself was rinsed with water for the same period of time as that above, the following results were obtained:

| | Desiccated | |
|---|---|---|
| | Yes | No |
| **Time spent in open environment** | Grade | |
| **2mins** | 2 | 1 |
| **5mins** | 3 | 1 |
| **10mins** | 2 | 1 |
| **30mins** | 3 | 2 |
| **1 hour** | 3 | 2 |
| **2 hours** | 3 | 2 |
| **6 hours** | 3 | 2 |
| **12 hours** | 4 | 1 |
| **24 hours** | 4 | 2 |
| **48 hours** | 3 | 1 |
| **5 days** | 2 | 1 |
| **1 week** | 1 | 1 |

**Table 11**

As can be seen this yielded much greater quality fingerprints than when the level of washing had been increased. This is most likely a result of a greater amount of fingermark residues being removed by the washing process itself when either scrubbed or washed with acetone. In the case of ‘rinsed with water’ those constituents which are not soluble in water will remain and thus have greater potential to corrode the metal further as time progresses. An example of the improvements that can occur are highlighted below.

**Figure 73 - Comparison between desiccated prints (right) and non-desiccated (left) at 24 hours (top 2) and 48 hours (bottom 2)**

The reason the level of quality dips again once a certain timeframe has passed is explained by the appearance of the metal itself at this point. There are dark ridges where the mark was deposited.

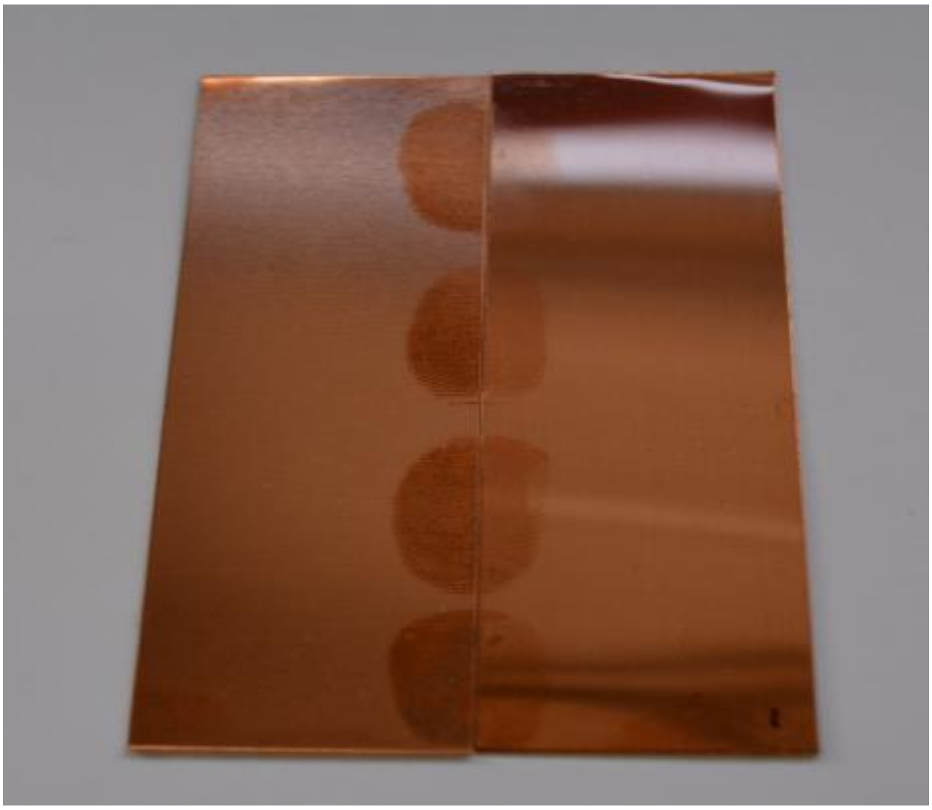


**Figure 74 - Dark ridges after fingermarks have been left on the metal post desiccation for 1 week (left) compared to when left for 24 hours (right)**

This colour matches that of copper oxide. The reaction seems to have reached it's end-point on the surface of the metal, and is resultantly very difficult to transfer onto the surface of the gelatine lifter when this is placed over it. Therefore the reaction with the rubeanic acid is occurring much less and the fingerprint is more difficult to visualise. This is compared to when there has been less time on the surface. Whilst oxidation has still occurred, the reaction still seems to be happening when the gelatine lifter is placed over the metal. This appears to be far easier to transfer onto the surface of the gelatine lifter and thus react with the rubeanic acid solution. For the earlier times (up to 30mins) the quality is also on occasion lessened. In this case it is believed that the fingermark has not necessarily had time to fully begin reacting with the metal surface, or has not done it to the required extent. Whilst this timing is important to the overall quality of mark obtained, it is also vital to note that when desiccated, there is still a consistent level of reasonable quality fingerprint development regardless, especially if the metal has not been thoroughly washed and scrubbed with soapy water and acetone.

The next step was confirming that 24 hours was sufficient time for the metal to spend in the desiccator and if leaving the metal in this environment for a longer (or shorter) period of time could further improve the quality of fingerprint developed.

Fingermarks from a range of donors were deposited on the surface of copper and left for 24 hours. These were then washed thoroughly using acetone and soapy water, and placed back into the desiccator. Each donor deposited 5 fingermarks, 1 from each finger. These were then separately left in the desiccator for a range of times. The times left were limited at 10 days as too long in the desiccator would be undesirable for obtaining results which can be analysed quickly.

| | | | Grade | | |
|---|---|---|---|---|---|
| | | | Time | | |
| **Donor** | 1 hour | 24 hours | 48 hours | 1 week | 10 days |
| **1** | 1 | 1 | 1 | 0 | 0 |
| **2** | 2 | 2 | 1 | 1 | 0 |
| **3** | 1 | 1 | 2 | 0 | 1 |
| **4** | 1 | 1 | 1 | 0 | 0 |
| **5** | 0 | 1 | 0 | 1 | 1 |
| **6** | 2 | 3 | 1 | 2 | 1 |
| **7** | 2 | 3 | 2 | 1 | 1 |
| **8** | 1 | 3 | 1 | 0 | 0 |
| **9** | 2 | 2 | 2 | 1 | 1 |
| **10** | 1 | 1 | 1 | 1 | 1 |

**Table 12**

What becomes apparent from these results is that 24 hours in the desiccator is the optimum period of time for the metal with fingermark deposit on it, to be in this environment. For longer periods, oxidation had still occurred to the point where the material of interest is 'blocked' from being lifted by the gels. For a shorter period of time, it can be explained by not enough corrosion occurring at this point, so the signature is not as easily examined via this procedure. There are still reasonable results which can be gathered at times other than 24 hours, however this appears to be optimum and also enables fairly quick analysis of results.

### 4.3.1 Washing eccrine fingermarks

Previous results have highlighted this techniques abilities to develop eccrine fingerprints of reasonable quality. As a result of the improved results from using a desiccator, it was now to be attempted again, however with eccrine marks deposited as opposed to natural ones. This would enable visualization even when there had been recent washing of the hands, a weapon a potential criminal could use. The same experimental procedure as outlined above was completed, with the only difference being those fingermarks deposited being eccrine as opposed to natural. These were prepared by an individual washing their hands and wearing latex or nitrile gloves for 10 minutes prior to deposition. The washing procedures were the same as for previous work in this chapter. The results here are highlighted below:

| | | | Grade | | |
|---|---|---|---|---|---|
| **Donor** | Unwashed | A | B | C | D |
| **1** | 1 | 1 | 1 | 0 | 1 |
| **2** | 2 | 2 | 1 | 1 | 1 |
| **3** | 0 | 0 | 0 | 0 | 0 |
| **4** | 1 | 0 | 1 | 1 | 0 |
| **5** | 1 | 1 | 0 | 0 | 0 |
| **6** | 2 | 1 | 0 | 0 | 0 |
| **7** | 2 | 2 | 2 | 0 | 1 |
| **8** | 1 | 0 | 1 | 1 | 0 |
| **9** | 2 | 1 | 1 | 1 | 0 |
| **10** | 1 | 1 | 1 | 0 | 0 |

**Table 13**

With zero washing, or minimal washing (techniques A and B) there can be, on occasion, fingerprints of a reasonable quality developed. However once more vigorous washing is introduced, the ability to develop high quality fingerprints is removed, as a result of the residues which can corrode the metal being removed. It appears that the corrosion signature which appears vital to development is much less apparent in eccrine prints than in those which are natural or sebaceous. With both washing and not washing, natural or sebaceous marks are developed with a great deal more success than eccrine, however this must not take away the great positives and potential such a method shows. This technique has great versatility with regard to developing fingermarks ranging from the highest quality, even when subjected to a reasonable degree of washing for natural and sebaceous fingerprints to mid quality fingerprints for eccrine deposits when washed with less vigour (just rinsed). Not only has this emphasised an excellent technique with regard to developing said fingerprints, but one which can remain non-invasive and has an additional step which can further enhance the quality of results which can be obtained via the desiccation (again non-invasive). This desiccation step is of great interest with regards to the improvements it yielded. It is theorized that when a fingermark has been deposited the residues present are slowly corroding the metal over time. This corrosion signature is what is being detected via the process outlined. By desiccating the metal, this signature can be both preserved and enhanced for a longer period of time and hence enables greater detection. When this is either left outside of this environment or removed from the desiccator for a given period of time (24+ hours) this effect is removed, and hence detection must be completed within a few hours of desiccation for the full effect to be visualized. Another theory is that the presence of a fingermark is mobilizing the $Cu^{2+}$ and thus allowing transfer to the gelatine lifter, which can then be detected via the rubeanate solution. Enough time must have passed by for this mobilization to have worked, however not enough so that a passivation layer has been created and there is minimal transfer between the fingermark residues on the metal and the gelatine lifters as a result.

The work involving desiccating fingermarks in this manner has been shown to follow a pattern. When metal is left for a relatively short period of time before development of the deposited fingermarks, there is little difference between using the desiccator and not. However when conditions are far from ideal, notable improvements can be made by using the desiccator as part of the process. Considering the likelihood of encountering a fresh fingermark so soon after deposition is going to be rare, the improvement seen in the presence of the desiccator is of great importance. Another pertinent feature of this procedure is the fact that the gel can lift the latent detail from the metal surface, and then be left for several hours before treatment with the rubeanic acid solution. As a result of this, where necessary a lift could be taken on site, transported back to the lab, and analysed with no adverse effects. The gel lifting process is discrete enough that the metal surface can be treated with other techniques; cyanoacrylate fuming, vacuum metal deposition, powers, etc.

### 4.3.2 Copper, brass, bronze comparison

As has been discussed, there is little/no difference between the results obtained between experimentation completed with copper, brass, or bronze. It appears that as long as there is a reasonable amount of copper present, it being the main element within an alloy, there will be excellent levels of detection when using rubeanic acid solution. These are shown below:

**Figure 75 - Comparison between Copper (left), brass (middle), and bronze (right)**

## 4.4 Fingerprints from lead

Because of the excellent detail which can be obtained from copper and its alloys when using rubeanic acid solution, it was now to be attempted with lead, the other metal which has previously shown to be sensitive to said solution. A natural fingermark was deposited on a lead block (the same as that used in chapter 3) and left for 24 hours in the open environment. A gelatine lifter was then placed over this and left for 2 minutes before being treated with rubeanic acid solution. This gave no indication of a fingerprints present. Due to the previous requirement of UV light to visualise the brown/orange colour indicative of leads presence, this gelatine lifter was then exposed to said UV light for 24 hours. This still yielded no indication of a fingermark, only leads presence in an orange/brown 'background'. The same process was attempted again, however with a sebaceous fingermark as opposed to a natural mark, to see if the addition of a greater level of corrosion to the lead would enable improved visualization. However this again did not produce any indication of a fingerprint. A third attempt was done with eccrine deposits, in case of a different reaction scheme to that with copper. This also yielded no fingerprint markings. The lack of markings here is most likely a result of leads decreased sensitivity to rubeanic acid solution in comparison to copper. It could also be that the residues within a fingermark which are corroding the surface of copper and its alloys are not reacting in the same way with lead, and hence there is no way of visualising the fingermark. These combination of factors all contribute to why this technique does not work with lead, and the same was also true of other metals which rubeanic acid solution has shown the ability to detect, such as nickel and steel.

## 4.5 The effect of gases on fingerprint development

To further establish a greater understanding of the technique, the effects of water vapour, oxygen, and nitrogen on the metal and how it interacts with a deposited fingermark were studied. A natural fingermark was deposited on the surface of 4 samples of copper by 10 different donors. This was then washed thoroughly with acetone and soapy water, before being placed in the open environment for 24 hours. The 4 pieces of copper for each individual were then placed in four different environments. One was the desiccator, the others were a desiccator that had been flooded with oxygen or nitrogen, and one kept in a superglue cabinet with humidity set to 80RH. This aimed to see if any particular feature of the desiccation was improving the results which had been obtained thus far, or any feature of the open environment which was hindering the development of high quality fingerprints.

| | | Environment | | |
|---|---|---|---|---|
| **Donor** | Desiccator | Nitrogen | Oxygen | Humidified |
| **1** | 1 | 1 | 1 | 0 |
| **2** | 3 | 2 | 2 | 1 |
| **3** | 1 | 1 | 1 | 1 |
| **4** | 1 | 2 | 1 | 0 |
| **5** | 2 | 2 | 1 | 0 |
| **6** | 2 | 2 | 2 | 1 |
| **7** | 3 | 1 | 1 | 0 |
| **8** | 2 | 2 | 1 | 1 |
| **9** | 2 | 1 | 1 | 1 |
| **10** | 2 | 2 | 2 | 0 |

**Table 14**

There are minimal differences between all three of the desiccated environments, with a general desiccation being marginally the best, however a study using a greater number would verify this. What is far clearer is the negative impact which humidifying the metal is having on the subsequent fingerprint development. Some minor details are present at best, in comparison to the other environments which all offer much better chances of reasonable fingerprint development. The same pattern was also true for both brass and bronze. What these results clearly suggest is that whilst the amount of oxygen or nitrogen present offers little change to the final result compared to desiccation in its general environment, humidifying the metal hugely decreases the likelihood of quality fingerprint development. As has been shown previously, background appears much earlier with a humid environment, however this is not the only problem arising in this particular study. The development itself is hindered in this case. It is put forth that this is a result of water vapour catalysing the formation of the passivation layer which then hinders the ability to visualise the developed fingerprint due to reduced mobility of $Cu^{2+}$. The other possibility is that a highly humid environment inhibits the ability of the fingermark to corrode the metal surface, possibly by reacting with the constituents of the fingermark themselves, and thus reducing its ability to react with the metal surface and form a corrosion signature which can then (or in this case cannot) be detected via rubeanate solution.

## 4.6 Analysis of fingermark components

In order to better understand the process when a fingermark reacts with copper and its alloys, a range of constituents from within a fingermark were analysed, to determine if they were able to react with copper and in turn rubeanate solution thus forming the blue/black precipitate. This could also yield some insight into why the process works better with sebaceous deposits when compared to eccrine. Amino acids are abundant in these eccrine deposits, whereas sebaceous have a greater range of fatty acids and salts.

As had been determined earlier in this chapter, the gelatine lifters have a great level of adhesiveness (with work later in this chapter further emphasising this). With this information, three amino acids were analysed at various levels of dilution. This could help determine if every amino acid present was reacting with the rubeanic acid, or if there were certain amino acids which had a greater affinity for said solution and hence had a greater contribution to the reaction which was occurring. This can then be compared to fatty acids, salt solutions, and water, to determine which specific features of a fingermark are contributing to the subsequent reaction with copper and rubeanate solution.

### 4.6.1 Serine

With serine being the amino acid which is most abundant in an eccrine fingermark deposit[115], the interaction of this with both a copper surface and rubeanate solution was analysed. A piece of copper was cut to size. On one piece, a drop of deionized water was placed on the surface and left to evaporate. This is the control, and proves that any reaction that does occur will be a result of the serine as opposed to the water. A 0.117M solution of serine was made up in distilled water, and then a 10x and 100x dilution was completed for this, to make concentrations up to 0.00117M. These were each then left to evaporate on the surface of copper.  After being left in the open environment for 24 hours, a gelatine lifter was placed over this circular droplet for 2 minutes.  Each serine solution has a clear dark circle in the characteristic colour of copper rubeanate formation.

**Figure 76 – Proof that amino acid is reacting with rubeanate solution**

Hence it appears to be clear that serine is causing the oxidation of copper which allows said reaction to take place.  In a standard fingerprint, the concentrations of amino acid can be as low as 0.0000025g/ml and hence even greater dilutions were attempted.  A solution of serine at concentration 0.00000117g/ml was made up.  Whilst being a lighter colour than at higher concentrations this there is still undoubted a reaction occurring, and hence it can be said with reasonable confidence that serine is an amino acid which is contributing to the reaction occurring between a fingermark deposit and the surface of copper.

**Figure 77 – This continues to occur at lower concentrations**

The distilled water had no reaction in any circumstance and hence this confirmed the serine as the cause of this reaction.  It is unlikely that only one amino acid is catalysing the formation of copper rubeanate, and hence the same process was completed for other amino acids.

### 4.6.2 Glycine

As this was the next most abundant amino acid present in an eccrine fingermark deposit, the same process as above was completed, with a solution of glycine in distilled water prepared.  Concentrations ranging from 0.0121M – 0.000121M were each placed onto the surface of the copper plate, which again had been cut to size.  For these concentrations there was still the same reaction occurring, suggesting that this particular acid does interact with the copper surface, and again catalyse the reaction occurring between cuprous ions and the rubeanate solution.  However, these concentrations are higher than what will usually be found within a fingermark deposit.  At greater dilutions, and concentrations less than this, the reaction was not occurring.  It was thought to be unlikely that serine would be the sole amino acid which is responsible and hence another amino acid which was less abundant was also attempted.

### 4.6.3 Aspartic acid

This amino acid was chosen due to its presence in a range of food and drink products.  As a result of this, its abundance will likely vary from individual to individual.  This could potentially give an insight into how diet may affect the ability of this technique, ie whether each individual has a differing level of susceptibility to said process. A solution with concentrations ranging from 0.00997M – 0.0000997M were examined. These each gave clear markings suggesting the acid was interacting with the copper surface in the manner expected. Again, further dilutions were completed thus forming a solution with a concentration of 0.0000000997M. Upon analysis using the gelatine lifters and rubeanate solution, there were still marks indicative of copper rubeanates presence.

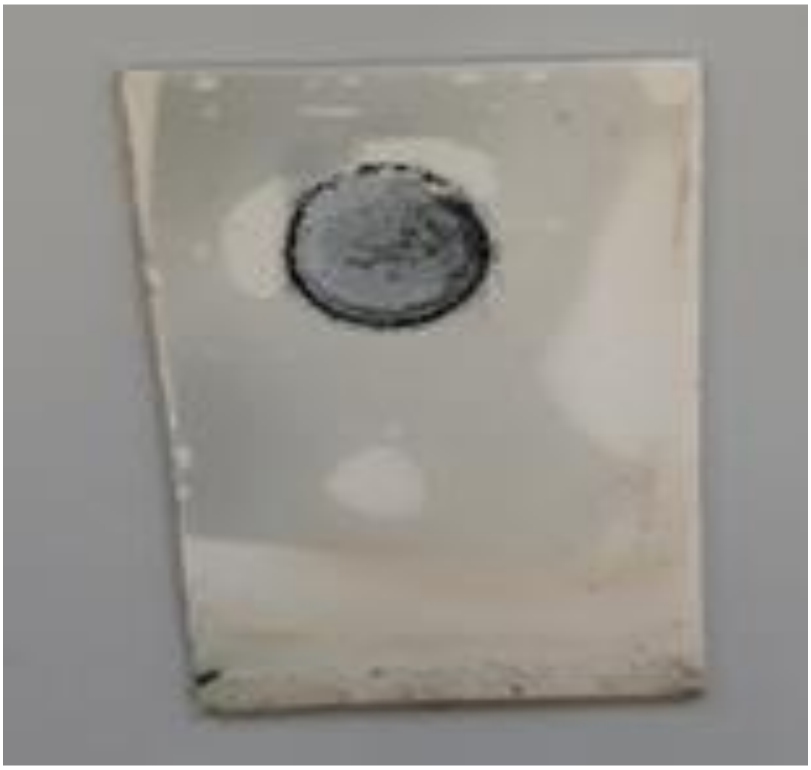


**Figure 78 - Aspartic acid**

What is interesting here is that aspartic acid appeared to have a greater contribution to this process than glycine, and gave identical results to serine, despite being far less abundant in an eccrine fingermark deposit (22% of the serine levels). This suggests that not all amino acids present in a fingermark are having the same contribution to the reaction occurring (between the amino acids and the copper surface) and hence the development of the fingerprint which is visualised using the rubeanate solution. Instead different amino acids will be contributing to the reaction that is occurring between a fingermark and the surface of copper.

### 4.6.4 Water

It can also be said with a reasonable degree of certainty that amino acids are not the sole cause of the reaction between a fingermark deposit and the surface of copper. This is clear, as sebaceous markings have shown much greater affinities towards this process. Sebaceous deposits do not have as many amino acids present as eccrine, yet are more sensitive to the process in general. This suggests many other constituents are contributing to the reaction occurring. Chlorides and various other inorganic constituents are the most notable of these that will contribute to said reaction. The reaction of other substances was confirmed when tap water was used rather than distilled water as a 'control'. A drop of general tap water was placed on the surface of copper, and left for the same period of time as outlined in the experiments above. Once this had evaporated onto the surface, it was lifted via the gels and then treated with rubeanate solution. As with the amino acids which were deemed to be having a contribution to the corrosion of the metal, the same was also true with the tap water. As this was not the case with distilled water, it was clearly not a simple case of $H_2O$ reacting with the elemental copper (thus causing the reaction with rubeanate). What is instead more likely is that the ions present in the water, such as chloride ions, are causing this corrosion. Bond et al have previously discussed the effect that said chloride ions have on brass and copper[100][146]. Hence it appears clear that this particular ion is contributing to the corrosive properties that result in fingermarks reacting with the surface of copper and its alloys in the way that it does.

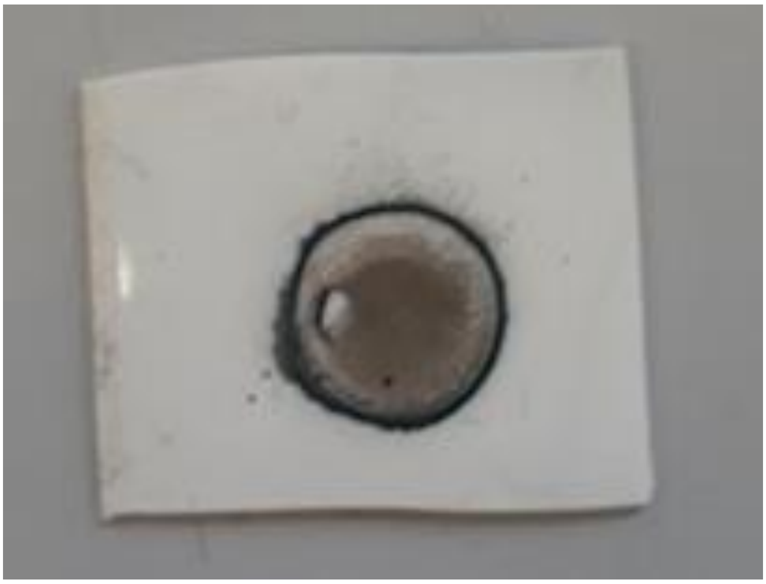


**Figure 79 - Tap water reacts with rubeanate solution**

### 4.6.5 Fatty acids

What was noted during the course of this research was that sebaceous fingermarks react more readily with copper and rubeanic acid solution to yield the characteristic blue/black colour. Therefore it stands to reason that fatty acids will also react readily with rubeanate solution and copper to produce this colouration. Fatty acids have previously being linked to a reaction with rubeanic acid[80][147] and so it was worth investigating their interactions here. Two fatty acids, myristic acid and palmitic acid were both analysed in the same manner as the above, to concentrations as low as 0.0000001M. Due to a poor solubility in water, both of these were made up in a solution that also had shown no reaction with rubeanate solution in ethanol. Rather than a drop being placed on the surface, the metal was dipped into the solution, so the crossover point where the reaction had stopped could be shown. This process is highlighted below:

**Figure 80 - Copper placed in solution of fatty acid**

Figure 81 - Gelatine lifter placed over this once evaporated (after 24 hours)

When developed, these both yielded identical markings, emphasising the reaction which was taking place.

