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The Conservation of Some Cast Iron Ammunition by the Alkaline Sulphite Method

Theo Skinner

Until recently the conservation of marine cast iron was problematic. However, in 1975, North and Pearson (1) published a method for the stabilisation of such iron which appeared to hold considerable promise. This so-called alkaline sulphite method was therefore applied to a large collection of cannonballs which the N.M.A.S. Conservation Laboratory received. These cannonballs (together with a few hand grenades) were part of a great amount of material treated at this laboratory, all derived from the site of H.M.S. Dartmouth, a fifth rate frigate sunk in 1690 off Eilean Rubha an Ridire in the Sound of Mull (2). The present author was not involved initially in this treatment, which was started by Sandra Dunbar and Helen Dalrymple in 1978. The complete treatment has taken four years, although during one of these years no work was done, and during much of the remaining period the only work necessary was the regular changing and monitoring of solutions.

Some Background Information

The process of making cast iron is a comparatively recent one in the Western world, although used in China much earlier. Cast iron first made an appearance in the West about the 14th century AD; before this iron was smelted in the solid state in the bloomery process which produced essentially pure iron which could be easily forged. Carburizing of this wrought iron produced steel, an iron-carbon alloy. The discovery of the blast furnace enabled higher temperatures to be reached, which produced a molten iron-carbon alloy, cast iron, which contains carbon from 2% to 4.5%, as opposed to the 0.1% to 1.5% found in steels, this increase in carbon content also reduced the melting point of the alloy. Early blast furnaces were fuelled with charcoal, and partly because the limited physical strength of this fuel limited the height of the blast furnaces, the temperatures reached were much lower than can be achieved using coke as a fuel, a technique developed in the early 18th century. The use of coke and the resulting higher temperatures allowed the reduction of silica in the furnace charge, producing a high silicon cast iron, as opposed to the low silicon alloys produced by the charcoal furnaces. The amount of silicon affects the microstructure of the cast iron: high silicon levels tend to produce a grey cast iron, with free graphite flakes, whereas low silicon levels tend to produce a white cast iron, in which all the carbon is present as cementite or iron carbide, Fig.6. However, the microstructure of the alloy is also affected by the cooling rate: rapid cooling favours the production of white cast iron whereas slow cooling tends to produce a grey cast iron microstructure, with flakes of free graphite.
As the Dartmouth sank in 1690, we must assume that the cast iron is the product of charcoal fuelled furnaces, i.e. it is a relatively low silicon cast iron. The cannonballs themselves certainly appear to be so: early attempts to section a specimen for metallographic analysis were consistently unsuccessful. White cast irons are noted for the difficulty involved in machining them, due to the extreme hardness of the cementite constituent. Although it has not yet been possible to properly section any of the cannonballs (for lack of a diamond saw) and obviously will not be feasible to section all of them, the lack of graphitisation (see below) indicates that they are all of white cast iron. The exact structure of the metal is important, as it affects not only the working properties of the metal but also the process of corrosion and the nature of the corrosion products. The differences between wrought and cast iron corrosion have long been noted, and conservators generally differentiate between the two types with regard to choice of treatment; however the differences between white and gray cast irons have received less attention, probably because the white cast irons are relatively rare. It is interesting to note that the condition of the Dartmouth’s guns (which being large, slow cooled, castings are presumably grey iron) contrasts starkly with that of the cannonballs. To quote one of the excavators:

"During the process it became apparent that all the complete guns on site were in an extremely soft and advanced state of deterioration to such an extent that it was possible to pass a knife blade through the metal of the barrel with ease". (5)

The Corrosion of Iron in Marine Environments

The process of the corrosion of iron is an extremely complex one. North (6) considered that the process could be divided into two stages: first a brief period following initial immersion, followed by a sustained period of corrosion after the deposition of concretion. To account for some of the variability in condition of material from wreck sites, one should add a third stage; the period before immersion. The cannonballs from H.M.S. Dartmouth provide a good example of the possible importance of this pre-immersion period: many of these cannonballs were probably carried as ballast, several being far too large for the largest calibre guns the ship carried (5). As such they were probably in a very different state to the shot which was to be used as ammunition: as ballast they would be exposed to the corrosive atmosphere of the depths of the hull; the conditions there were described by the Dartmouth's Lieutenant, William Kiggins:

"Our ballast being so bad, stinking and all of a quagmire and sandy that it stoaks the timbers, that the water has no course to the pumps. (2) p.34."

Under such conditions, with salt water and an unlimited supply of oxygen, ballast iron would no doubt corrode very rapidly,
even before burial. The iron in use e.g. the guns and ammunition, would also suffer to some extent from the salt laden atmosphere, even if this effect was reduced by the application of a protective coating. The exact effects of the surface conditions of iron objects prior to burial are not known, but they may well be a significant factor in further corrosion. For example, a thick protective oxide film formed in the air may reduce the effects of later marine corrosion.

In the period immediately following burial, and before the deposition of concretion on the surface of the object (a period of 1-3 years in Western Australian waters, according to North (6) p.76), the corrosion of iron is primarily dependent on the pH and Eh of the marine environment. These in turn are affected by factors such as the tidal flow, depth, type of sea bed (sand, silt), organic activity and salinity (7).

In general, on the sea bed the environment will tend to be anaerobic and of near neutral pH. Under such circumstances the corrosion of iron proceeds by the following reactions, driven by the difference in potential between the iron (-0.45V) and sea water (Eh = +4V), (6)p.76).

\[
\begin{align*}
\text{Anodic reaction} & : & \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- & (1) \\
\text{cathodic reaction I} & : & \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- & (2) \\
\text{or} & & & (3) \\
\text{II} & : & 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^- & (3)
\end{align*}
\]

The last reaction is catalysed by sulphate reducing bacteria, which operate under anaerobic conditions. The anodic and cathodic regions occur at points on the object surface: the more noble constituents will tend to be cathodic (e.g. graphite flakes, cementite); the less noble ferrite or pure iron phase, together with sulphide inclusions, anodic. The pH at the cathodic areas will gradually rise, with the result that calcium and magnesium carbonate in the sea water will precipitate on these areas, forming an inorganic concretion which gradually cover the whole object. The object then enters the second and most prolonged phase of corrosion.