Figure 82 - Blue/black colour forms on surface of gel (myristic acid)

Figure 83 - Palmistic acid

The fact that tap water also reacts in the manner described above suggests that ions that will be present in non-distilled water such as chloride, potassium, and sodium ions are also contributing to the reaction occurring. This theory is further enhanced when considering the fact that distilled water shows no such affinity for the rubeanate solution, and yet eccrine markings still react. It has been reported that eccrine fingermarks comprise around 98% water, and so the additional 2% which is comprised of these ions are contributing to the reaction that is occurring. This also yields insight into why the process is more sensitive to natural and sebaceous markings as opposed to eccrine, with far fewer constituents of an eccrine mark being sensitive to the rubeanate solution in comparison. These will mainly be certain amino acids, such as serine and aspartic acid, but also it would appear, inorganic constituents such as chloride and metal ions. Referring back to table 1[82] highlights the constituents of a fingermark deposit:

| **Source** | **Location** | **Inorganic Constituent** | **Organic Constituent** |
|---|---|---|---|
| Eccrine Glands | Most of the body, but exclusive to palms of the hands and soles of the feet | Water (>98%)<br>Chloride<br>Metal ions ($Na^+$, $K^+$)<br>Sulfate<br>Phosphate | Amino acids<br>Proteins<br>Urea<br>Lactic acid<br>Sugars<br>Creatine<br>Choline |
| Apocrine Glands | Groin and armpits | Water (>98%)<br>Iron | Proteins<br>Carbohydrates<br>Sterols |
| Sebaceous Glands | Most of the body except on palms of hands and soles of feet. Highest concentration is on the forehead and back. | - | Glycerides (30-40%)<br>Fatty acids (15-25%)<br>Wax esters (20-25%)<br>Squalene (10-12%)<br>Sterol esters (2-3%)<br>Sterols (1-3%) |

By looking at the evidence, it is reasonable to conclude therefore, that there are several constituents of a fingermark which are reacting with the rubeanate solution and copper, and producing the blue/black colour. Whilst this alone is not extensive in terms of the contributory factors to the reaction occurring between a fingermark and copper, is certainly noteworthy and has resulted in a clear indication as to what is occurring. The process is not a simple case of one component reacting with the metal and corroding it. Instead a range of contributory constituents are having an effect, which has been shown to include certain amino acids, fatty acids, and inorganic ions. What is also worth consideration is the fact that because this reaction is due to a range of substances which differ between individuals, it is likely that the process will be more sensitive towards some deposited marks than others.

## 4.7 Potential outside of a heritage crime context

Whilst the bulk of this research aimed to focus on lowering levels of metal theft with regard to heritage crime, the potential of the work done and the results obtained meant that examining how well such techniques can work on materials which would help lower more general levels of crime is also important. This primarily involved attempts at developing fingerprints from brass bullet casings, a surface which has proven to be very problematic for forensic examiners. The shape alone makes this particular surface difficult to analyse fingermarks on, and this situation is exacerbated when the bullet has been fired. The high pressure and temperatures, that it becomes exposed to, make any fingermarks deposited on the surface up until this point even more difficult to visualise.

The first issue which needed to be addressed was determining how the gelatine lifter was going to be applied. In the methods described earlier in this chapter, the gel could be placed on top of the metal in question, and then a fingerprint roller used to smooth and ensure minimal air bubbles which are present. With the shape of a bullet casing, this would not be possible. The first attempt involved ‘wrapping’ the gel around the bullet casing, and being held for the 2 minutes of contact between gel and casing.

**Figure 84 - 'Wrapping' the gelatine lifter around casing**

The second involved rolling the casing across the surface of the gel.

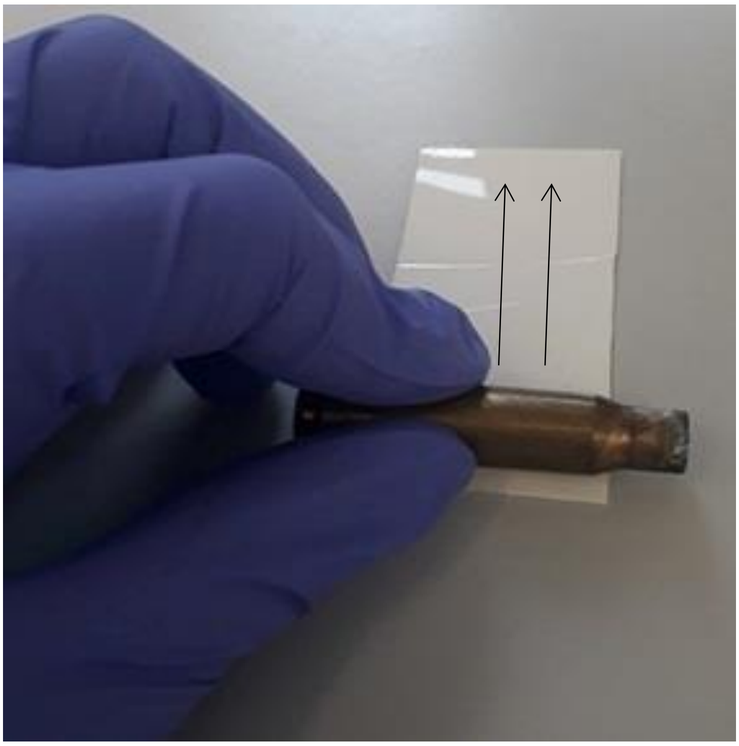


**Figure 85 - 'Rolling' casing across the gelatine lifter**

These gels were then treated with the rubeanate solution. This was done with 10 separate donors who each deposited a natural fingermark onto a casing which had not been fired.

| | Grade | |
|---|---|---|
| **Donor** | Wrapping | Rolling |
| **1** | 1 | 2 |
| **2** | 1 | 3 |
| **3** | 1 | 1 |
| **4** | 0 | 1 |
| **5** | 0 | 1 |
| **6** | 1 | 3 |
| **7** | 1 | 1 |
| **8** | 1 | 2 |
| **9** | 1 | 1 |
| **10** | 0 | 1 |

**Table 15**

As can be seen the rolling technique is the better of the two techniques however neither give consistently good quality fingerprints. The rolling technique did on occasion yield some good quality fingerprints however so highlighted clear potential. Because of this, the same experiment was completed on bullet casings which had been fired after the fingermark had been deposited on the surface. This gave the following results:

| | Grade | |
|---|---|---|
| **Donor** | Wrapping | Rolling |
| **1** | 0 | 1 |
| **2** | 0 | 0 |
| **3** | 1 | 1 |
| **4** | 0 | 0 |
| **5** | 0 | 1 |
| **6** | 0 | 0 |
| **7** | 1 | 1 |
| **8** | 0 | 1 |
| **9** | 1 | 1 |
| **10** | 0 | 0 |

**Table 16**

Obtaining useable results from fired cartridges via this technique proved to be very difficult. One of the greatest problems was the amount of background which was blocking any potential visualization.

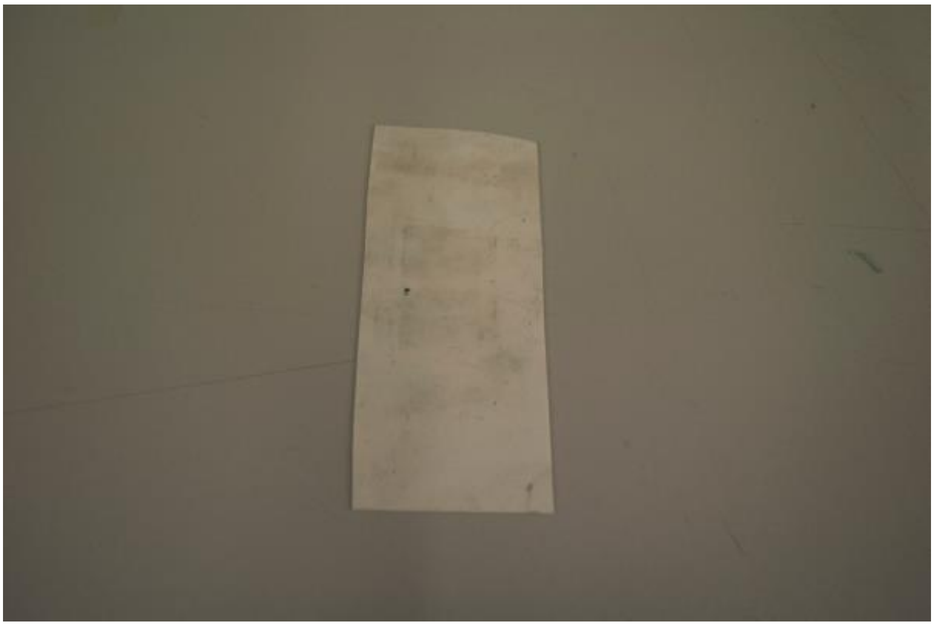


**Figure 86 - Background interfering with potential visualization from a bullet casing**

The gunpowder released upon firing was also picked up by the white gelatine lifters and would block much of the fingerprint should it be developed at all. As a result a method of cleaning the casing was attempted, as previous work has shown that even with washing on general metal, high quality fingerprints can be obtained. It is also worth considering that the excess material removed could also potentially give an insight into the weapon used or environment it was fired in. To do this, the casings were placed in an Eppendorf filled with water and then placed in a sonic bath for 2 minutes. This was then placed in a centrifuge at 15,000rpm for 30 seconds. The casings were then removed and rolled across the gelatine lifter. Whilst there was noticeably less 'background' there was no information suggesting the presence of a fingermark. There was a small amount of material still present in the Eppendorf that could be used for further analysis if required; this also shows that removal of this material is easily possible.

### 4.7.1 Invasively analysing bullet casings

Whilst remaining non-invasive is imperative for the work done focusing on those metals found at heritage sites, for materials like bullet casings, this is not as important and invasive procedures, if effective would be suitable. One such method again involved taking advantage of rubeanic acids high levels of sensitivity to copper.

Copper (II) acetate (0.503g) was dissolved in distilled water (50ml) to give a clear blue solution. A fingermark was deposited on the bullet casing, without being fired. This was kept in the open environment for 24 hours, then left in a desiccator for a further 24 hours. This casing was then dipped into the copper acetate solution for 30 seconds before being placed back into the desiccator for a further 1 hour. This was then rolled across the gelatine lifter and treated with rubeanate solution.

The above was completed with 10 donors and gave the following results:

| **Donor** | Grade |
|---:|---:|
| **1** | 3 |
| **2** | 2 |
| **3** | 3 |
| **4** | 1 |
| **5** | 2 |
| **6** | 3 |
| **7** | 3 |
| **8** | 2 |
| **9** | 3 |
| **10** | 3 |

**Table 17**

This showed clear promise as generally there was good quality fingerprints developed, and in some cases these were excellent. A grade 3 example is shown over the page.

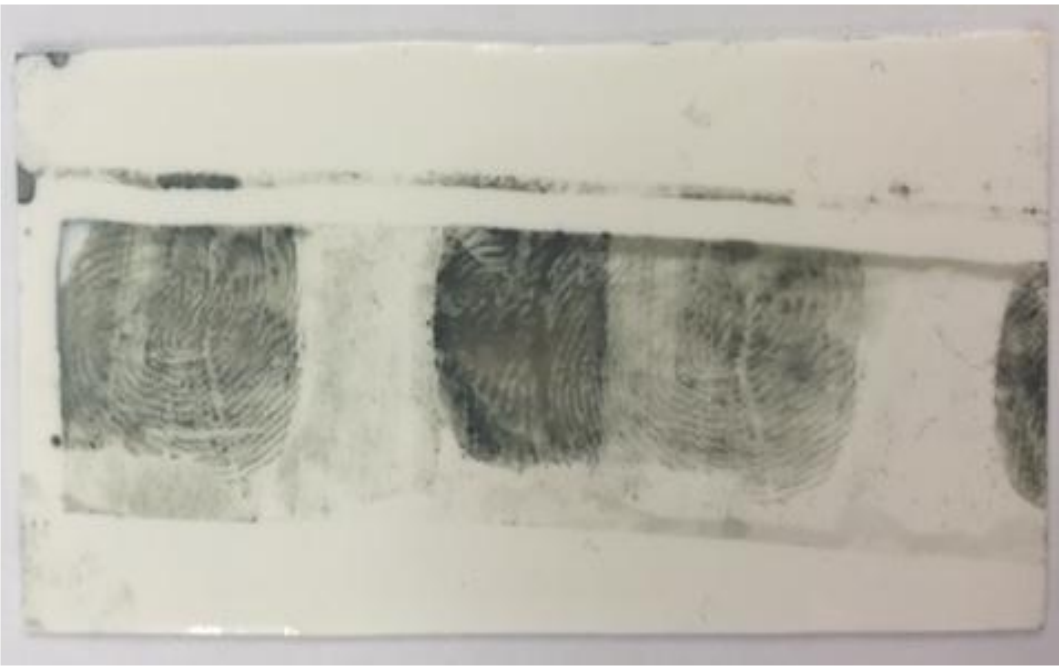


**Figure 87 - Good levels of detail obtained using copper acetate on a bullet casing**

The next step was to see if this continued to be the case with casings which had been fired, and hence subjected to high pressure and temperature. The same process as before was attempted on fired casings. This gave the following results:

| **Donor** | Grade |
|---:|---:|
| **1** | 1 |
| **2** | 1 |
| **3** | 2 |
| **4** | 1 |
| **5** | 0 |
| **6** | 1 |
| **7** | 0 |
| **8** | 1 |
| **9** | 2 |
| **10** | 1 |

**Table 18**

Whilst this showed considerable improvement to the non-invasive procedure, it was still clearly limited, and the action of firing appears to remove a large amount of the residues which are enabling the mobilization of the $Cu^{2+}$ or preventing the corrosion signature from being analysed fully. However the fact that there is some detail above, and excellent detail can be obtained when it has not been fired still suggests there is certainly the potential for future work. There is even an argument to be made that the technique could be used in instances where a casing which has not been fired, but has been handled, could be analysed by those tasked with finding a potential criminal. For example when a casing has been unknowingly dropped at a crime scene.

Another invasive attempt at fingerprint detection involved direct treatment of the casing with the rubeanate solution. This solution was made up as in all other cases (0.1% solution) but then the gelatine lifter step was removed. Instead the solution prepared was applied via an Ecospray directly to the bullet casing or metal surface itself. However this yielded no positive results under any circumstance. Whilst a reaction is most likely occurring, it is not possible to visualise the fingermark in this manner.

## 4.8 Developing fingerprints from other surfaces

Throughout the research outlined to this point, it is without doubt that rubeanic acid has a very high level of sensitivity to cuprous ions. It was thought that this sensitivity could be taken advantage of in order to develop high quality fingerprints from the surface of materials which themselves would not have this sensitivity. This was to be done by transferring small amounts of this copper and its ions to alternate materials, which could then react with the residues of a fingermark and then be transferred to the gelatine lifters and analysed as with previous methods of detection. As the survey noted, there are numerous materials which are vandalised or stolen at heritage sites, where being able to non-invasively obtain fingerprints from would be hugely desirable. There are surfaces which are commonly studied with regards to their interaction with fingermarks, however this is rarely done when it comes to analysing said surface with no chemical contact. For the purpose of this research the following materials were examined:

- Paper (This included material like a stamp, or an old map)
- Metals other than copper and lead (gold and steel)
- Fabric

To do this, the following procedure was followed.

A fingermark was deposited onto the surface of the material in question, and left for 24 hours. After this period of time a copper plate was then placed on top of the material in question (with fingermark deposit on it) and underneath a heavy lead weight. This was left for a further 48 hours inside a desiccator. After this, both the material chosen and the copper were placed on a gelatine lifter and treated with rubeanate solution.

### 4.8.1 Paper

The first surface this was attempted with was paper. It was thought that old books or documentation could be the victim of theft, and there were a few examples of this highlighted in the survey discussed in chapter 2. The first attempt was completed on A4 printer paper, and gave no information when lifted from the paper itself, although it did yield markings indicative of coppers presence, but these were just a smudge of colour. When lifting from the copper however there was the appearance of a faint fingerprint with some reasonable detail (2 on the Bandey Scale). As a result of this, older paper, more likely to be detected in a non-invasive manner was then examined in the same way. The paper used was from 2 items. The first was a penny red stamp, and the second was a map from 1840. However, this gave no information on any occasion, even when parameters were changed such as the heavy weight being left on top of the copper for a greater period of time (1 week). Because there has been no change in procedure, the reason for this not working must be because of the paper as opposed to the technique itself. The older paper may well be more porous and hence details of the fingermark will be harder for the cuprous ions to interact with. Even when a sebaceous mark is laid onto this surface it is impossible to see any detail with the naked eye, so it appears likely that this particular surface is especially problematic when it comes to analysing fingerprints non-invasively.

### 4.8.2 Gold and stainless steel

The same process was attempted with the non-porous metals gold and stainless steel. Both of these had showed much lower sensitivity to rubeanate solution than copper and so it was believed that there would be minimal background for the attempts here. For gold on both occasions, with gelatine lifted from both surfaces there was no evidence of fingerprint development, instead there was just a smudge of colour again. However stainless steel showed much greater promise with this particular technique and whilst lifting from the steel itself yielded little detail, lifting from the copper that had been in contact with said steel gave fingerprints of fairly good detail (3 on the Bandey Scale). It appears that with such a non-porous material, the ability of the fingermark residues to remain on the surface of steel, and hence react with the copper when this is placed on top of it is improved. This worked similarly with natural and sebaceous marks, however gave no such detail with eccrine deposits. It can therefore be concluded that the more robust components within a natural or sebaceous fingermark will remain present on the surface of steel, however this is not the case with eccrine deposits.

**Figure 88 – Fingerprint developed from stainless steel**

### 4.8.3 Fabric

When attempted with fabric, there was no detail at all apparent. There were again notes suggesting coppers presence however no detail to suggest presence of a fingermark.

What the above appear to suggest is that such a procedure seems to be limited to non-porous materials, where the fingermark residues can remain on the surface of said material, as opposed to becoming withdrawn into it, and hence impossible to interact with the copper plate, no matter how much weight is placed on top of it. Taking advantage of this kind of interaction shows similarities to the work done by Davis et al[148] where VMD (Vacuum Metal Deposition) was used to coat the surface of polymer notes with a thin layer of copper which interacted with deposited fingermarks on its surface. This technique clearly has great potential, in several arenas, however its invasive nature means alternatives like the one discussed in this thesis are required for those materials found at heritage sites.

### 4.9 Bacteriological information from gelatine lifters

Gelatine lifters have been incredibly useful tools that have been utilised throughout the course of this research. This has ranged from lifting trace metal residues to small amounts of loose material on stone samples. Therefore, it was believed that analysing the extent of the lifting capabilities of gelatine lifters was very important. It has already been shown that small traces of metal can be lifted and so it was understood that very small amounts of a material could be detected in this manner. Because of research on coppers abilities as an antimicrobial surface[149]; it was believed that using agar plates in conjunction with the lifters could yield insight into the extent of their capabilities. If so, there would be the potential of copper contact being proven as a result of its anti-microbial properties, as well as examining if a fingerprint can be visualised based on its bacteriological outline.

For the initial test the aim was to determine if bacteria from a finger can be picked up by the gelatine lifter and then transferred to an agar plate. Six standard agar plates were prepared and kept at 37°C. Six gelatine lifters were cut to size. On 4 of these a natural fingermark was deposited on the surface, whilst on the other 2 a fingermark was deposited directly onto the agar surface. The gelatine lifters were placed on the surface (with fingermark pressed against the agar) and left in an incubator at 37°C for 24 hours. For the 2 agar plates where the fingermark was pressed directly against the agar, there was clear bacterial growth, in the vague outline of a fingermark. In the case of those with the gelatine lifter being placed in the agar plate, it was discovered that the majority of the lifter broke down when left in contact with the agar for this period of time and the white colour had leaked into the agar and hence made any visualisation difficult. As a result the same process was completed again, however on this occasion the gel was placed in contact for 1 hour before being removed and agar then stored for a further 23 hours at 37°C. On this occasion all 6 agar plates gave the clear growth of bacteria in the outline of a fingermark.

In order to confirm that that was indeed the fingermark causing the growth a comparison was completed between a piece of gel which had a fingermark deposit on its surface, and one which had been left blank. These were both pressed against the agar plate for 1 hour before being left in the 37$^{o}$C incubator for a further 23 hours. The gel that had a fingermark on it produced clear bacteriological growth, however that which had been left blank had no such growth.

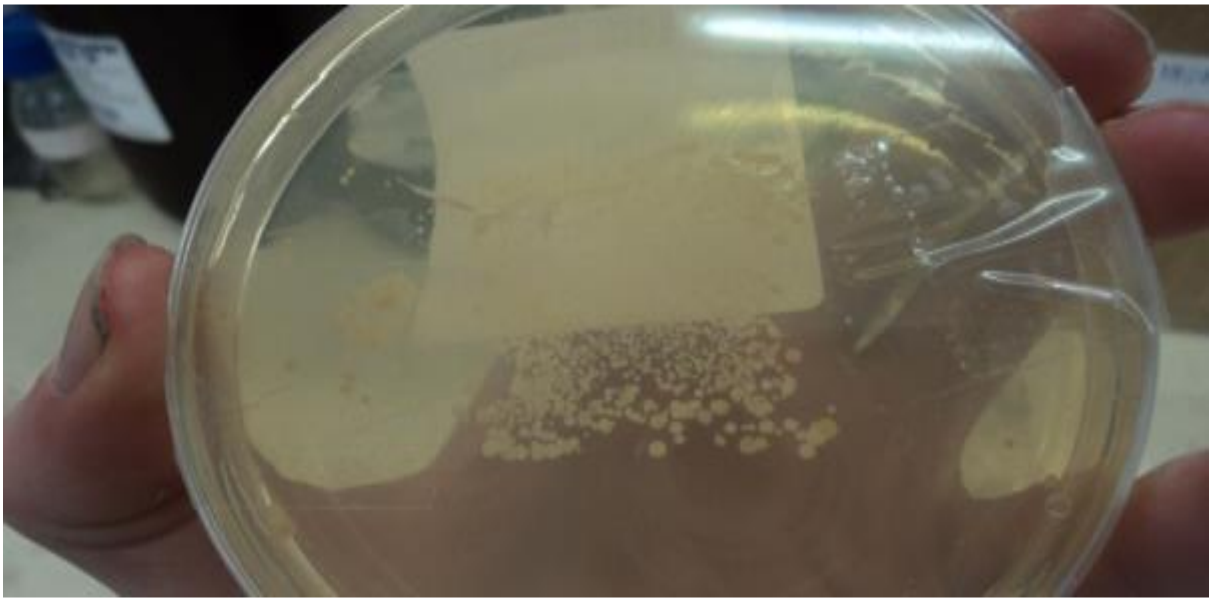


**Figure 89 – Outline of gelatine lifter can be seen via the bacteriological growth**

Hence it was shown that even bacteria on the fingers can be transferred onto the surface of the gels, such is their high levels of adhesiveness. With this information gathered, it was thought that a particular location on a specific piece which had been handled could be identified. It was also thought that it could yield some information concerning when certain materials had been recently held, such as copper which has a history of anti-microbial properties.

The initial point raised examined if the gels could be used to identify the exact point at which a latent fingermark deposit could be found. Hence a fingermark was deposited on an acetate sheet and left for 24 hours. A piece of gelatine lifter was then placed over this area, and a separate area elsewhere on the same sheet with no such fingermark deposited. These were each then placed on an agar plate for 1 hour, before being removed and left in an incubator at 37$^{o}$C for a further 23 hours. There was no growth when lifting in this manner in the outline of a fingerprint. On occasion there was slight growth, but this was in no particular pattern.

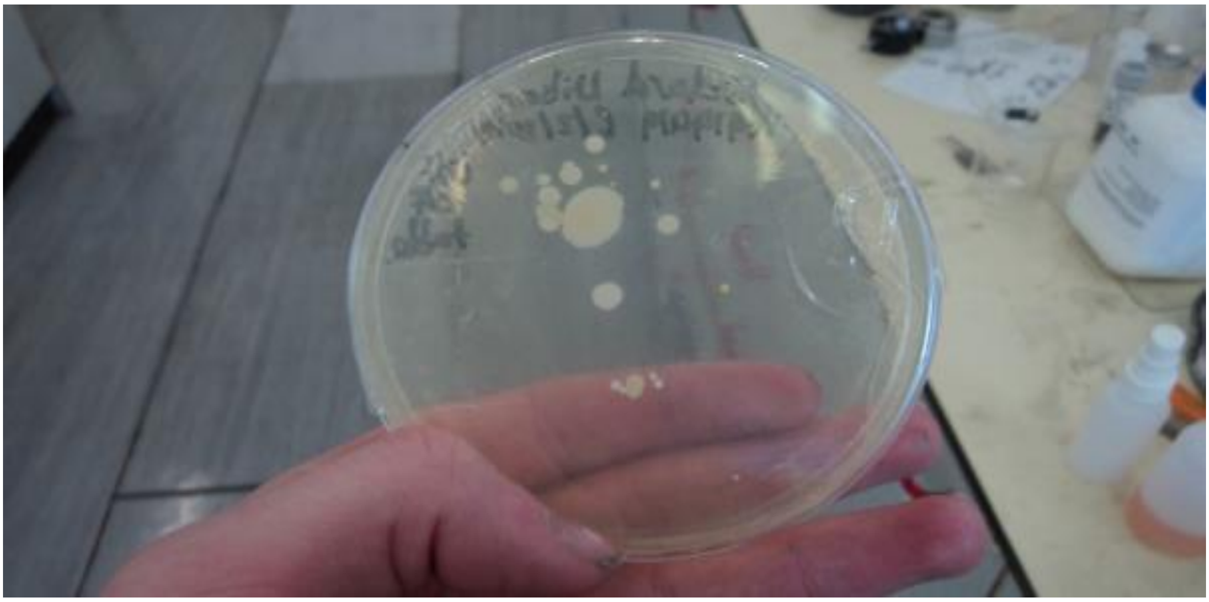


Figure 90 – No pattern with growth from alternate surface

It was also notable that both types of bacteria appeared identical to the naked eye and when looked at through a microscope. This experiment was completed with a range of materials other than acetate, such as from the laboratory desk, a copper pipe, or from the fabric of clothing. All gave identical results, suggesting that whilst small amounts of bacteria can be picked up via the gelatine lifters, this does not extend to lifting from other surfaces, and the bacteria from a fingermark must be directly deposited onto the gel, rather than lifted from another external surface. The fact that the bacteria which was growing was identical in each case also suggests that whilst bacteria being lifted using the gelatine lifters is most certainly notable, as it highlights their high levels of adhesiveness, the practical applications with regard to lifting bacteria is limited. Despite this, there is clear potential that is worth consideration when discussing future research in this field. Whilst the bacteria cannot be ‘mapped out’ using the lifters, it **can** transfer bacteria from finger to gel to plate, thus allowing visualisation. To progress further, confirming what this is reliant on, and if the amount of bacteria that is lifted can be increased must be determined.

Using an alternate form of analytical technique to examine the surface of the gel could yield further information with regard to what is being taken in from the skin, and increasing the adhesiveness could help this ability to map a fingermark using bacteria. Two differing gelatine lifters were used in this study, with one showing considerably better results than the other. The BVDA lifters which have been used throughout the rest of the research were not adhering to the agar and instead were falling away, or curling in the corners. As a way of tackling this, CSI lifters were used instead. These were backed with fabric as opposed to the usual acetate as is the case with BVDA. The additional weight ensured that the gelatine lifter had a constant contact with the surface of the agar. However in previous experimentation the CSI had a lower level of adhesiveness. Hence a technique which would enable the BVDA lifter to be used in this manner could possibly ensure an increased level of bacteriological material being lifted, and therefore be envisioned on the agar plate. With a larger amount of bacteria being lifted, it would be far clearer and easier to determine if there is a possibility that the presence of a fingermark is identifiable via this process. Whilst the research did not yield a specific practical application in terms of lowering levels of heritage crime, what it did, was yield further information about the gelatine lifters, something that is a key component of the research completed elsewhere within this project. It also provided an insight into the great levels which can be lifted via the lifters. When considering the reaction process that is occurring on the surface of the gelatine lifter in other areas of research, such as the trace levels of copper and its interactions with fingermark residues, it is important to understand any limitations of what can be lifted onto the surface in the first place. As a result of this particular area confirming that even bacteriological levels can be lifted, it stands to reason that there need only be a very trace amount of a residue present, for it to have an interaction with a metal surface.

Throughout all of the fingerprint detection techniques outlined within this chapter, there appears to be clear trends which can be noted.

- Sebaceous and natural fingermarks are much more likely to yield a positive detection using rubeanic acid as the developing agent.
- Eccrine fingermarks can, on occasion yield positive identification, however this is less consistent.
- Rubeanic acid is an equally good developing agent for copper, brass, and bronze.

- It is not possible to use rubeanic acid as the developing agent for lead, or any other metal that has showed an affinity for rubeanate solution other than copper and its alloys.
- The transfer of cuprous ions to other materials is far more likely to occur on non-porous materials.
- There is the potential of this technique being used outside of a heritage crime arena, most notably with brass bullet casings.

Work discussed thus far has focussed mainly on metal theft, and using rubeanic acid as a means of detection for items of historical importance. However the survey completed and outlined in chapter 2 also highlighted stone as a material under great threat at heritage sites worldwide. The following chapter discusses work completed focusing on stone detection which, when coupled with the work already discussed regarding metal detection, aimed to develop a well-rounded project focusing on the end goal of lowering levels of heritage crime.

## Chapter 5 – Stone Theft

Stone theft is a branch of crime it may be somewhat surprising to consider as financially and emotionally destructive which it can be. There are several examples of stone theft which have resulted in huge costs, these costs often must be paid for by heritage sites which struggle to source such means [56][127][132]. Stone is also stolen at an increasing level abroad[150][151][152], when considering this issue from a more global viewpoint. Whilst the original work proposed here would be used to create a database of information on a national scale, this could be a stepping stone to future progress in terms of improving the validation of a stones original location. A specific example of this could be from within differing countries when efforts are made to illicitly transport them across borders. With heritage crime being especially prevalent in war torn countries[8], the work proposed here could be an excellent tool to help improve prove the authenticity of potentially stolen artefacts when they are illegally transported and be a contributory factor in efforts to lower levels of this global trafficking.

Gravestones being stolen, or vandalised is a clear example of the emotional, as well as financial damage stone theft can cause[60]. Whilst instances like this can cause distress, they clearly highlight the issue and create a greater public awareness of an issue, which may surprise many outside of those which are tasked with protecting heritage sites. The occurrence of stone theft has received greater media attention over recent years, and the extent of the problem was further emphasised with the results of the survey completed during the course of this research[29] in which stone was the most commonly stolen non-metal material. Additionally, developing a detective method for stone and bricks has huge potential outside of heritage crime when considering the use of bricks as weapons, with examples such as the London riots (August 2011) clearly showing the desire to link an individual to brick or stone[63].

### 5.1 Aims

In response to the results obtained during the survey, and after initial research regarding the problem itself, where both Historic England and the Church Conservation Trust highlighted the extent of this problem, the decision was made to focus a degree of this study onto developing a technique which could be used to aid in lowering levels of stone theft. What was important here was ensuring any technique developed had the potential to be used by those who required such work being done. Hence an interview was conducted with a member of the Church Conservation Trust. From this the following key points were taken away:

- Developing a technique focusing on lowering stone theft would be very useful
- Remaining as non-invasive as possible was vital
- A small amount of material being removed for analysis would generally be suitable, however any more would be dependent on the particular piece and its historic value

As a result of the non-invasive requirements, the work done attempted to use as little of the stone for analysis as possible. With this, it was decided that the adhesive nature of the gelatine lifters would again be taken advantage of in order to ‘lift’ small amounts of stone which could in turn be analysed. It was hoped that this analysis could be taken advantage of in order to produce information regarding the surfaces of stone to determine its historical environment and location. Hence it could yield knowledge as to if a stone has been in a rural location, next to a busy road, or near a specific building. It was also hoped that it could yield information regarding its geographical location, whether this can be narrowed down to a county, or even the specific site itself. What was to be unique about this branch of research was it being a surface technique rather than analysing the entire stone, an area which would both be invasive, and unnecessary in this particular case.

Before this stage could be reached however, it first had to be confirmed that a given analytical process could yield information at all when the gelatine lifters were to be used as a substrate for said analysis. The techniques were unique in that trace amounts were being ‘lifted’ using the gels, and analysed whilst still on this surface. Any process had to first be optimized and any background minimized or, if possible removed entirely. If this could be achieved then it was hoped that further, more in depth analysis would yield greater levels of detail regarding stone.

The primary aim was to simply determine if the analytical technique in question (laser induced breakdown spectroscopy) could be used to analyse trace amounts of stone, and produce a spectrum which provided any insight into what the stone is comprised of. With this, it was also hoped that the gelatine lifters would not ‘block’ the visualization of any information of interest within the spectra produced.

More long term aims focused on the requirements for those tasked with lowering levels of stone theft at heritage sites nationwide. If the technique could provide unique information about each piece of stone, and its history both geographically and environmentally, then it could in theory be ‘matched’ to a specific location. It was therefore hoped that this technique could eventually enable a ‘database’ of information regarding stone to be developed, based on each individual piece of stones unique chemical fingerprint. Determining if this was possible, and if so, to what extent, was a key aim during this process.

## 5.2 Laser Induced Breakdown Spectroscopy (LIBS)

Laser induced breakdown spectroscopy, or LIBS, has been used for a great range of both analytical and forensic purposes. This has ranged from screening for gunshot residue[153] to analysing bakery products[154].

The technique itself involves a laser pulse impacting upon the surface of a given material, which then results in a small amount of said material being removed or ablated. This evaporated material then expands above the surface and due to the high pressure forms a plasma. The electrons, ions, and excited species of the ablated material make up the light emission which is then converted into a unique analytical signal[121] measured by the LIBS system. What appeared most promising about this technique with regard to this work, is the fact that such a small amount of material is ablated or removed that it can still be considered to be non-invasive. Because of this, the quantity of loose material that must adhere to the gelatine lifters is reduced as only a miniscule amount is needed for analysis. What also appealed about this technique was the fact that the laser itself could be focused onto one specific point, with a high level of accuracy, and the amount of laser pulses used could also be controlled. With the introduction of such steps, it was hoped that the amount of interference from the gel, could be minimized.

### 5.2.1 Experimental

A small piece of gelatine lifter was cut to a consistent size (3cm x 3cm) in order to obtain each specific sample. Gravestones were generally the samples chosen as they could yield some information regarding the approximate age of the stone that was being analysed. Each piece of gel was placed over the stone for 30 seconds; occasionally this needed to be held against the stone so it did not fall off, as it could not adhere to the stone if it had a particularly rough texture. Each piece of gel was covered with the acetate sheet once stone had been lifted, before being analysed using LIBS.

The instrument used for this analysis was an Ecco2 Elemental Comparator laser induced breakdown spectrometer. Within this was an actively Q switched Nd:YAG 1064nm laser. The detector used detected wavelengths across a range from 225-930nm with 0.14nm optical resolution in the UV.

After several preparatory samples, and a degree of trial and error, it was decided that only one laser pulse would be focused on a random piece of stone on each gelatine lifter.

Based on the information obtained during these preparatory studies, a stone group was added to the ecco2 database so these elements were labelled automatically. On the occasion where peaks were present that did not fall into this set of elements, they were analysed manually. This was done primarily as a time saving exercise. The elements within this group were:

- Sodium
- Iron
- Potassium
- Titanium
- Magnesium
- Silicon
- Strontium
- Calcium
- Barium
- Zinc
- Aluminium

Not all of these were commonly found, and this was cut down to focus on more specific elements based on initial findings, as will be discussed later in this chapter.

A range of stones were analysed. Whilst these were not definitively shown to be any particular type, both the results from the LIBS and a visual inspection prior to analysis highlighted similarities throughout. It was believed that all stones analysed were one of four types:

- Granite
- Limestone
- Slate
- Sandstone

After initial results were obtained, the same sites were all tested again 6 months later.

One issue that needed to be addressed was the ethics of the work, as the sites analysed are gravestones. In churches with large amounts of foot traffic, and a churchwarden that was readily available, permission was asked for (and granted) prior to analysis. However in more rural areas it was often not possible to find the correct person for this permission to be granted. This was why very old gravestones (over 100 years) were generally analysed, as the likelihood of a person visiting this gravestone was drastically reduced.

## 5.3 Results and discussion

The amount of material lifted varied considerably from each individual stone. On some occasions, there was almost entire coverage across the gel, whereas on others there were only isolated pieces of stone present on the lifter. Whilst only a minute amount of stone is required for LIBS, this did limit the availability of stone to analyse on certain samples. The initial step that this process required was noting any differences between the gel alone, and the stone that was analysed on the gels surface. This was done in order to determine both the level of 'background' present when a stone sample was analysed, and also which particular elements are abundant within the gel and must therefore be taken into account when results are obtained.

The bulk of the differences in all samples were between the wavelengths of 250-700nm. Outside of these there were many similarities as a result of elements found within the chamber itself such as oxygen and nitrogen.

When placed in the ecco2 chamber, laser pulses were set at three random points of the gel. Upon analysis, all gave identical results. Unsurprisingly there was a significant peak due to titanium, because of the titanium oxide, which was abundant in the lifters due to its properties as a whitening agent. There was also high levels of strontium and sodium. All of these were taken into account when analysing stone samples.

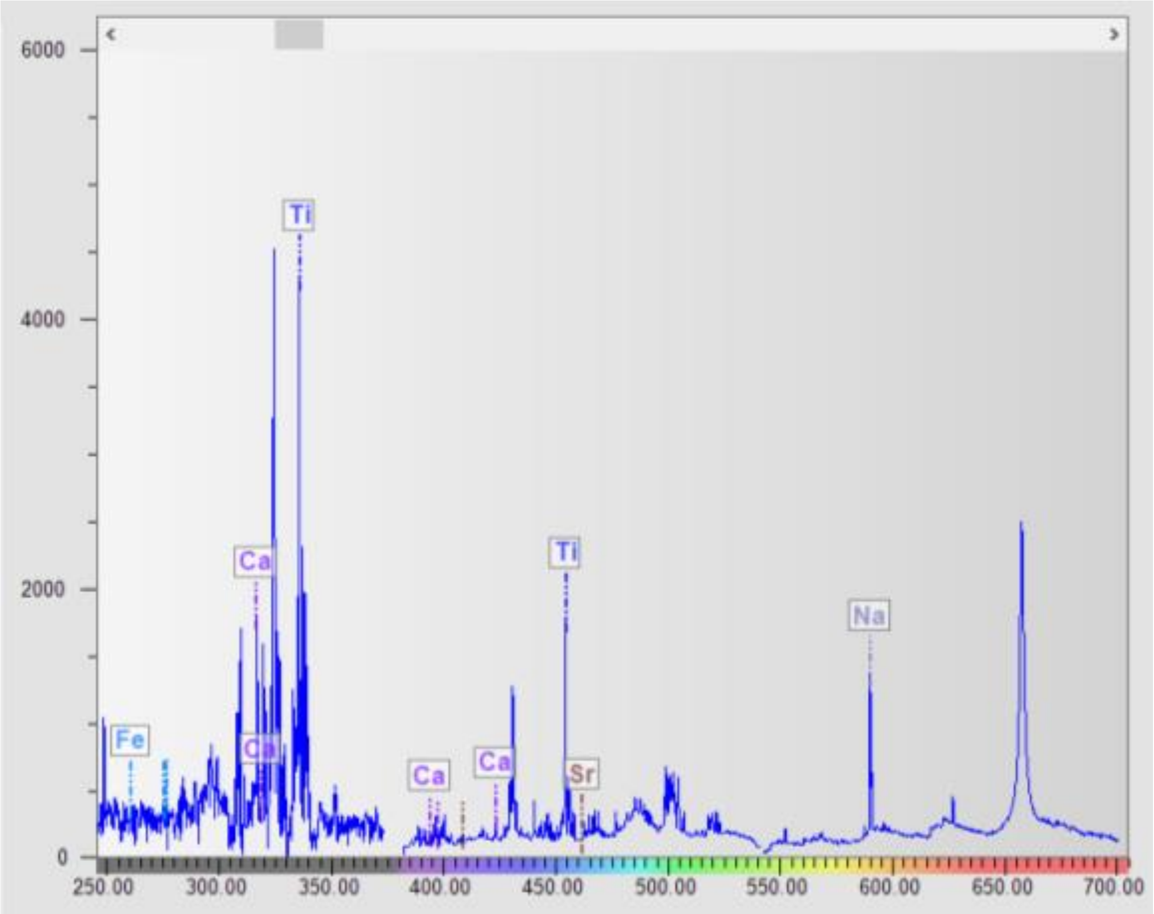


**Figure 91 - Gelatine lifter**

The unlabelled peak at 656nm was due to Scandium. The first step was to confirm that upon analysis of stone, there were any differences at all, and that something other than the gel was being detected. A grave from Mansfield shown below highlights that whilst there are several similarities suggesting some gelatine lifter is being detected, a few great differences prove that stone is the bulk material being analysed.

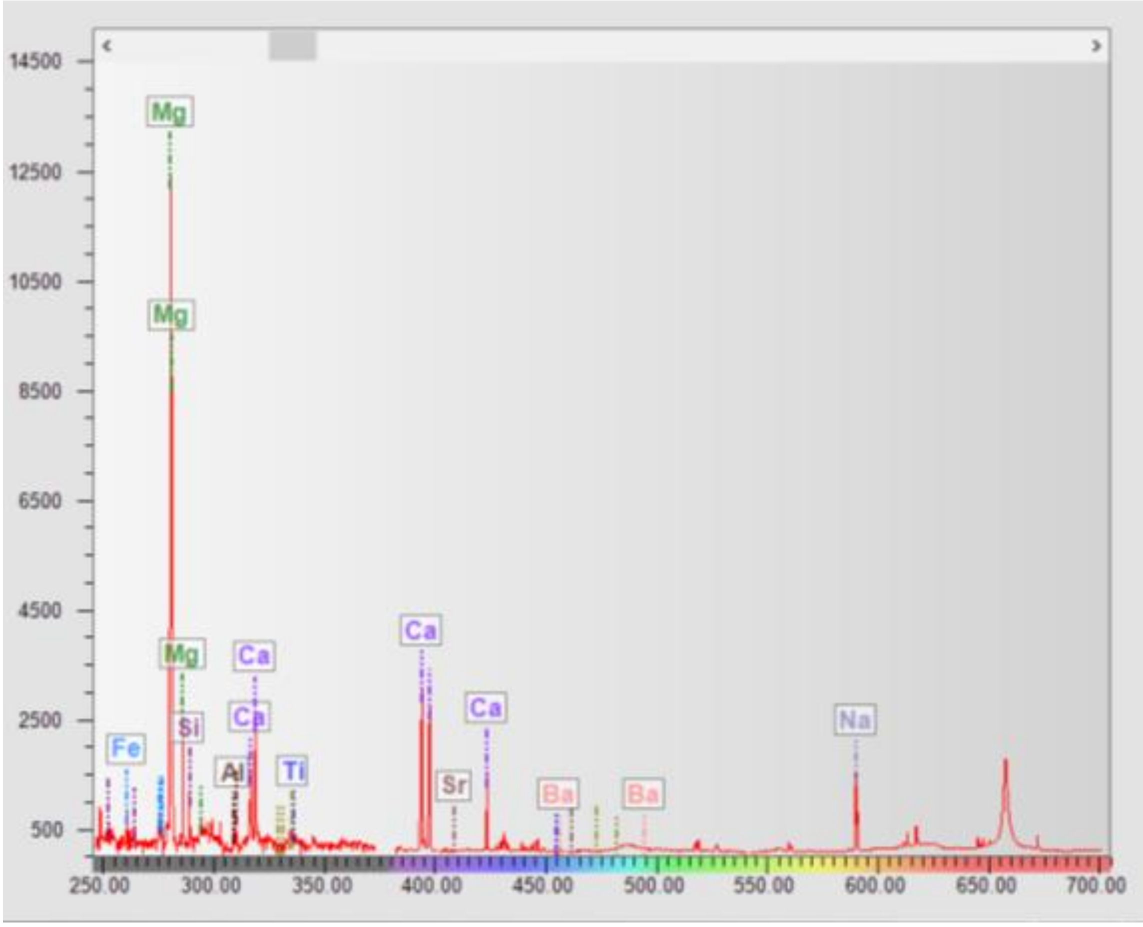


**Figure 92 - Results from a stone sample (Mansfield)**

As can be seen there are notable differences here, highlighting that stone is being detected as well as the gelatine lifter. Other stones also produced spectra notably different the the gelatine lifter, and similarities (such as the peak at 656nm) are easily discounted, whilst differences (such as the magnesium doublet peak at 279nm) are clear.

Following on from this success in terms of the primary goal (differences between lone gel, and stone on gel), the next step was examining if there were any differences between pieces of stone on the same piece of gelatine lifter. Ensuring there was a degree of consistency, and therefore the position on stone that was chosen had little importance was imperative. Highlighted below is the same site in Mansfield, however analysed at a different point on the same gelatine lifter.

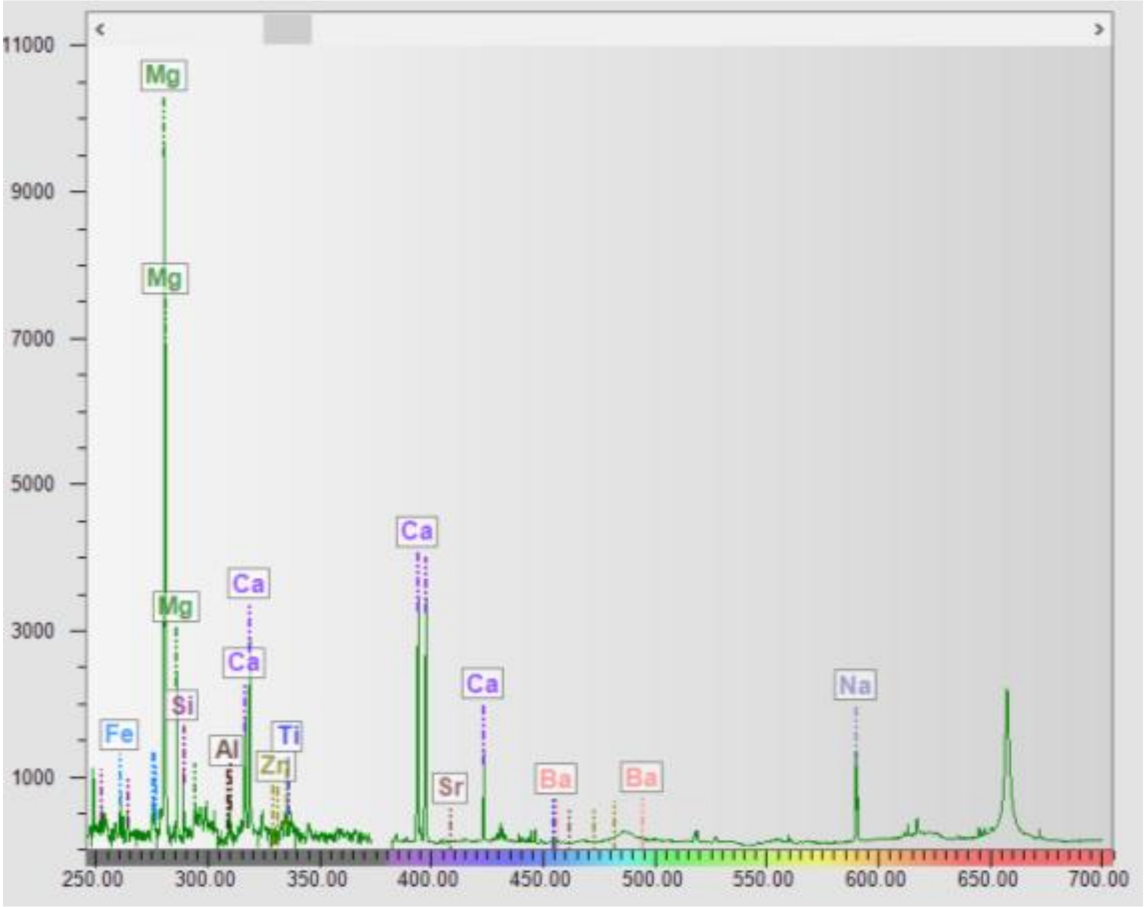


**Figure 93 - A different point on the gelatine lifter**

The peak positions are near identical to the first scan of this stone. The intensities differ slightly, and this is likely due to factors such as how robust the stone is, or how much gelatine lifter is being picked up aside from the stone itself. Such influences will be difficult to avoid with this technique, and when the differences are as minimal as here, the problems that it results in are minimal. The similarities between the samples are much greater than the differences, and as a result it appeared that this aim was successful as well.

Below is a zoomed in section of these spectra which clearly highlight both the similarities between the two Mansfield samples, and how they differ from the lone gel:

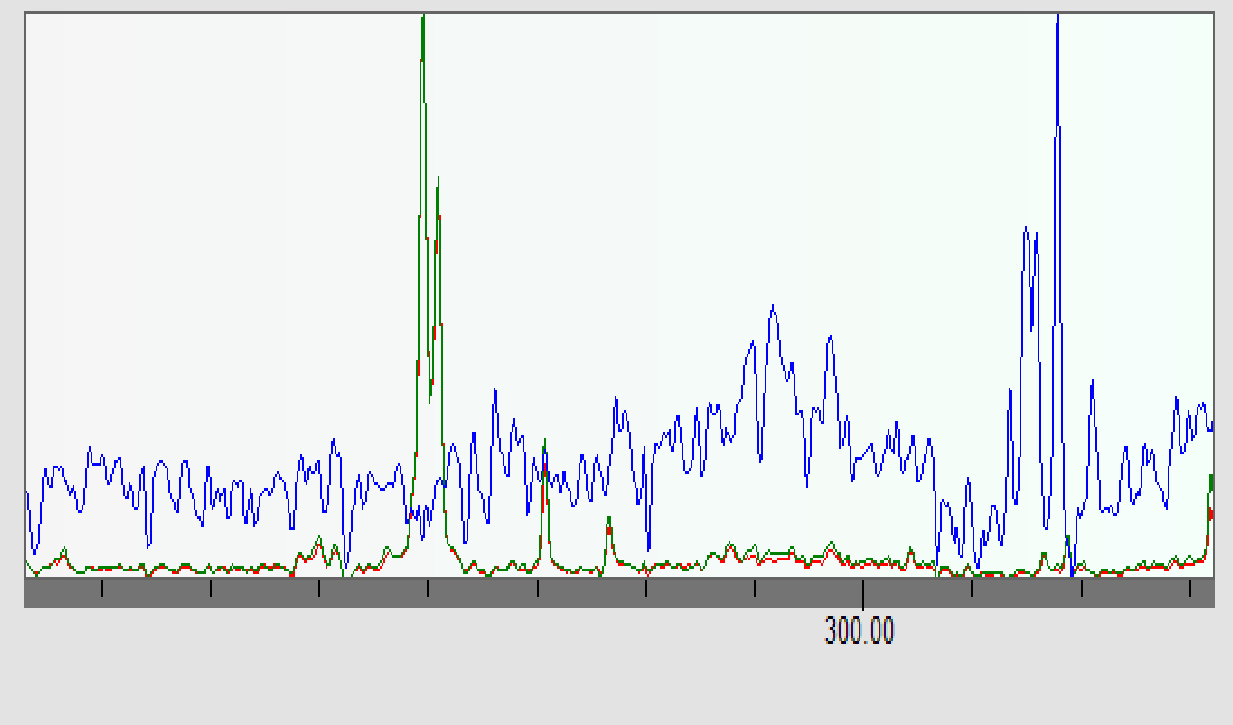


**Figure 94 - Gelatine lifter (blue) notably differs from when stone is involved**

The highest peak for both stone samples is due to magnesium, where there is no notable peak for the gel alone. On the other hand, there is a peak in matching intensity for the lone gel on the right of this figure which is due to aluminium.

At this point two clear goals had been achieved with regard to this technique.

- The stone produced different results to the gelatine lifter, and the two could be differentiated.
- Across a small piece of area like a single 3cm x 3cm piece of gelatine lifter, the stone analysed produced near identical spectra, highlighting consistency which was imperative to compare on a greater scale.

The next step was to analyse if there were any trends which could yield further information about a stone, or if each piece of stone produced a near identical spectrum.

### 5.3.1 Geographical comparison

Determining if the LIBS can be used as a way of identifying key details about a stone has the potential to be an excellent tool for those tasked with protecting such material from theft at heritage sites. Identifying any patterns of information regarding a stone's elemental makeup could be an excellent way of doing this, as any piece of stolen material could then be 'matched' to its original location. In this section, the differing geography of stone was compared, ie stone found in several different towns or cities was analysed to determine the differences, if there are any, between each. In each site, the environment was kept as similar as possible for this process. In the case here, they were all taken from sites on a main road close to the centre of the town or city as it was hoped that several external factors could potentially have influenced the chemical makeup of a stone here, for example emissions from cars.

One site in each location was analysed initially. The simplest way of comparing these was attempted first, which was that done above. Simply noting differences visually in the spectrum produced by each. In total there were five samples analysed at this point. These were in the following years, in which all were within a 14 year timeframe.

- Leicester 1871 (blue spectra)
- Edinburgh 1880 (red)
- Loughborough 1855 (green)
- Mansfield 1872 (orange)
- Nottingham 1866 (purple)

When analysed it was clear that there were several similarities which made visualising differences in the most simplistic way difficult. Whilst there are certain differences, there are not enough for this to be the only step required.

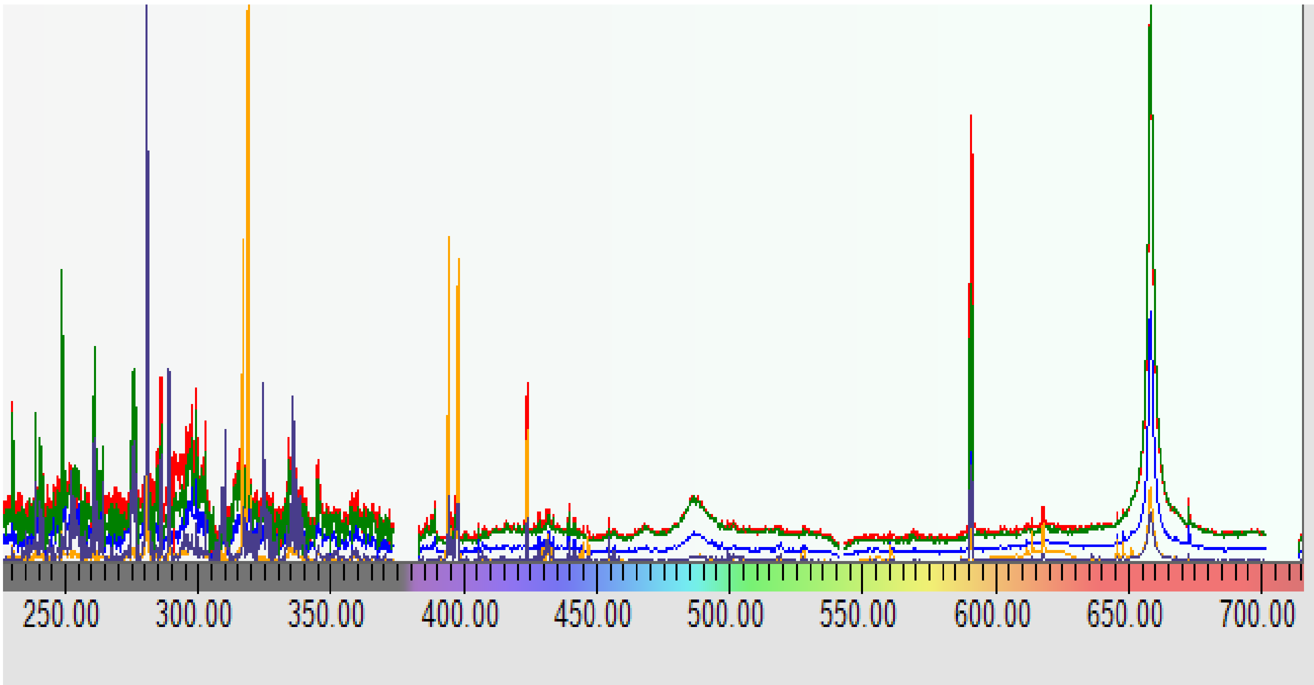


**Figure 95 - Whole spectra of interest**

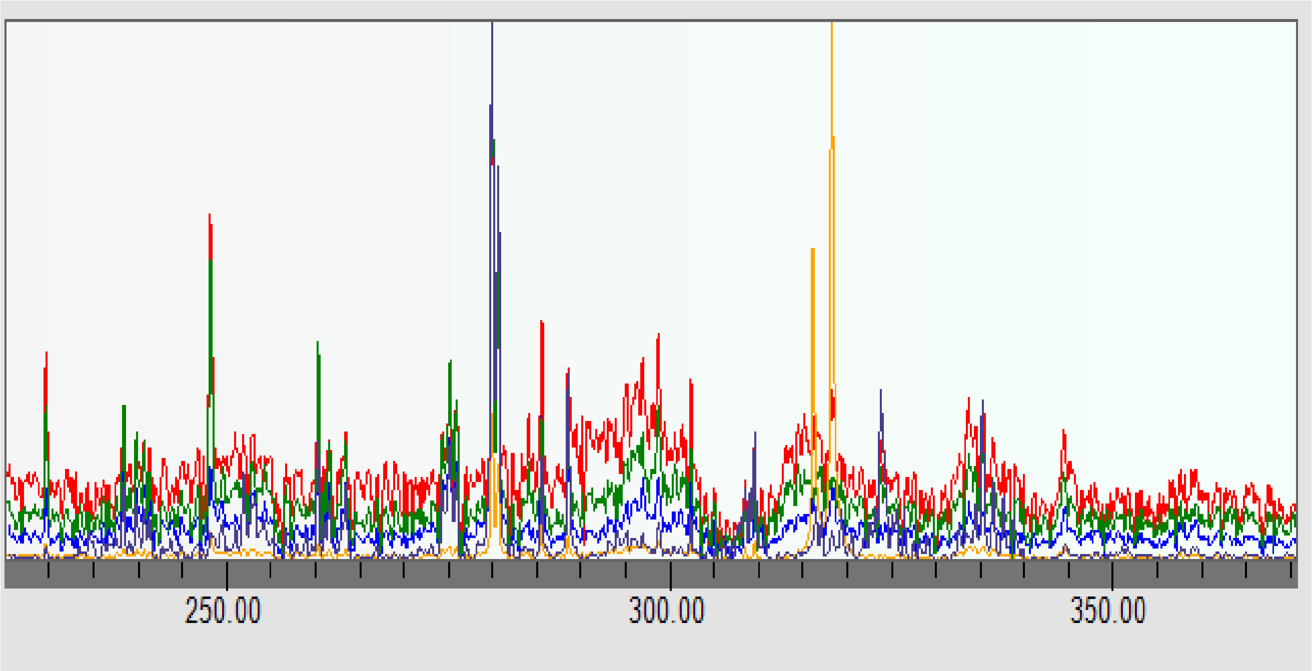


**Figure 96 - 230-370**

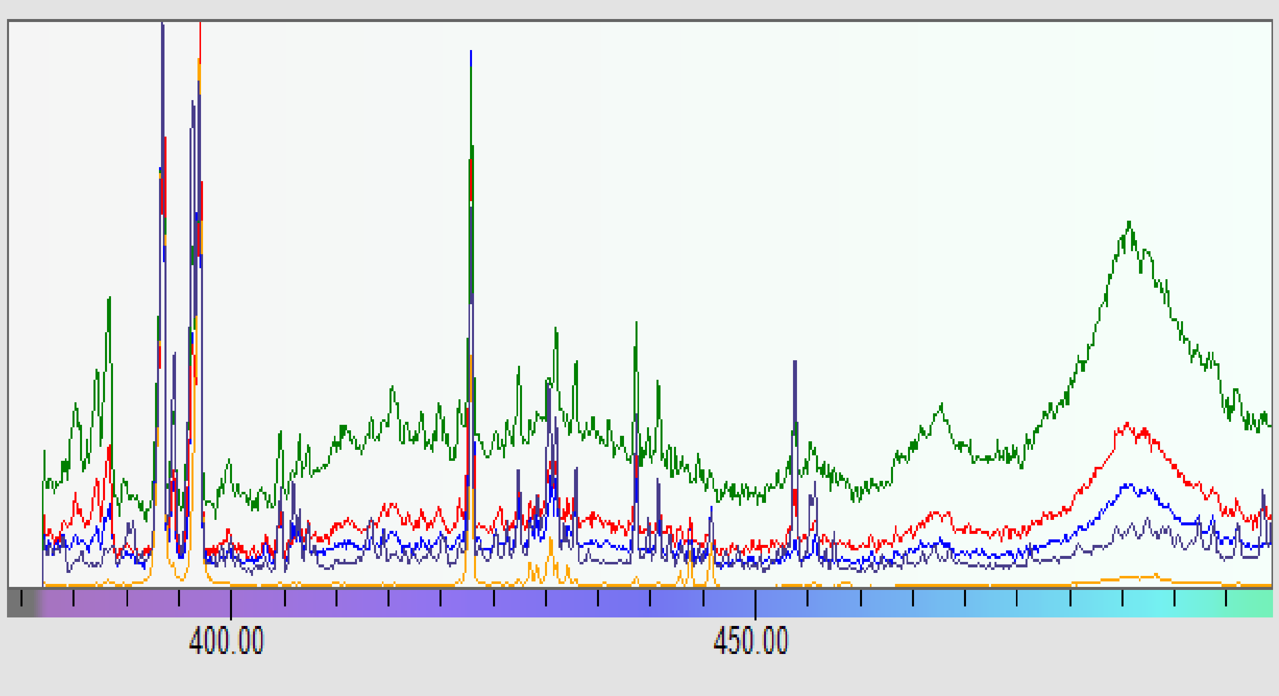


Figure 97 - 370-550

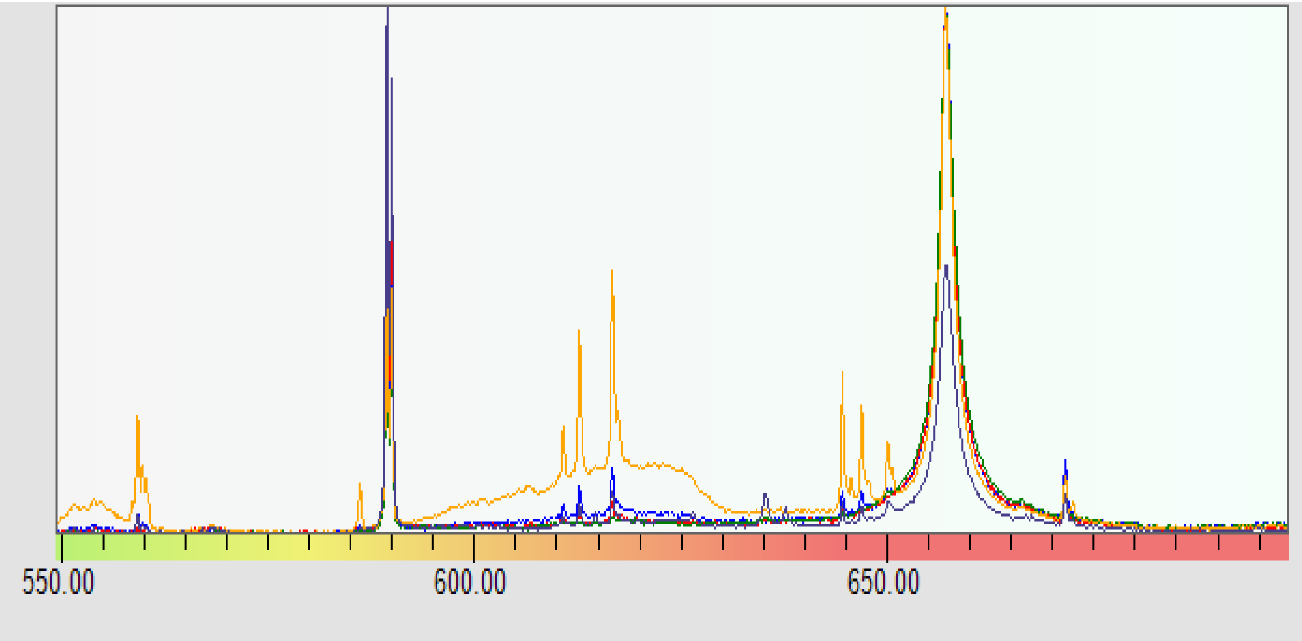


Figure 98 - 550-670

The peak height differences at calcium 317nm is just one example of a difference between the peaks, however the other results obtained here highlight few differences between samples.  Another five samples taken from elsewhere on the same site in each were then analysed identically to the process described above. This produced near identical results for each. Because of this, further analysis, noting any differences was required. This involved noting the levels of certain elements within the samples, and comparing ratios across the differing locations.

Five of the most common elements found in stone were chosen for this primary comparison. These were:

- Iron (260nm)
- Magnesium (279nm)
- Silicon (288nm)
- Aluminium (309nm)
- Calcium (317nm)
- Titanium (453nm)

Titanium is rarely as abundant as the other elements listed here; however, it was believed that it could yield insight into the level of gelatine lifter, which was being analysed, as this was particularly abundant for the gelatine lifter alone.

Five pieces of stone were again analysed at each of the locations (25 samples in total, comparing results based on a piece of stone's geographical location). Upon inspection of the spectra itself, finding any particular pattern was not possible.

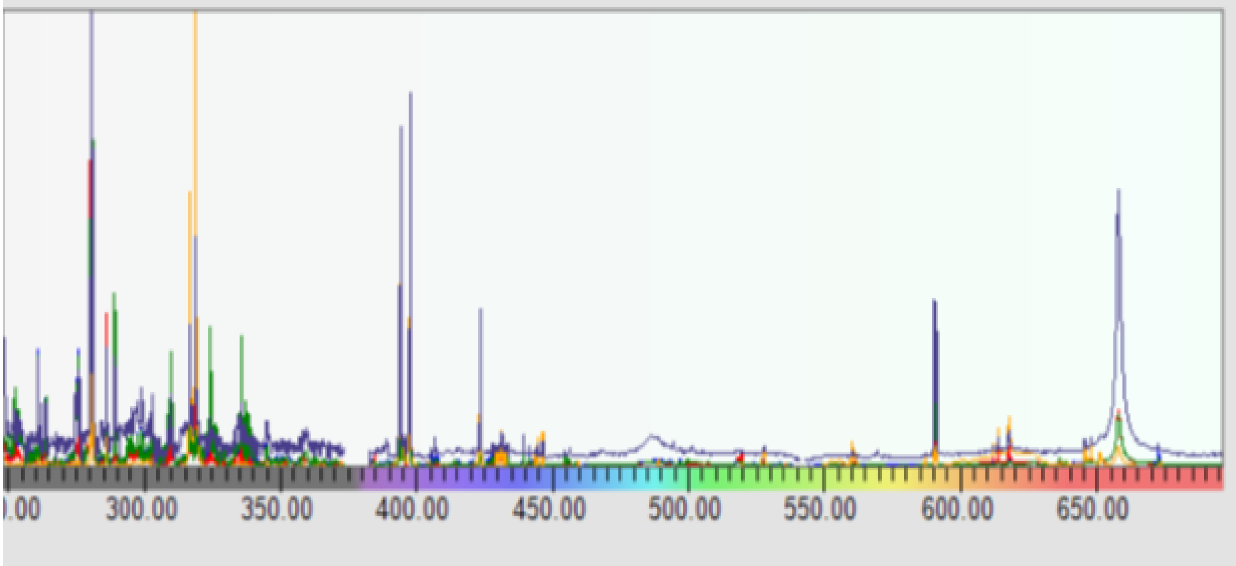


**Figure 99 - Five spectra at different locations**

A snapshot (above) of five spectra at differing locations emphasise the difficulty in noting differences between each aside from intensity. This is also the case when looking at each individually:

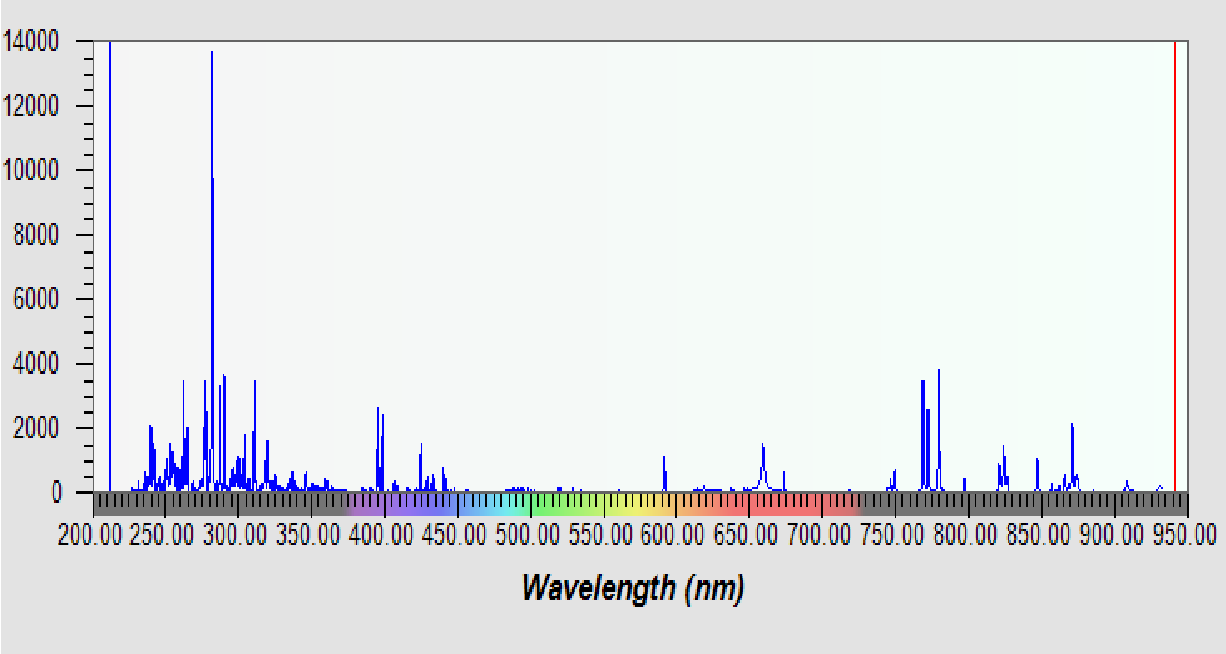


**Figure 100 - Leicester**

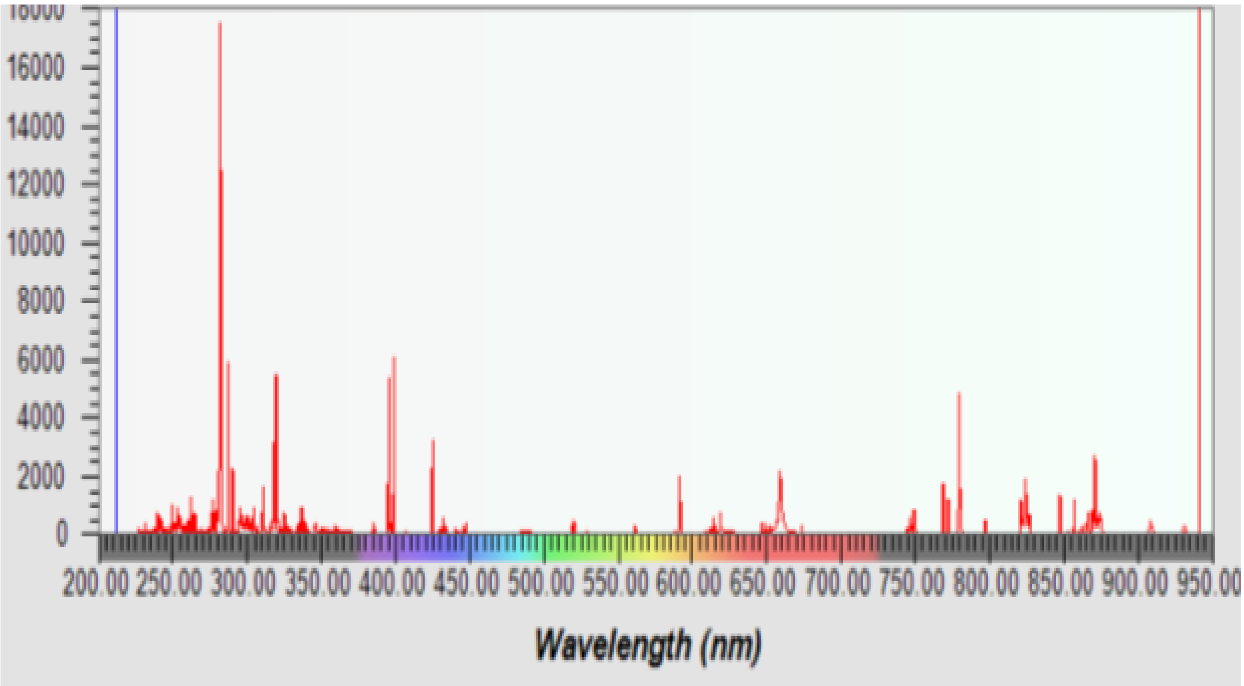


**Figure 101 - Edinburgh**

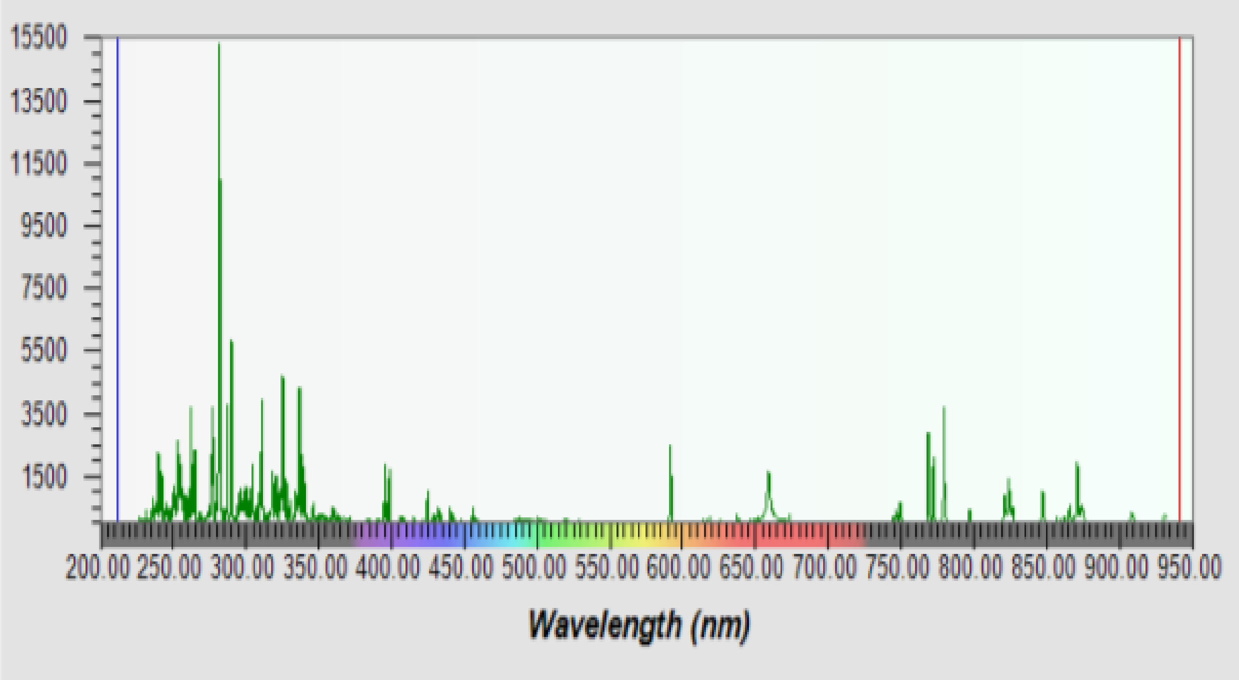


**Figure 102 – Loughborough**

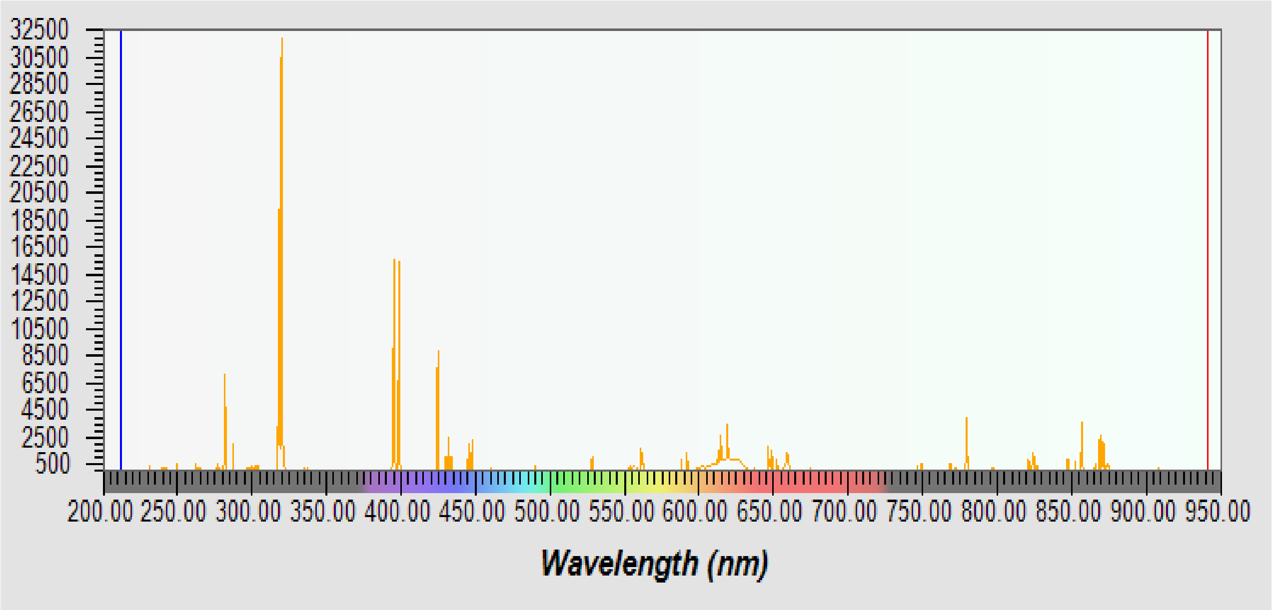


**Figure 103 - Mansfield**

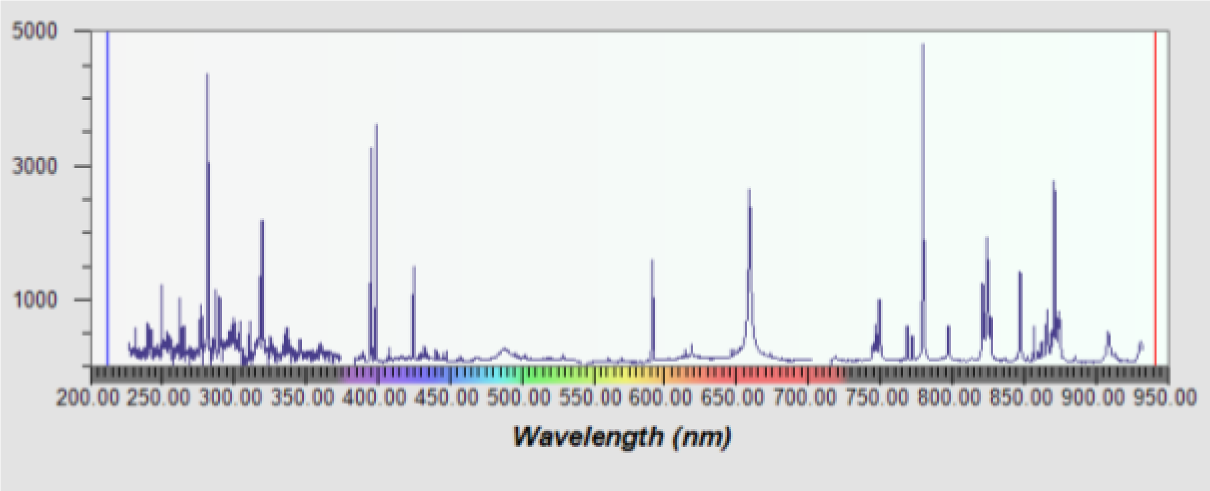


**Figure 104 - Nottingham**

On four of these occasions there are minimal differences in the dominant peak (Mg279nm) the differences only being in the intensity of this peak. On the fourth sample there is a very dominant peak for calcium, however magnesium is still abundant. What this small snapshot highlights is the difficulty in differentiating between samples when looking at the spectra alone. More detailed insight is required.

Because of this, rather than comparing the visual spectra, the ratios of the intensities for elements that were most abundant were compared across sites in order to determine if there was any pattern developing.

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.242 | 0.0127 | 0.0922 | 0.121 | 0.161 |
| 2 | 1 | 0.546 | 0.000818 | 0.173 | 0.0899 | 0.172 |
| 3 | 1 | 0.196 | 0.00832 | 0.0504 | 0.0549 | 0.0777 |
| 4 | 1 | 0.976 | 0.115 | 0.377 | 0.597 | 0.989 |
| 5 | 1 | 0.299 | 0.00749 | 0.157 | 0.0356 | 0.0195 |

**Table 19 - Leicester**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.103 | 0.00827 | 0.209 | 0.175 | 0.218 |
| 2 | 1 | 0.124 | 0.0647 | 0.218 | 0.233 | 0.348 |
| 3 | 1 | 0.839 | 0.483 | 0.486 | 0.431 | 0.668 |
| 4 | 1 | 0.745 | 0.0722 | 0.501 | 0.709 | 0.914 |
| 5 | 1 | 0.299 | 0.00749 | 0.157 | 0.0356 | 0.0195 |

**Table 20 - Edinburgh**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 0.374 | 1 | 0.00391 | 0.0682 | 0.0256 | 0.0561 |
| 2 | 0.589 | 1 | 0.00313 | 0.0505 | 0.0394 | 0.0558 |
| 3 | 0.0997 | 1 | 0.00928 | 0.071 | 0.0487 | 0.0846 |
| 4 | 0.806 | 1 | 0.0426 | 0.224 | 0.385 | 0.712 |
| 5 | 1 | 0.111 | 0.00847 | 0.201 | 0.173 | 0.222 |

**Table 21 - Mansfield**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.422 | 0.0169 | 0.12 | 0.0885 | 0.149 |
| 2 | 1 | 0.178 | 0.0507 | 0.228 | 0.213 | 0.333 |
| 3 | 1 | 0.254 | 0.0289 | 0.25 | 0.138 | 0.221 |
| 4 | 0.392 | 1 | 0.0197 | 0.104 | 0.0583 | 0.0844 |
| 5 | 1 | 0.315 | 0.0135 | 0.126 | 0.0904 | 0.148 |

**Table 22 - Loughborough**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 0.454 | 1 | 0.0262 | 0.157 | 0.144 | 0.167 |
| 2 | 1 | 0.365 | 0.124 | 0.256 | 0.13 | 0.222 |
| 3 | 1 | 0.0815 | 0.0393 | 0.286 | 0.24 | 0.36 |
| 4 | 1 | 0.881 | 0.0859 | 0.236 | 0.154 | 0.183 |
| 5 | 0.159 | 1 | 0.00651 | 0.0127 | 0.00458 | 0.0105 |

**Table 23 - Nottingham**

The results outlined above bore very little insight into each piece of stone in terms of where it could be located. The most abundant element was either magnesium or calcium on each occasion, both elements which are expected to be abundant in stone. In Mansfield, calcium was more often the most abundant, possibly a result of the stone commonly found in this area; Further credence is added to this theory when considering the additional presence of calcium in a number of samples from Nottingham. More work is required to confirm any trend however, as this was not always the case. This technique is perhaps not the ideal for such a conclusion anyway. There would be many methods which could determine the chemical makeup of a piece of stone, and experts would likely be able to do so by visual examination. What this technique hoped to do was yield information regarding the surface of a stone, and how the environment may have affected this over a certain period time. Because of this, elements like magnesium and calcium, which will be abundant in the majority of the samples tested, yield little information other than proving the accuracy of the technique. Instead, patterns of note like the slightly higher levels of iron found in Edinburgh compared to other locations were deemed more worthy of further investigation as this could be a feature specific to either Edinburgh itself, or larger cities in general.

These sites were investigated further with an additional five samples from each area.

These produced the following results:

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.218 | 0.0259 | 0.236 | 0.183 | 0.293 |
| 2 | 1 | 0.0678 | 0.0526 | 0.343 | 0.369 | 0.482 |
| 3 | 1 | 0.566 | 0.0317 | 0.184 | 0.113 | 0.19 |
| 4 | 1 | 0.195 | 0.0181 | 0.144 | 0.12 | 0.176 |
| 5 | 1 | 0.124 | 0.0165 | 0.278 | 0.142 | 0.245 |

**Table 24 - Leicester**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.0298 | 0.0501 | 0.153 | 0.129 | 0.223 |
| 2 | 1 | 0.156 | 0.0599 | 0.383 | 0.137 | 0.35 |
| 3 | 1 | 0.452 | 0.0384 | 0.221 | 0.171 | 0.212 |
| 4 | 0.794 | 1 | 0.102 | 0.489 | 0.317 | 0.331 |
| 5 | 1 | 0.199 | 0.0172 | 0.283 | 0.124 | 0.187 |

**Table 25 - Edinburgh**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.0191 | 0.0689 | 0.157 | 0.199 | 0.304 |
| 2 | 1 | 0.154 | 0.0767 | 0.434 | 0.131 | 0.208 |
| 3 | 0.406 | 1 | 0.013 | 0.0868 | 0.0902 | 0.0906 |
| 4 | 1 | 0.295 | 0.0329 | 0.254 | 0.207 | 0.249 |
| 5 | 1 | 0.192 | 0.1 | 0.176 | 0.124 | 0.192 |

**Table 26 - Mansfield**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.16 | 0.071 | 0.414 | 0.152 | 0.246 |
| 2 | 1 | 0.109 | 0.0498 | 0.294 | 0.249 | 0.419 |
| 3 | 1 | 0.054 | 0.0598 | 0.317 | 0.301 | 0.457 |
| 4 | 1 | 0.196 | 0.0649 | 0.179 | 0.248 | 0.474 |
| 5 | 1 | 0.569 | 0.0391 | 0.221 | 0.139 | 0.219 |

**Table 27 - Loughborough**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.216 | 0.0756 | 0.221 | 0.0939 | 0.126 |
| 2 | 1 | 0.193 | 0.0547 | 0.146 | 0.158 | 0.348 |
| 3 | 0.451 | 1 | 0.0123 | 0.0587 | 0.0371 | 0.0547 |
| 4 | 1 | 0.105 | 0.257 | 0.202 | 0.171 | 0.255 |
| 5 | 1 | 0.377 | 0.0208 | 0.375 | 0.0713 | 0.119 |

**Table 28 - Nottingham**

As can be seen, this provided very little information regarding such trends. Magnesium again proved to be the element that was most abundant in the majority of samples. On occasion, calcium was higher than this; however monitoring any geographical trend regarding this was not possible, with calcium contributing the most intense peak in samples found in four of the five locations studied.

Edinburgh again had a slightly higher contribution due to iron as a general trend, but this was not such a significant amount in comparison to other locations. Whilst the average ratio was higher than the other locations, on occasion it was lower. This particular trend perhaps offers promise; however, this would require a vast study, over a significant number of locations, both within Edinburgh and across other cities. The possibility of iron being present was taken into account when analysing differences in a piece of stones environmental location, discussed later in this chapter.

As can be seen, whilst there are similar trends on occasion, this is not always the case, and the amount of information that could be garnered this way is limited. For the LIBS to be able to match a piece of stone to a specific location there must be minimal chance of misidentification. In the cases noted, whilst there are some patterns shown, the limited consistency of this suggested alternate methods of observing this process were required.

Each location produced very similar results for the most abundant elements found, and whilst this information was interesting in terms of the information it produced regarding a piece of stone, the practical use this could have in terms of tracing a stolen piece of stone back to its original location was minimal.

The trends themselves are just one technique in which a piece could be identified. Another method would be to compare all samples and note all peaks produced if each piece did indeed produce a unique chemical fingerprint. However what prevented this from being possible was the minor differences that did occur each time across the whole stone. Whilst the results were generally identical within a small area like the gelatine lifter, across the whole stone the results did differ marginally upon each scan. An example of the minor differences that can occur across a single piece of stone is shown below:

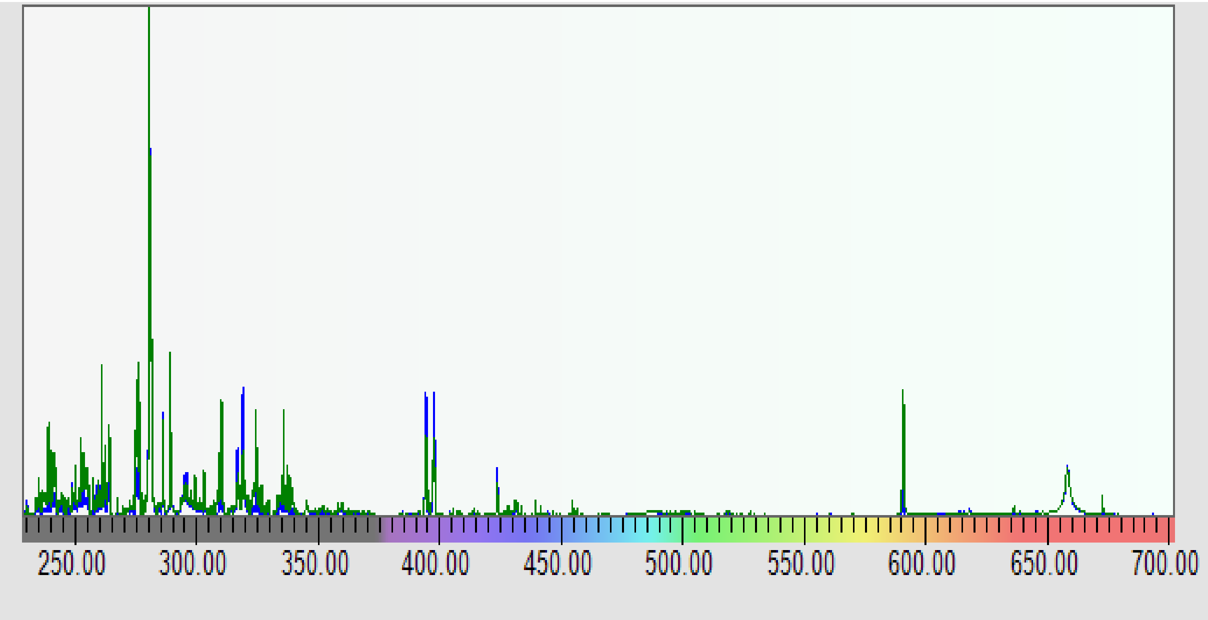


**Figure 105 - Same stone at two different points**

As can be seen above, whilst the peaks produced are generally at the same wavelengths, the intensities can differ across a single piece of stone. This can also occur on a single gel lift, but is rare. When the same stone is lifted from various points on the same piece, the above occurs the majority of the time. This is likely due to differing levels of erosion across a stone resulting in alternate levels of thickness and other such variants which affect how much of the stone, and how much of the gelatine lifter is analysed within the chamber.

As a result of what has been outlined thus far, similar work was then completed on five other sites, however this time the focus was to be on differing environmental locations to see if this produced a clearer trend which would allow greater matching to a location via the LIBS.

### 5.3.2 Environmental comparison

Geographical information regarding stone is available in certain formats already[155]. Whilst the study above hoped to yield information regarding the surface of said stone, the results suggest that there are few differences that can be found via LIBS. Where there has been less analysis, is how the environment a piece of stone is in over a lengthy period of time may have affected the stone, particularly its surface. It stands to reason that if two pieces of identical stone are then placed in two vastly different locations, then their surface would likely be affected as a result. For example, if a stone was next to a main road for a prolonged period of time, have the fumes released near to it affected the surface of the stone compared to a stone sample left in a more rural environment? Finding differences based on a stones environment has greater potential than simply comparing their bulk constituents. Various other analytical techniques, and experts in the field would likely be able to provide the information regarding levels of calcium in a stone for example. By using the LIBS in the manner discussed here though, trace elements that may be detected on the stone could offer more information than has previously been provided concerning a stone sample, and a piece of discovered stone could be 'matched' back to its original location. Therefore once it was confirmed that magnesium and calcium were the most abundant elements within the majority of samples, the primary goal within this section was to note any other patterns developing, and highlighting the appearance of other elements which are not as closely associated with a stone's chemical makeup prior to its years spent in a particular environment. The environments which were compared within this section are as follows:

- On a busy main road (blue)
- Middle of a city centre, so few roads, but a busy area (green)
- Outskirts of a city, in a very large cemetery (red)
- A rural churchyard in the countryside (yellow)

Each stone appeared similar based on a visual examination. As with the geographical study, the first point of comparison was to simply note differences between the spectra when analysing visually. Below shows four different samples.

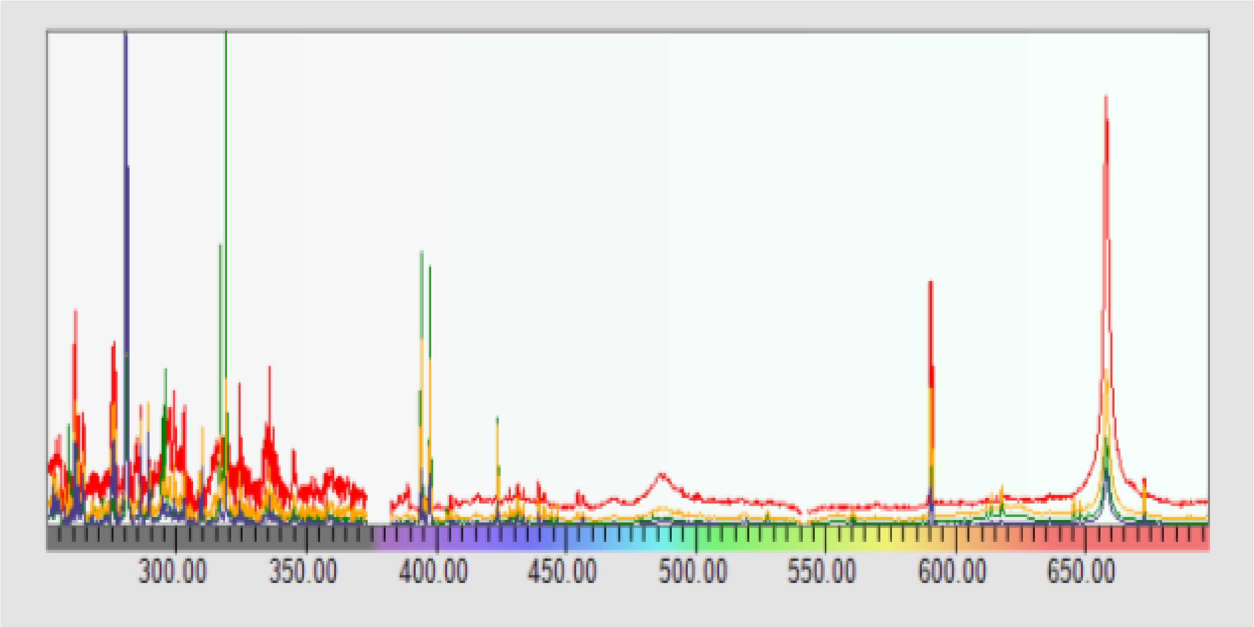


Figure 106 - Comparison across spectra

As with the geographical comparison, this technique of visual comparison of the spectra was limited.  Each produced peaks at similar wavelengths albeit of differing intensities.  Even when the spectra was analysed across a narrow band, the information yielded was minimal.

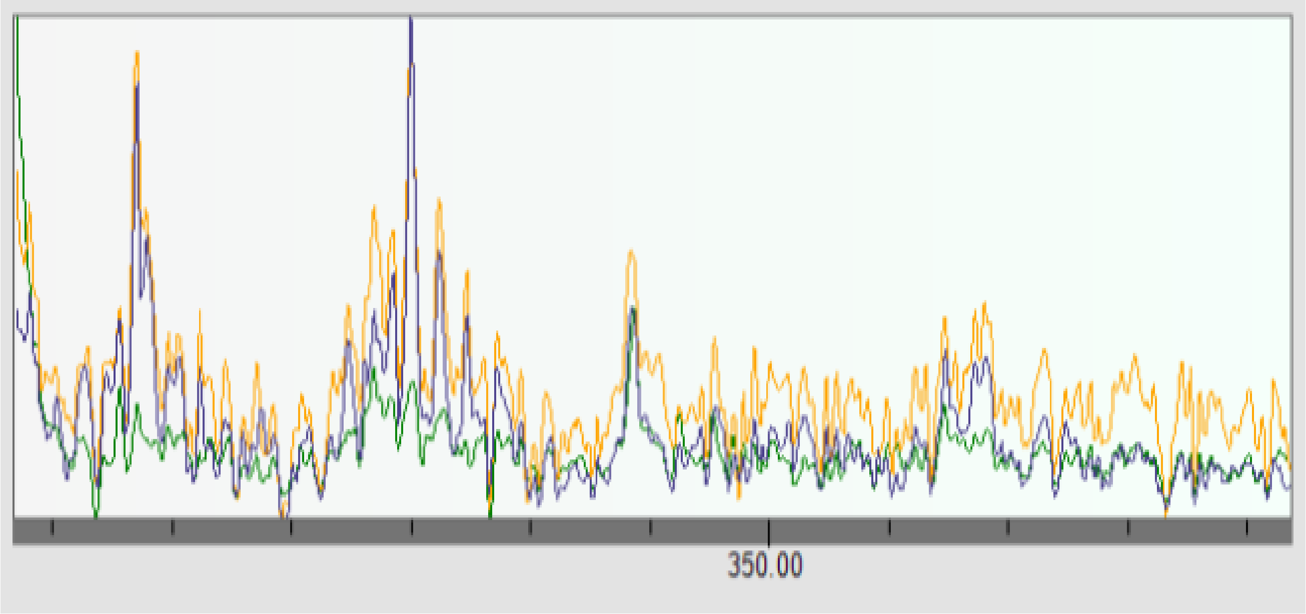


Figure 107 - Narrowed band

It was also noteworthy that the spectra show striking similarities to those assembled when comparing across geographical location.

Therefore, it was deemed that noting the ratio of these abundant peaks (as in the previous section) was necessary in determining any possible trends across these samples from differing environmental locations. The city in question was Edinburgh.

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.355 | 0.1 | 0.333 | 0.246 | 0.279 |
| 2 | 1 | 0.35 | 0.0622 | 0.291 | 0.383 | 0.56 |
| 3 | 1 | 0.385 | 0.0198 | 0.217 | 0.114 | 0.167 |
| 4 | 1 | 0.881 | 0.0859 | 0.236 | 0.154 | 0.183 |
| 5 | 1 | 0.154 | 0.0767 | 0.434 | 0.131 | 0.208 |

**Table 29 - Main road**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.194 | 0.0587 | 0.405 | 0.112 | 0.178 |
| 2 | 1 | 0.276 | 0.0599 | 0.214 | 0.0817 | 0.15 |
| 3 | 1 | 0.37 | 0.0397 | 0.229 | 0.0799 | 0.137 |
| 4 | 1 | 0.106 | 0.0412 | 0.227 | 0.246 | 0.356 |
| 5 | 0.567 | 1 | 0.809 | 0.346 | 0.186 | 0.379 |

**Table 30 - City centre**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.489 | 0.0311 | 0.173 | 0.132 | 0.182 |
| 2 | 1 | 0.222 | 0.0206 | 0.138 | 0.801 | 0.136 |
| 3 | 1 | 0.269 | 0.0205 | 0.144 | 0.151 | 0.197 |
| 4 | 1 | 0.271 | 0.0201 | 0.15 | 0.0825 | 0.105 |
| 5 | 1 | 0.303 | 0.0384 | 0.232 | 0.11 | 0.156 |

**Table 31 - City outskirts**

| | Mg 279 | Ca 317 | Ti 453 | Fe 260 | Al 309 | Si 288 |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.414 | 0.035 | 0.198 | 0.112 | 0.17 |
| 2 | 0.155 | 1 | 0.00651 | 0.0126 | 0.00458 | 0.0105 |
| 3 | 0.392 | 1 | 0.0197 | 0.104 | 0.0583 | 0.215 |
| 4 | 1 | 0.1 | 0.0137 | 0.175 | 0.124 | 0.192 |
| 5 | 0.226 | 1 | 0.00915 | 0.0207 | 0.0134 | 0.0165 |

**Table 32 - Rural location**

The levels of iron in sites next to a main road appear markedly higher than those found in rural environments. Despite this generally being the case, there were still instances where levels of iron were lower or higher than anticipated as is shown by sample 1 in a rural environment. Whilst the results do show promise, they also highlight a level of limitation with regard to this technique which has been touched upon previously in this chapter. This is that for a piece of potentially stolen stone to be linked to a specific location, there must be as much consistency as possible so there is little doubt regarding the conclusions drawn. Thus far, aside from the most abundant of peaks (magnesium and calcium), any trend that has become apparent has had a small number of contradictory results.

The findings outlined here are difficult to explain. There are possible theories that may provide some insight into the presence of iron that have been considered however. The first is that it is simply a material that is more commonly found within the rocks used for gravestones at this particular site. Whilst this was the case at the sites analysed, it is not necessarily the case across the whole city.

Another theory is that the stones which have a lower level of iron have been protected from an environmental factor which has resulted in greater iron levels prior to the analysis. This could be natural, or physical shelter preventing iron traces being taken into the stone's chemical makeup.

There is little certainty with regards to either of these however, and judging by the inconsistencies of the results obtained during the course of this work, to do so would require a very large scale project taking into account many sites from numerous locations.

Aside from this however, as was the case with the comparison across geographical locations, there was little/no trend across environmental locations when considering these five most abundant peaks. Magnesium and Calcium generally are the only elements that form the majority peak in any sample.

The insight which can be gathered via comparison of magnesium and calcium is minimal. From the samples obtained, those which had calcium as their most intense peak were generally far whiter in appearance. It was therefore concluded that the presence of an intense calcium peak was likely due to the fact that these particular stones were made of limestone, or a similar stone. Whilst non-invasively determining this via the LIBS is noteworthy, it is also unnecessary as such information will be easily gleaned by those which interact with such stones on a regular basis, negating the requirement for scientific analysis in such cases. Despite this, it can certainly be taken as a positive that such a technique provided this insight, and emphasises the potential of the process.

The insight which such comparisons can yield is minimal. Proving that magnesium or calcium is largely present in a piece of stone is promising with regards to the development of the technique, however using this to prove a potentially stolen piece of stone's original location would be nearly impossible. Therefore other trends needed to be analysed. In order to do this, each spectrum was visually inspected in great detail, to note any differences across environmental locations. Another method used to determine which elements to compare across locations was the matching system which was present in the LIBS. This was part of the system which compared the simulation for each element to the sample which was being analysed. The accuracy of this was reduced when considering that not all bands are used for this correlation, but it gives a useful indicator as to how likely an element is to be in a given sample.

Upon inspection, it was clear that generally, there were few peaks which appeared in one stone sample that differed from another. There were two which were noticeable in any form. The first was a peak corresponding to Nickel at 230nm, shown below:

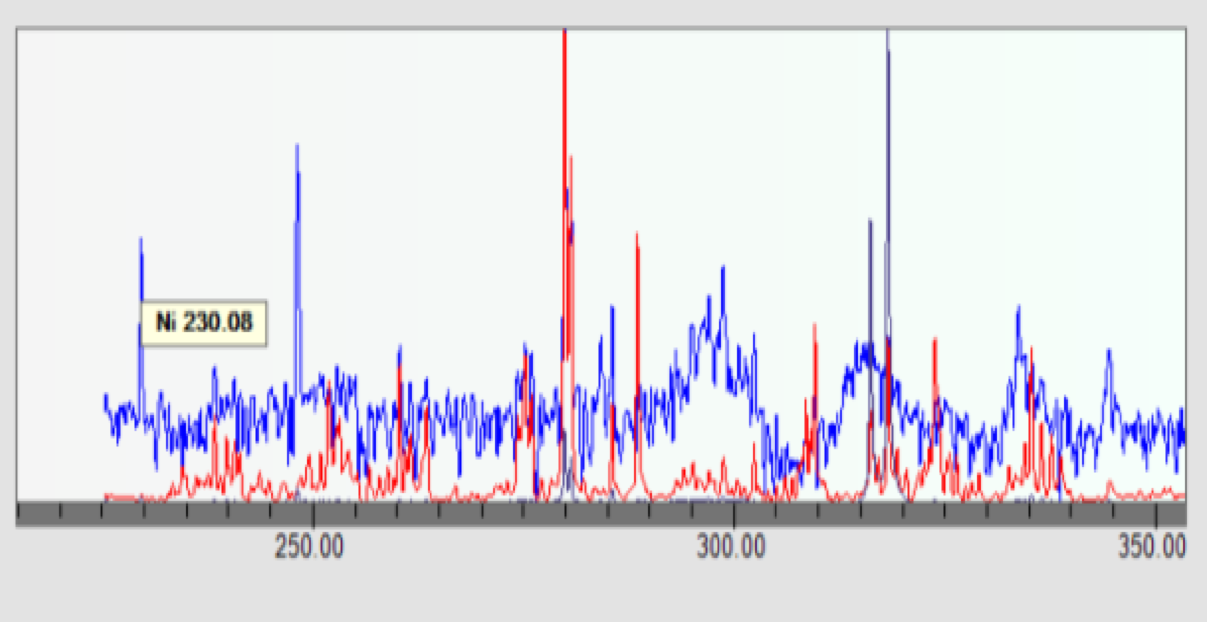


Figure 108 - Nickel 230nm peak

As can be seen there is a minor peak for the sample in blue (Leicester 1901) whereas the red sample (Mansfield 1888) had no such peak. The peak shown however was not of great intensity, and only appeared in this one sample out of all those tested. As a result of this anomaly, the levels of nickel in the blue sample were compared to that in the lone gel sample. This is shown below, with the stone sample in blue and lone gel in red:

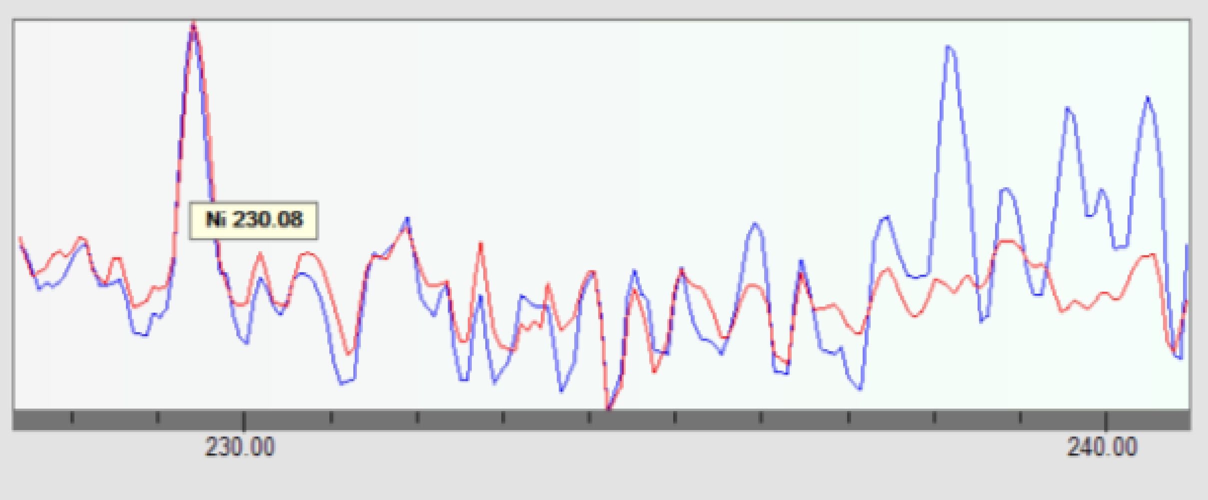


Figure 109 - Stone sample (blue) compared to lone gel (red)

As can be seen, it seems clear that the presence of this nickel peak is present as a result of the gelatine lifter itself being detected. It is also striking that there are differences elsewhere in the spectra, therefore the stone is being detected, but is not likely to be responsible for the nickel peak at 230nm.

A clearer example of an unexpected element being noted was that of gold at 323nm. This was found in three samples all within the same site. This was from a site which was nearby to a main road.

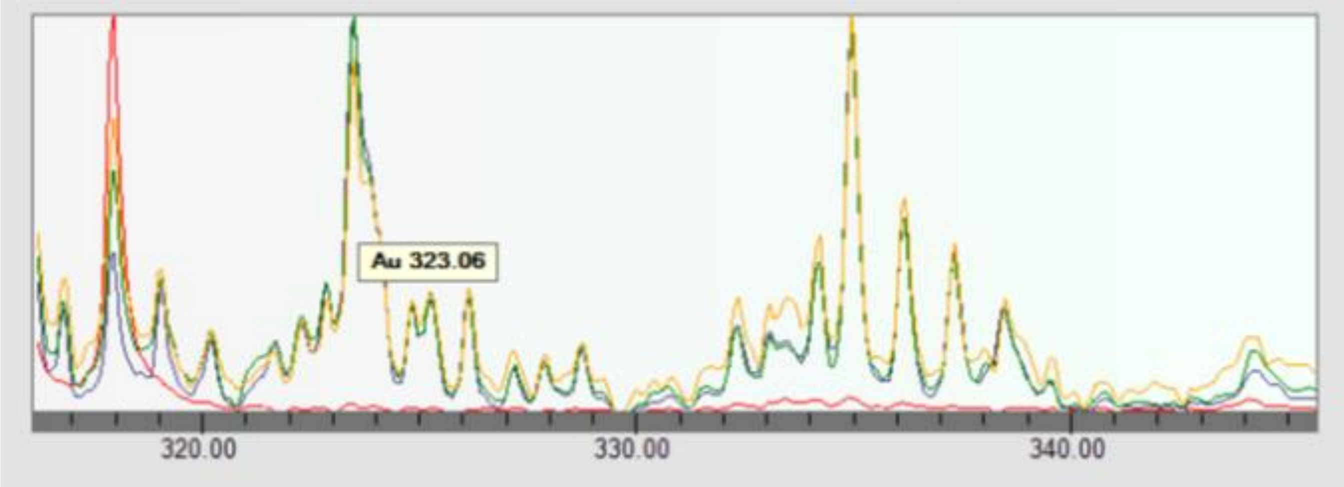


**Figure 110 - Presence of gold peak at 323nm in three samples**

The above compares the sites mentioned (blue, yellow, and green) to another stone found elsewhere at the same site (red) which did not produce said gold peak within the spectra. The peak itself for gold was not abundantly clear at first glance, and its initial presence was discovered via the matching system. Based on the values within this, anything above an 80% match is deemed to be 'very likely' present within a sample detected. Three of the samples analysed produced values greater than an 80% match for gold (81, 83, and 83%). Upon inspection at the wavelength corresponding to gold (323nm) the above peak was apparent. What was interesting regarding this discovery was the locations of the gravestones in question. All were found in a direct line in a surrounding area of Nottingham in a rural environment. There were no visual clues as to why this may be the case i.e. the stone did not have gold writing on for example. There was no such gold traces found anywhere else within the same site which samples were taken from. Taking this into account, the ability to 'match' this stone because of the gold traces was minimal, as it was not found throughout the same location. What is certainly noteworthy however is the fact that differences are found in the first place. The reason for gold traces being present was unclear, one possible theory is that decorative gold was once present, but over time has eroded to the point where it is no longer visible by eye. This theory has supporting evidence as when the stone that produced a gold peak was analysed identically at different points on the stone, the gold peak was not always present. Theoretically this was because there was no such decoration at this point. Additionally, this would also go some way to explaining why there was no such gold peak on other stone samples within this location, the decoration was either not present, or was at a different point on the stone, which was not within the area covered by the gelatine lifter analysed. Another theory as to why gold was present was its usage in certain catalytic converters in cars[156][157]. However this appeared to be unlikely as if this was the case, it would surely be present in more sites found in such environments.

There were other elements that were investigated across the spectra, that it was believed could differ across an environmental location. Platinum was the main example of this, as its common usage in catalytic converters[156] suggest that this is an element which may be found more commonly at sites near to a main road as opposed to in a more rural setting. Therefore the spectra for such samples were analysed for signs of such elements which could be present as a result of such factors (such as gold as was previously noted). However there were no samples analysed which suggested the appearance of such precious metals aside from the gold samples discussed previously. This could simply be because there is not enough platinum around in these environments to contribute significantly to a piece of stones chemical makeup, or alternatively, to do so would require a greater period of time within an environment where there are higher levels of said element. Again, a very long term project may yield more insight into such questions, however for the course of this research such factors did not provide enough insight to be able to identify a stone based on its environmental location in this manner.

What must also be noted is that only four different types of stone were analysed within the course of this work. Whilst this will limit the great differences across samples, this is a necessary step, as the gravestones analysed comprised of the most commonly used stone samples across the country[158]. Therefore it made sense to analyse the differences within these specific forms of stone. It also ensured that any differences found were limited to those found via the LIBS system as opposed to differences a casual visual inspection could have done as effectively.

What appears to be clear from the results obtained is that whilst the technique clearly works, in that notable amounts of stone are being detected from the surface of the gel, background from this substrate is still apparent. If this were a consistent amount, the problem could simply be negated as it could easily be discounted from the analysis. However, what became clear was that the amount of gelatine lifter that can be detected varies from sample to sample in a manner that is difficult to predict or account for.

Despite some minor differences based on both geography and the environment of the stone analysed, the majority of the samples all produce similar spectra. Whilst intensities differ across samples, the information this yields is minimal, as that is to be expected to an extent when considering this particular form of analysis.

All sites were visited 6 months after the initial analysis and produced near identical results, highlighting this similarity being maintained even after a reasonable period has elapsed. A longer term project that could measure changes annually and beyond would yield greater insight into whether changes do occur due to the environment, and if so what these changes are.

Whilst peak height is proportional to the concentration of an element within a sample, the laser pulse energy can vary, and the relationship between pulse energy and signal is non-linear, therefore it is not possible to quantify via absolute signal (however there is a relationship between the two). As well as this, the matrix, in this case the stone, can also have an effect on the elements themselves meaning 100ppm of one element in stone does not necessarily show the same signal as 100ppm of another element[159]. Another reason intensity is perhaps not the ideal method of comparison is the use of gelatine lifters in this particular technique. Whilst they are clearly capable of lifting trace levels of loose stone from the surface of this material, the depth that this stone has will vary across samples. With this, the amount of gelatine lifter which is also detected will vary as well. Whilst efforts have been made to reduce this variable, and the problem itself is minimal, maintaining the consistency required to see a pattern develop definitively was proven to be very challenging via this technique.

Throughout the process, it is believed that four types of stone were analysed. Granite, slate, sandstone and limestone are four of the most commonly used stones used in such a manner (headstones). Based on their appearance it is believed that these make up the majority, and if not, all of the samples analysed. The work done here aimed to analyse minute differences across samples based on the geography and environment each of these will have been situated in. This was true in some cases, with certain elements becoming apparent in relatively high concentrations that would be unexpected in the stones specified (e.g. iron). What is of greater note however is the differing ratios that are present throughout, even though the actual types of stone remain fairly consistent. This therefore suggests that the conditions are having some effect on the elemental composition. Whilst the levels of this are still unclear, the mere fact that differences are occurring with the same types of stone is a clear positive step moving forward. The eventual goal of identifying each individual stone in a unique manner is one step closer because of this.

From the results obtained it is clear that there are both positive and negative outcomes from the LIBS system being used in the manner outlined. The original strategy had key aims which were addressed, with some being met, whilst others proved challenging. What must first be considered is that the mere presence of useable data can be deemed a success as it provided useful and unique information regarding each piece of stone analysed. There was no instance where no data was acquired, and therefore the work done highlighted a novel use of an analytical technique non-invasively providing information about the surface of stone. This provides a clear ‘snapshot’ of a piece of stone at a specific place and time, and checking back on this after a substantial amount of time has passed would be an interesting area for future work. The other aim at the beginning of this research was to provide evidence of trends relating to a stone’s location based on its chemical makeup which is provided by the LIBS. Again, information, and trends were both evident, however it must also be noted that this did have limitations. The consistency of the process was perhaps the most challenging aspect of this work. Whilst across small patches of gel results were generally near identical, when analysing various points of the same stone there were notable differences. With this it would be hard to track any trends without a degree of doubt surfacing over the results gathered. Across all geographical and environmental locations, there were similarities in that magnesium and calcium were heavily abundant. Where this technique shows promise however is the levels of detection providing insight into elements which are less abundant in stone. Whilst such instances highlighted during this chapter (like gold) are difficult to explain categorically, a much longer term study, analysing such stone over a greater period of time, may provide a greater insight into why such elements become apparent in a given location. A longer term study with such work would have additional benefits in that changes in a stones chemical makeup can be tracked over years as opposed to the months which were studied here. With this, a more definitive answer could be provided as to why such elements become apparent, and after how long in a set environment do changes to said makeup begin to appear. Rain for instance has a slight affect in terms of how well the gel can adhere to the stone. However the chemical changes long term this causes are more difficult to see. Analysis during each season of the year would also be a worthy study, to see how environmental conditions can effect chemical makeup of a stone. With these answers, determining why such changes occur is likely to be much clearer.

The work completed here is certainly notable, despite limitations, and can be classed as an important step towards tackling stone theft. This is a form of crime that has proven to be very difficult to police, and the current techniques which are used to prevent or detect such crime do not always correspond to the delicate manner in which historic stone must be treated. By taking such steps towards non-invasively detecting stone, it is hoped that this work, whilst limited, can be a stepping stone for further improvement for lowering levels of stone theft at heritage sites.

## 5.4 Fingerprints from brick and stone

In addition to analysing the surface of stone to aim to help develop a database of information, efforts were also made to detect latent fingermarks which had been deposited on the surface of brick or stone. As with previous chapters this aimed to utilize rubeanic acid and its sensitivity to copper.

A sebaceous fingermark was deposited on the surface of both a standard brick, and stones with a range of textures, ranging from smooth to very rough.

Figure 111 – Brick used to develop fingermarks from

This was left for 24 hours before copper plating, or tape in the case of curved stone, was placed on the brick or stone under a lead weight for a further 24 hours. The copper was then removed and left in a desiccator for 24 hours before being placed under the gelatine lifter for 2 minutes and treated with rubeanate solution. This gave no useable results. On occasion there would be markings of the outline of a fingermark however this gave no ridge detail.

Figure 112 – Poor quality fingerprint developed from brick

The following attempt aimed to utilize copper acetate solution as had also been attempted with reasonable success on other materials such as laminate surfaces and stainless steel. Copper acetate (0.497g) was dissolved in distilled water (50ml). The brick or stone was then dipped in this solution for 30 seconds. After being left to air dry for 1 hour, a copper plate or tape was then placed over this for a further 24 hours, again under a heavy lead weight. The copper was removed and left in a desiccator for 24 hours again. This was then gel lifted for 2 minutes before being treated with rubeanate solution. This produced rough markings on some samples, however only minimal detail was obtained, and this was not always the case. The ability to detect any markings appeared to be based on how rough the texture was. Both the copper and gelatine lifter appeared to have better interactions with smoother stones. This is most likely because any cuprous ions will be transferred much less onto the rough surface, and the gel itself is much less adhesive on said rough surface. When this is the case, very little of the cuprous ions vital to the reaction which results in fingerprint development, will then be transferred to the gelatine lifter. As a result there will be no visible fingerprint. On smoother stone, whilst more is transferred than with a rough texture, it is still not enough to yield high quality fingerprint development. This highlights why stone and brick have been such problematic materials for those attempting to analyse latent fingermarks, and whilst the outline of said fingermark suggests promise in this area, for the course of this research there was little workable information obtained. The combination of the unusual and often rough texture of stone, its semi-porous nature, and the often unusual shape of stone appear to make fingermarks difficult to develop, especially when using gelatine lifters. Other techniques may be better suited to these surfaces, such as electrostatic lifting[116].

## 5.5 Future work on stone, and what must be overcome for positive results to be established

it is clear that LIBS has some potential with regard to developing a technique which could help to lower levels of stone theft at heritage sites in this country and beyond. Early discussions made it apparent that the most desirable outcome would be to develop a 'database' of information which could match a piece of damaged or stolen stone to its original location. Practically this is of great importance, as stone will often be moved miles from its original location in order to be sold. By having such a database in place, a piece of stone could be analysed and not only be confirmed as stolen, but simultaneously have its actual location where it was stolen from proven. It is easy to see why such a process is highly desirable by those tasked with lowering levels of such theft. The gelatine lifters do not damage the stone being analysed in any way, only removing material that is already loose. This highlights the clear importance of such research, and the development of key ideas which focus solely on stolen items from a heritage viewpoint. This is also true on a global scale, with the work proposed having clear potential in terms of improving checks on provenance in stone items.

Despite certain restrictions, any information that can be added to the overall knowledge currently present is beneficial. Whilst not all sites will show a trend, this will almost certainly not be the case countrywide. As has already been seen with just the small sample set obtained thus far, some areas have differences which can contribute a degree of knowledge as to a stones original location. Slightly higher levels of iron in city centres as opposed to more rural areas are the main example of this. This was true with different types of stone, with both granite and limestone producing this trend. Whilst alone this is unlikely to be enough to directly link a stone to a specific location, it could be used as part of a case of evidence where an examiner could say a stone is likely from a certain location or environment. In the current scenario where stone theft levels are rising and the work towards tackling this issue scientifically is still very low, this work has proven to show unmistakeable potential, and highlights a clear pathway which could be taken into establishing information regarding stone, and theft thereof on a national scale.

The work completed during this project is not conclusive regarding this technique and its ability to lower stone theft. Instead it emphasises the potential of the work and has established a novel use of an analytical technique. With this though there are areas where future work would be required should this technique have real life applications with regard to tackling heritage crime. One such area of study would be to look at the effect of moving stone from one environment to a completely different one, and see if that changes its surface elemental composition, and if so how soon it will do this. If a piece was stolen, it is likely to be moved to a different setting and hence it would be necessary information with regard to linking this stone to its original location. As has been touched on previously however, the largest task left facing this work is to develop a much greater range of results. Trends have been made apparent from the samples analysed here, so comparing these countrywide would enable the actual applicability to those tasked with finding stone thieves to be determined.

What is also noteworthy is the novel use of an analytical technique that has been a feature of this work. This is an area where links between science and lowering heritage crime has great potential. Utilizing as many people from as many differing backgrounds, all focusing towards the set goal of lowering such crime is vital in order for real and noticeable progress to be made.

## Chapter 6 Conclusions and further work

The primary goal of this research was to examine whether the increasing levels of heritage crime could be tackled by a chemist, and to develop a technique which focused solely on this particular issue, particularly theft of metal and stone. Whilst current forensic techniques can be used at heritage sites, a clear example being forensic marking techniques like SmartWater, these are not applicable at every site. The expense such techniques can result in coupled with the often invasive nature of said procedure can rule out certain sites from taking advantage of the most recent advancements. This is primarily because previous work done has focused on detection at all costs, even if this results in the destruction of, or compromises the historical value of a particular item. Whilst some materials found at heritage sites can be examined via more traditional means, such as copper piping or lead sheeting, there are many more examples where this would not be desirable at all. Because of this, the techniques available to those tasked with lowering levels of heritage crime have been limited. The early course of this research focused on developing a survey which could be used as a reference point and justify the scientific analysis that was done. The expectation was that metal theft would be highlighted as the crime which posed the greatest threat to such sites, and this did prove to be the case. What was more of a surprise however was the results which stated that stone theft was also of great concern. The survey achieved its main goal, which yielded useful information about the type of crime which is most problematic, and emphasised that this form of crime is of particular concern currently. As was the aim of the survey, this paved a clear path for the forensic and analytical research which was completed throughout the rest of the study, and justified what was done by confirming the problems faced.

Metal theft was without doubt the greatest threat facing heritage sites, and hence was the issue which was to be initially focused upon. A technique was developed which has undoubted promise when considering the aim of lowering the levels of metal theft. Focusing mainly on metals which are particularly appealing to metal thieves (copper and lead) a technique has been successfully developed which can now link a potential suspect to a stolen item. What was most satisfying about this development was the non-invasive nature of the technique, and the sensitivity which can be achieved with it. Both of these are especially important in terms of tackling theft from an historical context as there is no need to damage the metal in question, or to involve direct chemical contact with a potential suspect.

The work completed here for tackling metal theft then progressed further with the development of a technique which analysed the metal itself as opposed to an individual. This again remained non-invasive, and utilised the understanding that desiccation can improve the quality of fingermark deposits which can, in turn, be developed using the gelatine lifters and rubeanic acid solution. Again, this focused on remaining non-invasive, a factor which was vital in terms of maintaining the aim of tackling heritage crime specifically. Despite this being the objective, the potential is clear in terms of detection from a more general standpoint.

Aside from metal theft, other forms of crime such as stone theft were also tackled. This is an area which has received far less attention from the forensic community and as a result the information garnered could potentially act as a starting point for future work to be completed focusing on lowering levels of stone theft. Whilst this technique would require further work in order to be utilized on a larger scale, the results obtained are very promising as it provided clear evidence of an analytical technique providing information regarding a stone samples chemical makeup. It also provided proof of basic trends occurring based on a stone’s geographical or environmental location. Again, remaining as non-invasive as possible, a technique has been developed which can clearly show that the surface of stone varies between sites. Trends have been noted which, whilst not infallible, do highlight differences which thus far can be linked to a particular geographical or environmental location.

The importance of the research conducted was made abundantly clear by the media attention which it drew. Whilst developing novel techniques and proving the potential of collaborating chemists with a heritage crime taskforce was the primary goal of this research, raising public awareness of the issue at hand was an important adjunct to this. Metal theft was understood to be a particular concern generally, and so the additional goal of protecting heritage sites (an issue which many care passionately about) proved an interesting story to tell. The success of the work completed with regards to this ensured that a welcome light was shone on a topic of concern. The work completed regarding metal theft was showcased and discussed through both local newspaper articles[160] and a live appearance on BBC's Crimewatch Roadshow[161].

The rise in the public's awareness was not limited to metal theft at heritage sites however. The initial work done on stone theft also garnered interest from several media outlets[162][163], going onto cite the troublesome rise in such crime over recent years. Whilst there are often cases where scientific research receives public attention in the case of this research it is imperative. Heritage sites are an integral part of our culture and history. Whilst scientific progress is necessary, removing the ignorance surrounding this form of crime and the widespread harm it can cause is integral. By developing tools which we can use to tackle this problem, and taking advantage of the attention this often receives, it is firmly believed that this project has successfully achieved the initial goals which were outlined. Whilst a negative side of this may be alerting criminals of ways around such techniques (notably wearing gloves or washing hands thoroughly after handling metal), this could easily be sidestepped by releasing selective information regarding a technique to the general public via the media. It is hoped that by providing improved methods of detection, the likelihood of an individual committing a crime can be reduced as the fear of getting convicted of a crime increases.

This work has been unique, in that it has focused on what is an expanding form of crime which the general public care a great deal about. It is vital to protect the historical sites not only in this country, but worldwide. Each item found at a given heritage site is an insight into the history and culture of a specific location. With this in mind, it is hugely important that long term projects focusing solely on this issue continue further down the line. Whilst there are areas outlined here which have proven successful in identifying a gap in knowledge for those tasked with lowering heritage crime, other areas could act as a springboard for future work. Whilst metal theft has criminal links outside of a heritage context, and hence has been focused on in other arenas, problems like stone theft have received less attention in the media or from scientific study. Involving individuals from as many backgrounds as possible has been outlined both in the survey completed here, and further echoed by Historic England themselves, as being exceedingly important. It is believed that the work completed here, as well as developing novel scientific techniques will also provide certain proof that science, and specifically in this case chemistry, can be taken advantage of, and in turn effectively lower levels of heritage crime.

## Appendix

Full list of questions asked in the survey outlined in chapter 2.

**Section A - Background Section**

1. **Thinking about the ways in which you interact with the historic environment, would you consider yourself predominantly:**

- Owner
- Manager
- Tenant
- Employee
- Volunteer
- Visitor
- Other (please specify)

2. **Are you a member of any heritage organization(s)?**

- National Trust
- English Heritage
- Society for the Protection of Ancient Buildings
- Alliance to Reduce Crime against Heritage (ARCH)
- Council for British Archaeology
- Society for the Protection of Ancient Buildings
- Ancient Monuments Society
- Society of Antiquaries London
- Other (please specify)

3. **The following question asks for some details about your experiences of heritage crime. If you are answering on behalf of a specific site or organisation, please provide details here: (if you are answering as an individual state this.)**

## Section B – Heritage Crime Experiences

4. **Thinking about the heritage site(s) you interact with most, was there any heritage crime at this site in the last 12 months? If 'no' or 'Don't know' skip to question 6.**

- Yes
- No
- Don’t know

**4a. If yes, approximately how many times was crime experienced at this site?**

- 1
- 2-5
- 6-10
- More than 10
- Don’t know

5. **What crime type(s) were experienced at this site?**

- Criminal damage (vandalism)
- Criminal damage (arson)
- Theft of architectural material (metal)
- Theft of architectural material (non-metal)
- Theft of other material
- Illicit metal detecting
- Theft of general metal
- Other (specify)

**5b. Which of the above was most frequently experienced?**

**5c. Which caused most concern or damage?**

6. **Of the following, who do you think should take responsibility for tackling heritage crime?**

- Site owner
- Manager
- Tenants
- Visitors
- Police
- Scientists
- Other (please specify)

6b. Which of these do you think is most responsible?

7. **What materials are present in the heritage site you interact with most? Please include materials which are inherent to the structure (for example as part of a building), as well as those that are removable (for example in art work and displays).**

- Copper
- Lead
- Pewter
- Bronze
- Brass
- Stainless steel
- Stone
- Wood
- Don't know
- Other (please specify)

8. **Of the following, which materials do you think are at risk of being stolen at the heritage site you interact with most?**

- Copper
- Lead

- Pewter
- Bronze
- Brass
- Stainless steel
- Stone
- Wood
- Don’t know
- Other (please specify)

**8b. Of these, which do you believe is most at risk?**

**Section C – Lowering heritage crime levels**

9. **Which of the following security measures are present at the heritage site most relevant to you?**

- Security cameras
- Security guards
- Fences
- The use of SelectaDNA, SmartWater, or other forensic marker
- Alarms
- None
- Don’t know
- Other (please specify)

10. **If the following crimes were committed, which, in your opinion, would pose particular problems upon attempting to discover that a crime had occurred?**

- Criminal damage (vandalism)
- Criminal damage (arson)
- Theft of architectural material (metal)
- Theft of architectural material (non-metal)

- Theft of other material
- Illicit metal detecting
- Theft of general metal
- Other (specify)

**10b. Which would be the most problematic?**

**11. In your opinion, which of the following materials would be difficult to replace, if stolen or damaged?**

- Copper
- Lead
- Pewter
- Bronze
- Brass
- Stainless steel
- Stone
- Wood
- Don’t know
- Other (please specify)

**12. Are there any issues regarding heritage crime, not discussed here, that need particular consideration? If yes, then please specify**

**13. Are you willing to be contacted with regards to the answers given in this survey? If yes then please provide an email or phone number, if no then please leave blank.**

**14. Would you be interested in receiving information about the results in this survey?**

## References

[1] UNESCO, *The World's Heritage*, 4th edition. Collins, 2015.

[2] Press Association, "40 million adults flock to Britain's castles and heritage sites," *The Guardian*, 2016. [Online]. Available: https://www.theguardian.com/culture/2016/dec/01/tourism-visitors-britain-castles-heritage-sites-historic-buildings. [Accessed: 16-Jul-2017].

[3] Historic England, "What is Listing?," *Historic England*, 2017. [Online]. Available: https://historicengland.org.uk/listing/what-is-designation/. [Accessed: 16-Jul-2017].

[4] B. Andrews, "Increases in Metal Theft Poses Challenge for Listed Building Owners," *AssetSure*, 2012. [Online]. Available: http://www.assetsure.com/increases-in-metal-theft-poses-challenge-for-listed-building-owners/. [Accessed: 03-Sep-2016].

[5] D. Bradley, C. Young, M. Coombes, L. Grove, and S. Thomas, "6165 The extent of crime and anti-social behaviour facing designated heritage assets Final Report David Bradley Jane Bradley Mike Coombes Louise Grove Suzie Thomas Chris Young March 2012 6165 The extent of crime and anti-social behaviour facing designated," no. March, 2012.

[6] English Heritage, "Alliance to Reduce Crime against Heritage," no. February, 2011.

[7] Historic England, "Theft from Places of Worship," *Historic England*, 2016. [Online]. Available: https://historicengland.org.uk/advice/caring-for-heritage/places-of-worship/places-of-worship-at-risk/metal-theft/. [Accessed: 14-Jun-2016].

[8] L. Grove *and S. Thomas.*, *Heritage Crime Progress, Prospects and Prevention*. Palgrave Macmillan, pp 1-10, 2014.

[9] G. Sheldrick, "New law cuts thefts of scrap metal by a third," *The Express*, 2015. [Online]. Available: http://www.express.co.uk/news/uk/559569/Legislation-cuts-scrap-metal-theft. [Accessed: 28-Dec-2016].

[10] T. Winter, "Clarifying the critical in critical heritage studies," *Int. J. Herit. Stud.*, vol. 7258, no. January, 2018.

[11] D. Wickmann, "Destruction of the Armenian Cemetery at Djulfa," no. June, pp. 2006–2007, 2007.

[12] R. Bevan, *The Destruction of Memory: Architecture at War*. Reaktion books, 2007.

[13] S. Al-Houdalieh and R. Sauders, "Building Destruction: The Consequences of Rising Urbanization on Cultural Heritage in the Ramallah Province," *Int. J. Cult. Prop.*, vol. 16, no. 1, 2009.

[14] S. Fiscor, "Metal Prices Gain Momentum," *E&Mj-Engineering Min. J.*, vol. 212, no. April, p. 72, 2011.

[15] T. Naylor, "The underworld of gemstones: Part II: In the eye of the beholder," *Crime, Law Soc. Chang.*, vol. 53, pp. 211–227, 2009.

[16] A. Hewitt, "Gold demand rises 2 % in 2016 as investment surges to four-year high," no. February, pp. 4–6, 2017.

[17] C. Alder, D. Chappell, and K. Polk, "Perspectives on the organisation and control of the illicit traffic in antiquities in South East Asia," Organised crime in art and

antiquities, (Milan, ISPAC, (2009).

[18] N. Brodie, J. Doole, and P. Watson, “Stealing History: The Illicit Trade in Cultural Material,” 2000.

[19] Lavenham Church, “Fantastic fundraising achieves target for lead theft roof repair,” *Wordpress*, 2015. [Online]. Available: https://lavenhamchurch.wordpress.com/2015/10/13/fantastic-fundraising-achieves-target-for-lead-theft-roof-repair/. [Accessed: 28-Jan-2018].

[20] Church Buildings Council, “Alternative roofing materials to lead,” *ChurchCare*, 2012. [Online]. Available: http://www.exeter.anglican.org/wp-content/uploads/2014/10/CBC-alternative_roofing_materials.pdf. [Accessed: 08-Aug-2017].

[21] English Heritage, “Theft of Metal from Church Buildings,” *The Heritage Alliance*, 2015. [Online]. Available: http://www.theheritagealliance.org.uk/hrba/wp-content/uploads/2015/01/theft-metal-church-buildings.pdf. [Accessed: 08-Aug-2017].

[22] L. Grove, “Heritocide? Defining and Exploring Heritage Crime,” *Public Archaeol.*, vol. 12, pp. 242–254, 2013.

[23] Historic England, “Heritage and the Economy,” pp. 1–6, 2015.

[24] Historic England, “Historic England and the English Heritage Trust,” *Historic England*, 2016. [Online]. Available: https://historicengland.org.uk/about/what-we-do/historic-england-and-english-heritage/. [Accessed: 19-Jul-2017].

[25] A. Hough, “75,000 ‘heritage crimes’ committed in a year,” *The Telegraph*, 2012. [Online]. Available: http://www.telegraph.co.uk/news/uknews/crime/9149420/75000-heritage-crimes-committed-in-a-year.html. [Accessed: 02-Jun-2016].

[26] Mark Harrison, “Memorandum of Understanding (MOU),” *Historic England*, 2016. [Online]. Available: https://historicengland.org.uk/advice/caring-for-heritage/heritage-crime/memorandum-of-understanding/. [Accessed: 13-Jun-2016].

[27] I. Bokova, “At last, the destruction of heritage has been recognised as a weapon of war,” *The Guardian*, 2016. [Online]. Available: https://www.theguardian.com/global-development/2016/sep/28/destruction-of-heritage-weapon-of-war-timbuktu-shrines-irina-bokova. [Accessed: 19-Jul-2017].

[28] S. Thomas, “Searching for answers: a survey of metal-detector users in the UK,” *Int. J. Herit. Stud.*, vol. 18, no. September, pp. 49–64, 2012.

[29] R. Wilson, “Summary | Survey ‘Heritage crime in your area’ | Analyse,” 2014. [Online]. Available: https://admin.onlinesurveys.ac.uk/account/lboro/analyse/68074/. [Accessed: 08-Jan-2016].

[30] A. Sidebottom, J. Belur, K. Bowers, L. Tompson, and S. D. Johnson, “Theft in Price-Volatile Markets: On the Relationship between Copper Price and Copper Theft,” *J. Res. Crime Delinq.*, vol. 48, no. 3, pp. 396–418, 2011.

[31] English Heritage, “Listed Building Consent,” *Http://Www.English-Heritage.Org.Uk*,

2014.

[32] H. Sherwood, “Suffolk churches count ‘devastating’ cost of lead roof thefts,” *The Guardian*, 2015. [Online]. Available: http://www.theguardian.com/uk-news/2015/oct/10/suffolk-churches-targeted-by-lead-thieves. [Accessed: 09-May-2016].

[33] Historic England, “ARCH The Alliance To Reduce Crimes Against Heritage,” 2016. [Online]. Available: https://historicengland.org.uk/advice/caring-for-heritage/heritage-crime/get-involved/.

[34] Historic England, “Heritage at Risk,” 2008. [Online]. Available: https://historicengland.org.uk/advice/heritage-at-risk/. [Accessed: 23-May-2016].

[35] English Heritage and Historic Scotland, “War Memorial Theft Prevention and solutions,” *War Memorials Trust Leaflet*, 2009. [Online]. Available: http://www.warmemorials.org/uploads/publications/189.pdf. [Accessed: 08-Aug-2017].

[36] Hayley Dixon, “War memorials vandalised,” *The Telegraph*, 2013. [Online]. Available: http://www.telegraph.co.uk/news/uknews/crime/10082647/War-memorials-vandalised.html. [Accessed: 14-Jun-2016].

[37] C. Goodman, “Chesham War Memorial defaced with ‘disgusting’ graffiti,” *Getbucks*, 2016. [Online]. Available: http://www.getbucks.co.uk/news/local-news/chesham-war-memorial-defaced-disgusting-11271939. [Accessed: 14-Jun-2016].

[38] M. Broomhead, “Chesterfield war memorial vandalised AGAIN,” *Derbyshire Times*, 2016. [Online]. Available: http://www.derbyshiretimes.co.uk/news/chesterfield-war-memorial-vandalised-again-1-7864976. [Accessed: 14-Jun-2016].

[39] BBC, “Metal theft in Sheffield rises by 72% over 5 years,” 2011. [Online]. Available: http://www.bbc.co.uk/news/uk-england-south-yorkshire-15333118. [Accessed: 10-May-2016].

[40] S. Durlauf and D. Nagin, “Imprisonment and crime,” *Criminol. Public Policy*, vol. 10, no. 1, 2011.

[41] Historic England, “Theft from Places of Worship.” 2011.

[42] Association of British Insurers, “From trains to drains Metal theft crime wave now costing over 1 million every week,” 2012. [Online]. Available: https://www.abi.org.uk/News/News-releases/2012/05/From-trains-to-drains--Metal-theft-crime-wave-now-costing-over-1-million-every-week. [Accessed: 13-May-2016].

[43] S. Marsden, “Britain’s most prolific church lead theft gang jailed,” *The Telegraph*, 2012. [Online]. Available: http://www.telegraph.co.uk/news/uknews/law-and-order/9743715/Britains-most-prolific-church-lead-theft-gang-jailed.html. [Accessed: 14-Jun-2016].

[44] A. Sloman, “Church Buildings Council Report of the working party on metal theft,” *Church Engl.*, vol. 1, pp. 1–7, 2015.

[45] Ecclesiastical, “Why Metal Theft is Good Business (but not for you…),” *Church Build*, 2011. [Online]. Available: http://www.churchbuildingprojects.co.uk/metal-theft-church-buildings/. [Accessed: 23-May-2016].

[46] BBC, “Metal thefts ‘down by a third’ in England and Wales,” 2015. [Online]. Available: http://www.bbc.co.uk/news/uk-31561871. [Accessed: 17-May-2016].

[47] G. Sievers, “Losing Your Mettle: is the law failing to stand up to metal theft?,” *Vacant Property Specialists*, 2015. [Online]. Available: https://www.journalism.co.uk/press-releases/losing-your-mettle-is-the-law-failing-to-stand-up-to-metal-theft-/s66/a564947/.

[48] M. F. J. Vijlbrief, “Looking for displacement effects: Exploring the case of ecstasy and amphetamine in the Netherlands,” *Trends Organ. Crime*, vol. 15, pp. 198–214, 2012.

[49] J. R. Nesselroade, S. M. Stigler, and P. B. Baltes, “Regression Toward the Mean and the Study of Change,” *Psychol. Bull.*, vol. 88, no. 3, pp. 622–637, 1980.

[50] D. P. Farrington and B. C. Welsh, “How Important is ‘Regression to the Mean’ in Area-Based Crime Prevention Research?,” *Crime Prev. Community Saf.*, vol. 8, pp. 50–60, 2006.

[51] C. Buckley, “Rail police: cable crime is biggest threat after terror,” *The Times*, 2007. [Online]. Available: http://www.thetimes.co.uk/tto/business/industries/engineering/article2169203.ece.

[52] M. P. Ashby, “Is metal theft committed by organized crime groups, and why does it matter?,” *Criminol. Crim. Justice*, p. 1748895815603777, 2015.

[53] Mark Harrison, “Heritage Metal Theft Workshop,” 2016.

[54] D. Shaw, “Police forces all face major budget cuts,” *BBC News*, 2015. [Online]. Available: http://www.bbc.co.uk/news/uk-31771456. [Accessed: 14-Jun-2016].

[55] S. Efford, “Budget cuts will radically change policing,” *Association of Police and Crime Commissioners*, 2015. [Online]. Available: http://www.apccs.police.uk/press_release/budget-cuts-will-radically-change-policing/. [Accessed: 14-Jun-2016].

[56] J. Brown, “Rising toll of York stone thefts from Leeds pavements has cost council £50k in a year - Yorkshire Evening Post,” *Yorkshire Evening Post*, 2015. [Online]. Available: http://www.yorkshireeveningpost.co.uk/news/latest-news/top-stories/rising-toll-of-york-stone-thefts-from-leeds-pavements-has-cost-council-50k-in-a-year-1-7178990. [Accessed: 11-Aug-2015].

[57] S. Swinford, “Stone theft hits ‘epidemic’ levels.” [Online]. Available: http://www.telegraph.co.uk/news/uknews/crime/11694827/Stone-theft-hits-epidemic-levels.html. [Accessed: 11-Aug-2015].

[58] J. Doward, “Stone thieves are dismantling Yorkshire’s heritage, warn police,” *The Guardian*, 2015. [Online]. Available: https://www.theguardian.com/uk-news/2015/jun/27/yorkshire-stone-thieves-region-heritage. [Accessed: 14-Jun-2016].

[59] H. Sime, “Rural England hit by surge in theft of paving slabs as thieves target daylight raids | Daily Mail Online,” *The Daily Mail*. [Online]. Available: http://www.dailymail.co.uk/news/article-3142700/Surge-theft-paving-slabs-thieves-posing-workmen-high-viz-jackets-target-rural-properties-brazen-daylight-raids.html. [Accessed: 11-Aug-2015].

[60] P. Dinham, “Thieves steal expensive paving stones from a cenotaph memorial

dedicated to the memory of murdered soldier Lee Rigby," *Daily Mail*, 2016. [Online]. Available: http://www.dailymail.co.uk/news/article-3699367/Paving-stones-dedicated-Lee-Rigby-stolen-Middleton-cenotaph-memorial-dedicated-memory-murdered-soldier.html. [Accessed: 20-Jul-2016].

[61] D. Wilkinson, "Lee Rigby memorial cenotaph targeted by 'absolutely disgusting' crooks who stole dozens of paving slabs," *Daily Mirror*, 2016. [Online]. Available: http://www.mirror.co.uk/news/uk-news/lee-rigby-memorial-cenotaph-targeted-8454112. [Accessed: 18-Jun-2017].

[62] David Millward, "Surge in stone thefts," *The Telegraph*, 2011. [Online]. Available: http://www.telegraph.co.uk/news/uknews/8853296/Surge-in-stone-thefts.html. [Accessed: 20-May-2016].

[63] L. Davis and R. Fisher, "Fingermark recovery from riot debris: Bricks and stones," *Sci. Justice*, vol. 55, no. 2, pp. 97–102, 2015.

[64] "Wenlok Jug stolen from Stockwood Discovery Centre," *BBC News*, 2012. [Online]. Available: http://www.bbc.co.uk/news/uk-england-beds-bucks-herts-18056773. [Accessed: 24-Jun-2016].

[65] E. Forde, "Criminal gangs targeting high-value works of art in UK," *BBC News*, 2013. [Online]. Available: http://www.bbc.co.uk/news/uk-24956337. [Accessed: 24-Jun-2016].

[66] R. Sloggett, "Art crime: fraud and forensics," *Aust. J. Forensic Sci.*, vol. 4000, no. June, pp. 1–7, 2014.

[67] W. F. Libby, "Radiocarbon dating, memories, and hope," Los Angeles, 1972.

[68] P. Wilson, "Goldrush?," *Current Archaeology*, 2009. [Online]. Available: https://www.archaeology.co.uk/articles/opinion/gold-rush.htm. [Accessed: 28-Jan-2018].

[69] D. Gill, "The Portable Antiquities Scheme and the Treasure Act: Protecting the Archaeology of England and Wales?," *Institute of Archaeology*, 2010. .

[70] S. M. Bleay *et al.*, "Non-invasive detection and chemical mapping of trace metal residues on the skin," *RSC Adv.*, vol. 4, p. 19525, 2014.

[71] M. and E. Bobtelsky, "The Compounds of Gold and Palladium with Rubeanic Acid. Composition, Structure and Analytical Use," *Anal. Chim. Acta*, vol. 17, 1957.

[72] S. Sykes and J. W. Bond, "A Comparison of fingerprint sweat corrosion of different alloys of brass," *J. Forensic Sci.*, vol. 58, no. 1, pp. 138–141, 2013.

[73] Smartwater, "Smartwater," 2016. [Online]. Available: http://www.smartwater.com/.

[74] Mark Waugh, "National Campaign to Reduce War Memorial Theft," 2011. [Online]. Available: http://www.warmemorials.org/uploads/publications/313.pdf. [Accessed: 27-Mar-2017].

[75] Trace-In-Metal, "a uniquely comprehensive metal protection system," 2016. [Online]. Available: http://www.trace-in-metal.com/index. [Accessed: 21-Jun-2016].

[76] SelectaDNA, "Advanced Forensic Marking," *SelectaDNA*, 2004. [Online]. Available: https://www.selectadna.co.uk/history. [Accessed: 21-Jun-2016].

[77] I. Fraser, “Antique brick thefts plague east London as prices rise 9pc,” *The Telegraph*, 2016. [Online]. Available: http://www.telegraph.co.uk/business/2016/03/21/antique-brick-thefts-plague-east-london-as-prices-rise-9pc/. [Accessed: 22-Jun-2016].

[78] A. Donche and S. Loyan, “Development of Latent Fingerprints on Stones,” *J. Forensic Identif.*, vol. 46, no. 5, pp. 542–555, 1996.

[79] C. Lennard, “Fingerprint detection: future prospects,” *Aust. J. Forensic Sci.*, vol. 39, no. July, pp. 73–80, 2007.

[80] B. C. Shah, “Novel Fingerprint Development Techniques,” Loughborough University, 2013.

[81] C. Champod, C. Lennard, P. Margot, and M. Stoilovic, *Fingerprints and other ridge skin impressions*. 2004.

[82] H. Lee and R. Gaensslen, *Advances In Fingerprint Technology*. CRC Press, 2001.

[83] J. Szumera, M. Wełniak, A. Olejniczak, and J. P. Lukaszewicz, “Transfer of triazine-iron(II) chromic complexes left by iron items on textile background and human skin,” *J. Forensic Sci.*, vol. 55, no. 4, pp. 944–952, 2010.

[84] M. Stevens and H. Messier, “The trace metal detection technique (TMDT): a report outlining a procedure for photographing results in color, and some factors influencing the results in controlled laboratory tests.,” 1974.

[85] H. Messler and J. Stevens, “Fluorescence Photography of the Trace Metal Detection Technique,” *Photogr. Appl. Sci. Technol. Med.*, vol. May, pp. 24–25, 1975.

[86] W. Kokocinski, J. Brundage, and J. D. Nicol, “A Study of the Use of 2-Nitroso-1-Naphthol as a Trace Metal Detection Reagent,” *J Forensic Sci*, pp. 810–814, 1980.

[87] D. C. G.L.Goldman, B.S and J.I. Thornton, “A New Trace Ferrous Metal Detection Reagent,” *J. Forensic Sci.*, vol. 21, no. 3, pp. 625–628, 1976.

[88] L. Thornton and D. Grim, “An Improved Ferrous Metal Detection Reagent,” *J Forensic Sci*, vol. 22, no. 4, pp. 739–741, 1977.

[89] A. Leifer, H. Wax, and J. Almog, “Who Held the Gun ?: Decipherment of Suicide-Homicide Cases Using the PDT Reagent *,” *J. Forensic Identif.*, vol. 51, pp. 346–360, 2001.

[90] A. Olejniczak, A. W. Cyganiuk, and J. P. Lukaszewicz, “1,2,4-Triazine-Based Chromogenic Reagents for the Detection of Microtraces of Various Metals Left on Human Skin,” *J. Forensic Sci.*, vol. 55, no. 3, pp. 747–752, 2010.

[91] C. Lee and M. Phil, “The Detection of Iron Traces on Hands by Ferrozine Sprays : A Report on the Sensitivity and Interference of the Method and Recommended Procedure in Forensic Science Investigation,” *J Forensic Sci*, no. Ii, pp. 920–930, 1986.

[92] H. . E. A. Bandey, *Fingermark Visualisation Manual*. 2014.

[93] F. Nizam, W. Knaap, and J. D. Stewart, “Development of fingerprints using electrolysis: a technical report into the development of fingerprints on fired brass cartridge cases,” *J. Forensic Identif.*, vol. 62, no. 2, p. 129, 2012.

[94] B. W. Given, “Latent fingerprints on cartridges and expended cartridge casings.,” *J. Forensic Sci.*, vol. 21, no. 3, pp. 587–94, 1976.

[95] C. M. a Girelli, B. J. M. Lobo, A. G. Cunha, J. C. C. Freitas, and F. G. Emmerich, “Comparison of practical techniques to develop latent fingermarks on fired and unfired cartridge cases,” *Forensic Sci. Int.*, vol. 250, pp. 17–26, 2015.

[96] Y. Migron, G. Hocherman, E. Springer, J. Almog, and D. Mandler, “Visualization of sebaceous fingerprints on fired cartridge cases: a laboratory study.,” *J. Forensic Sci.*, vol. 43, no. Imi, pp. 543–548, 1998.

[97] Chemistry and Industry, “A Smoking Gun,” *Forensic Sci. Chem. Ind.*, no. July, pp. 28–31, 2012.

[98] A. D. A. W. Geraint Williams, H. Neil McMurray, “Latent Fingerprint Detection Using a Scanning Kelvin Microprobe,” *J. Forensic Sci.*, vol. 46, no. 5, pp. 1085–1092, 2001.

[99] J. W. Bond and E. Lieu, “Electrochemical behaviour of brass in chloride solution concentrations found in eccrine fingerprint sweat,” *Appl. Surf. Sci.*, vol. 313, pp. 455–461, 2014.

[100] Bond. John W, “Visualization of Latent Fingerprint Corrosion of Metallic Surfaces,” *J. Forensic Sci.*, vol. 53, no. 4, pp. 812–822, Mar. 2008.

[101] J. W. Bond, “On the electrical characteristics of latent finger mark corrosion of brass,” *J. Phys. D. Appl. Phys.*, vol. 41, no. 12, p. 125502, 2008.

[102] J. W. Bond, “Effect that the relative abundance of copper oxide and zinc oxide corrosion has on the visualization of fingerprints formed from fingerprint sweat corrosion of brass,” *J. Forensic Sci.*, vol. 56, no. 4, pp. 999–1002, 2011.

[103] C. G. Worley, S. S. Wiltshire, T. C. Miller, G. J. Havrilla, and V. Majidi, “Detection of visible and latent fingerprints using micro-X-ray fluorescence elemental imaging,” *J. Forensic Sci.*, vol. 51, no. 1, pp. 57–63, 2006.

[104] C. Flynn, K., Maynard, P., Pasquier, E., Lennard, C., Stoilovic, M., and Roux, “Evaluation of Iodine-Benzoflavone and Ruthenium Tetroxide Spray Reagents for the Detection of Latent Fingermarks at the Crime Scene,” *J. Forensic Sci.*, vol. 49, no. 4, pp. 1–9, 2004.

[105] I. Hefetz, A. Cohen, Y. Cohen, and A. Chaikovsky, “Development of latent fingermarks from rocks and stones,” *J. Forensic Sci.*, vol. 59, no. 5, pp. 1226–1230, 2014.

[106] M. and B. . Bobtelsky, “A Quick and Direct Micro-Heterometric Determination of Traces of Copper with Rubeanic Acid in Metals and Alloys,” *Anal. Chim. Acta*, vol. 15, no. 2, pp. 62–72, 1956.

[107] Freidrich Wohler, “Ueber Cyan Verbindungen,” *Poggendorfls Annln*, vol. 2, no. 2, pp. 177–182, 1825.

[108] R. Ray, P., Ray, “Metallic Compounds of Rubeanic Acid,” *Q. J. Indian Chem. Soc.*, vol. 118, no. 3, 1926.

[109] P. Ray and J. Xavier, “Review of rubeanic acid and derivatives as chelating ligands and analytical reagents,” *J. Indian Chem. Soc.*, vol. 38, no. 8, p. 535, 1961.

[110] M. Abboudi, A. Mosset, and J. Galy, “Metal complexes of rubeanic acid. 3. Large-Angle x-ray scattering studies of amorphous copper(II) and nickel(II) complexes,” *Inorg. Chem.*, vol. 24, no. 2, pp. 2091–2094, 1985.

[111] G. Nilsson, “A Characteristic Reaction of Dithio-oxamide with Ferrous Iron,” *RSC*, no.

500, pp. 500–503, 1939.

[112] S. K. Bhowal, “Spectrophotometric determination of osmium with rubeanic acid,” *Anal. Chim. Acta*, vol. 69, pp. 465–468, 1974.

[113] H. H. Willard, C. Michigan, A. Arbor, and R. E. Mosher, “Determination of Copper by Dithio-oxamide in Magnesium and Magnesium Alloys Metallic Contaminants in Fluid Cracking Catalyst,” *Anal. Chem*, vol. 21, no. 5, pp. 20–21, 1949.

[114] K. Kanaizuka, R. Haruki, O. Sakata, M. Yoshimoto, Y. Akita, and H. Kitagawa, “Construction of highly oriented crystalline surface coordination polymers composed of copper dithiooxamide complexes.,” *J. Am. Chem. Soc.*, vol. 130, no. 47, pp. 15778–9, Nov. 2008.

[115] S M Bleay *et al.*, “Fingerprint Source Book,” *United Kingdom Home Off.*, p. Chapter 10-11, 2013.

[116] S. Wiesner, T. Tsach, C. Belser, and Y. Shor, “A Comparative Research of Two Lifting Methods: Electrostatic Lifter and Gelatin Lifter,” *J. Forensic Sci.*, vol. 56, no. January, pp. 58–62, 2011.

[117] Y. Shor, T. Tsach, S. Wiesner, and G. Meir, “Removing interfering contaminations from gelatin lifters.,” *J. Forensic Sci.*, vol. 50, no. 6, pp. 1386–1393, 2005.

[118] Exeter Analytical, “Elemental Analyser Theory of Operation,” 2016. [Online]. Available: http://www.exeteranalytical.co.uk/theory-of-operation/. [Accessed: 27-Jul-2016].

[119] L. Azaroff, *X-Ray Diffraction*. 1974.

[120] D. A. Radziemski, Leon J.; Cremers, *Handbook of Laser-Induced Breakdown Spectroscopy*. 2006.

[121] F. J. Fortes, J. Moros, P. Lucena, L. M. Cabalín, and J. J. Laserna, “Laser-induced breakdown spectroscopy,” *Anal. Chem.*, vol. 85, pp. 640–669, 2013.

[122] C. Pasquini, “Near infrared spectroscopy: Fundamentals, practical aspects and analytical applications,” *J. Braz. Chem. Soc.*, vol. 14, no. 2, pp. 198–219, 2003.

[123] H. W. M. Paine, H.L. Bandey, S.M. Bleay, “The effect of relative humidity on the effectiveness of the cyanoacrylate fuming process for fingermark development and on the microstructure of the developed marks,” *Forensic Sci. Int.*, vol. 212, pp. 130–142, 2011.

[124] D. A. Dillman, *Mail and Internet Surveys. The Tailored Design Method.*, Second Edi. John Wiley and Sons, 2007.

[125] L. Grove, G. Farrell, D. Farrington, and S. D. Johnson, “Preventing Repeat Victimization: A Systematic Review,” The Swedish National Council for Crime Prevention, Loughborough University, 2012.

[126] G. Farrell, C. Phillips, and K. Pease, “Like taking Candy. Why does Repeat Victimization Occur?,” vol. 35, no. 3, pp. 384–399, 1995.

[127] N. Tweedie, “Was your kitchen floor stolen from a church? Steep rise in theft of ancient slabs from churchyards, paths and walls fuelled by homeowners’ desire for ‘lived-in’ stone,” *Daily Mail*, 2015. [Online]. Available: http://www.dailymail.co.uk/news/article-3150483/Was-kitchen-floor-stolen-church-

Steep-rise-theft-ancient-slabs-churchyards-paths-walls-fuelled-homeowners-desire-lived-stone.html. [Accessed: 21-Aug-2016].

[128] K. Pickering, “PLUNDERED: Stone thefts are stripping away our heritage,” *The Telegraph and Argus*, 2016. [Online]. Available: http://www.thetelegraphandargus.co.uk/news/news_behind/14532151.PLUNDERED__Stone_thefts_are_stripping_away_our_heritage/. [Accessed: 21-Aug-2016].

[129] A. Daubney, “Floating culture: the unrecorded antiquities of England and Wales,” *Int. J. Herit. Stud.*, vol. 23, no. 9, 2017.

[130] J. Bergold and S. Thomas, “Participatory Research Methods: A Methodological Approach in Motion,” *Forum Qual. Soc. Res.*, vol. 13, no. 1, 2012.

[131] W. P. D. and H. C. Bond, John, “Visualization of Latent Fingerprint Corrosion on a Discharged Brass Shell Casing,” *J. Forensic Sci.*, vol. 54, no. 4, pp. 1034–1041, 2009.

[132] S. M. Bleay, P. F. Kelly, and R. S. P. King, “Polymerisation of S2N2 to (SN)x as a tool for the rapid imaging of fingerprints removed from metal surfaces,” *J. Mater. Chem.*, vol. 20, no. 45, p. 10100, 2010.

[133] I. Cobain, “Tough case to crack: the mystery of Britain’s falling crime rate,” *The Guardian*, 2014. [Online]. Available: https://www.theguardian.com/uk-news/2014/aug/31/tough-case-mystery-britains-falling-crime-rate. [Accessed: 03-Sep-2016].

[134] L. Bennett, “Assets under attack: Metal theft, the built environment and the dark side of the global recycling market,” *Environ. law an Manag.*, no. 20, pp. 176–183, 2008.

[135] B. Kooi, “Guide No. 58,” *US Dep. Justice, Off. Community Oriented Polic. Serv.*, vol. 58, 2010.

[136] Ecclesiastical, “Guidance Notes - Theft of Metal,” 2007.

[137] UK Legislation, *Scrap Metal Dealers Act*. 2013.

[138] J. W. Bond, S. V. Hainsworth, and T. L. Lau, “Lead theft-A study of the ‘Uniqueness’ of lead from Church roofs,” *J. Forensic Sci.*, vol. 58, no. 4, pp. 1003–1007, 2013.

[139] F. Saverio Romolo and P. Margot, “Identification of gunshot residue: A critical review,” *Forensic Sci. Int.*, vol. 119, pp. 195–211, 2001.

[140] W. I. Ltd, “WG Handheld Explosive & Narcotics Detector,” 2014. [Online]. Available: https://www.wi-ltd.com/product/explosive-narcotics-detector-hand-held/. [Accessed: 06-Aug-2017].

[141] Arrowhead Forensics, “Ferrotrace,” 2017. [Online]. Available: http://www.crime-scene.com/store/A-2090M.shtml. [Accessed: 08-Aug-2017].

[142] J. Almog, “Forensic science does not start in the lab: The concept of diagnostic field tests,” *J. Forensic Sci.*, vol. 51, no. 6, pp. 1228–1234, 2006.

[143] B. Glattstein, a Zeichner, a Vinokurov, N. Levin, C. Kugel, and J. Hiss, “Improved method for shooting distance estimation. Part III. Bullet holes in cadavers.,” *J. Forensic Sci.*, vol. 45, pp. 1243–1249, 2000.

[144] R. Kumar, N. Patial, and S. Singh, “Identification of Tool Marks of a Sickle on a Telephone Cable,” *J. Forensic Sci.*, vol. 58, no. 1, pp. 217–219, 2013.

[145] C. P. Garcia, “Rubeanic acid: a general spray reagent for the detection of steroids on thin-layer plates,” *J. Chromatogr.*, vol. 350, pp. 3–5, 1985.

[146] J. W. Bond, “Visualization of latent fingerprint corrosion of brass,” *J. Forensic Sci.*, vol. 54, no. 5, pp. 1034–1041, 2009.

[147] L. Holczinger, “Histochemischer Nachweis freier Fettsauren,” *Acta Histochem.*, vol. 8, pp. 167–175, 1959.

[148] L. W. L. Davis, P. F. Kelly, R. S. P. King, and S. M. Bleay, “Visualisation of latent fingermarks on polymer banknotes using copper vacuum metal deposition: A preliminary study,” *Forensic Sci. Int.*, pp. 1–7, 2016.

[149] G. Grass, C. Rensing, and M. Solioz, “Metallic Copper as an Antimicrobial Surface,” *Appl. Environ. Microbiol.*, vol. 77, no. 5, pp. 1541–1547, 2010.

[150] K. B. Ahmad, “Kashmir heritage: Tale of a mammoth loss,” *Greater Kashmir*, 2018. [Online]. Available: http://www.greaterkashmir.com/news/opinion/kashmir-heritage-tale-of-a-mammoth-loss--part-3/272047.html. [Accessed: 04-Feb-2018].

[151] Reuters, “Nazi victim memorial stones stolen in Berlin, police probe,” *Today Online*, 2017. [Online]. Available: http://www.todayonline.com/world/nazi-victim-memorial-stones-stolen-berlin-police-probe. [Accessed: 04-Feb-2018].

[152] J. M. Freyer, “China to crack down on brick-by-brick theft of Great Wall,” *The Guardian*, 2016. [Online]. Available: https://www.theguardian.com/world/2016/jul/28/china-to-crack-down-brick-by-brick-great-wall-theft. [Accessed: 04-Feb-2018].

[153] Foster and Freeman, “LIB Spectrometry for the detection of gun shot residues,” *Foster and Freeman*, 2016. [Online]. Available: http://www.fosterfreeman.com/trace-evidence/311-ecco-applications.html. [Accessed: 22-Jul-2017].

[154] Ç. S. Bilge G, Boyacı İH, Eseller KE, Tamer U, “Analysis of bakery products by laser-induced breakdown spectroscopy.,” *Food Chem*, vol. 181, pp. 186–190, 2015.

[155] English Heritage, “Strategic Stone Study A Building Stone Atlas of Nottinghamshire,” no. July, 2013.

[156] S. Zhang, Yanlin ; Cattrall, Robert ; McKelvie, Ian ; Kolev, “Gold, an alternative to platinum group metals in automobile catalytic converters,” *Gold Bull.*, vol. 44, no. 3, pp. 145–153, 2011.

[157] World Gold Council, “Gold in catalytic converters,” 2016.

[158] J. Jenkins, “The Definitive Guide to Choosing a Gravestone,” *GravestonesHQ*, 2014. [Online]. Available: http://www.gravestoneshq.co.uk/. [Accessed: 04-Feb-2018].

[159] S. Clement, R. King, and R. Wilson, “LIBS Meeting,” 2017.

[160] F. Dryden, “Loughborough University scientists develop new technique to help catch metal thieves,” *Leicester Mercury*, 2014. [Online]. Available: http://www.leicestermercury.co.uk/loughborough-university-scientists-develop-new/story-22915901-detail/story.html. [Accessed: 22-Feb-2017].

[161] “Crimewatch Roadshow Season 7 Episode 18,” BBC, United Kingdom, 2015.

[162] R. Trager, “Stone ‘blueprinting’ to tackle heritage thefts,” *Royal Society of Chemistry*,

2015. [Online]. Available: https://www.chemistryworld.com/research/stone-blueprinting-to-tackle-heritage-thefts/8816.article. [Accessed: 08-Aug-2017].

[163] M. B. Griggs, "Scientists In The United Kingdom Are 'Fingerprinting' Stolen Rocks," *Popular Science*, 2015. [Online]. Available: http://www.popsci.com/scientists-united-kingdom-are-fingerprinting-stolen-rocks. [Accessed: 08-Aug-2017].

## List of figures

## Publications

S.M. Bleay, L.E. Grove, P.F. Kelly, R.S.P. King, K. Mayse, B.C. Shah, R. Wilson, Non-invasive detection and chemical mapping of trace metal residues on the skin. RSC Advances, 2014. 4(37): p. 19525-19528. 23. D. Philipson and S. Bleay,

## Courses and conferences attended

Teaching skills parts A, B, C, Loughborough University, March 2014.

Radiation legislation and protection training, Loughborough University, March 2014.

Fire safety training, Loughborough University, December 2013.

IR spectroscopy training, Loughborough University, March 2014.

XRD training, Loughborough University, January 2014.

Presented posters at Science Matters conference, Loughborough University, 2014, 2015, 2016. Best poster award for secure and resilient societies section 2016.

Presented poster at East Midlands policing conference, Loughborough University, June 2014.

Presented poster at Heritage crime conference, University of Kent, June 2014.

Presented poster at New Frontiers in Forensic Science conference, University of Leicester, April 2015.

Attended CAST academia/industry meeting, Foster and Freeman, April 2015.

Presented research live on BBC's Crimewatch Roadshow, Cardiff, July 2015.

Presented at Top of the Bench event, Loughborough University, April 2016.

Presented at Inspiring Research conference, Loughborough University, November 2015. Runner up award.

Presented ‘What is a PhD?’ to undergraduate students, Loughborough University, February 2016.

Student Mentor 2015-2016

Laboratory Demonstrator 2013-2016

Attended all seminars and health and safety training within the department 2013-2016