Within the concretion, conditions are very different to those pertaining outside. North (6) found that the pH and Eh values within concretions were 4.8 ± 0.1 and -0.412V to -0.247V, respectively. In such circumstances the anodic and cathodic reactions must be separated such that the anodic reaction occurs at the metal surface whilst the cathodic reaction occurs within the concretion layer:

\[
\begin{align*}
\text{at anode} & : & \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- & (1) \\
\text{at cathode} & : & 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- & (3)
\end{align*}
\]

North favours reaction (3) as the cathodic reaction; the evidence in favour of this is firstly the appreciable quantities of gas released when concretions are broken open in situ; and the poor correlation between dissolved oxygen concentrations and observed corrosion rates for iron, together with the high sulphide levels.
commonly present in concretions. The acid conditions within the concretion are thought to be the result of hydrolysis i.e.:

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$$

Although these processes occur in both wrought and cast iron artefacts, the results are very different. In wrought iron the steady dissolution of the ferrite matrix and the diffusion of the ferrous ions through the concretion layer leaves no trace of the original shape of the object, save what is left as an impression in the concretion itself. Eventually one may be left with a complete void surrounded by the concretion shell, from which a replica of the original object may be cast, using a suitable material.

In cast irons, the presence of resistant phases in the microstructure of the metal retains the original shape and form of the object within the concretion. The nature of these constituents depends on the composition of the alloy. Grey cast irons contain graphite flakes: these are cathodic to the iron and consequently are not attacked. The result is a layer of graphite flakes with an infilling of iron corrosion products. This layer is generally soft and friable and one may easily "pass a knife blade through /It/ with ease". As corrosion proceeds, the metal/oxide interface recedes until a completely graphitised object remains.

In white cast iron objects, a similar process operates but in this case the corrosion resistant phases are the cementite, Fe₃C, and the ternary eutectic, of ferrite, iron carbide and iron phosphide. Pearson (8) draws a contrast between the soft, porous graphitised layer found in grey cast iron and the hard coherent layer formed in white cast iron by the extremely hard cementite and the ternary eutectic. Weier (7) considers the effect of variations in alloy composition on the survival of iron objects; however it is difficult to draw conclusions as there is little real data, most observations seem to be based on only one or two analyses (9),(10). However it seems likely that the proportions of silicon, phosphorous and carbon are important in determining both the rate of corrosion and the form of the corroded layer. The compactness of this layer will determine the rate at which ions can diffuse in and out of the interior, and this will also be controlled by the porosity of the concretion. Weier (7) states that the compact concretion formed in cold waters are more protective than the more porous concretions formed in warmer waters.

A further barrier to diffusion which may affect the rate of corrosion in sea water is that produced by coverings of microorganisms such as bacteria, fungi or algae. Such a situation existed on the Dartmouth site (Martin (2) p.33) and helped in part to preserve the material at this rather unpromising site. Other factors which appear to have helped preserve material from the Dartmouth are the limited fetch and sea horizon, extensive fissuring of the sea bed, together with a fair proportion of sedimentary deposit (Muckleroy (12)p.55).
The action of sulphide in the corrosion of artefacts from the Dartmouth is very evident - the concretions have a typically black appearance in general, although one or two cannonballs were covered in a very much thinner whitish concretion. Copper and copper alloy artefacts were generally covered with a thick layer of covellite, CuS, and a silver spoon was almost completely converted to silver sulphide; these are typically the result of corrosion in an anaerobic environment. However, the diversity of the site must be emphasised and some of the objects must have corroded in fairly oxidising conditions. A number of lead scupper liners were recovered; these were covered with the remains of macro-organisms and a thin layer of white corrosion product. In an anaerobic environment one would have expected these to be extensively converted to black lead sulphide or galena. This is explained by the fact that the scupper liners were found lying proud of the bottom (Martin (2), p.37) whereas many other objects were found buried in a trench dug by the keel as the ship settled (2)(p.39). The source of sulphide must in general have been the result of bacterial activity, however it is interesting to note that a great amount of coal was found on the site. Part of this appears to have derived from the galley, but the modern wrecks nearby also contained a great amount of coal, which generally contain large quantities of sulphur.

The corrosion products formed as the result of the anodic dissolution of iron depend largely on the anions present in the corrosive medium, and the rate of corrosion is influenced by the nature of the compounds these form with the dissolved iron. In some cases an insoluble material is produced which slows the rate of corrosion. Thus iron corroding in an environment containing phosphate ions may form a protective layer of insoluble vivianite Fe₅(PO₄)₂·8H₂O. This often accounts for the preservation of iron buried together with bone or other organic material. In a marine environment, the anions present are mainly chloride, sulphate, sulphide and carbonate. The first two produce soluble compounds with ferrous ion and are responsible for the corrosion of iron. The sulphide tends to precipitate in the concretion (North, 6,p.78): only low levels appear to be found actually in the corrosion layer. This is not surprising in view of the acidic conditions existing within the concretion which would tend to keep any sulphide in solution rather than precipitate it as iron sulphide. However, in the alkaline region of the concretion, precipitation of iron sulphides would be expected, and here North (6,p.78) finds high levels of sulphide and elemental sulphur, between 1 and 6%. Some small amount of dissolved hydrogen sulphide may however be present at the metal/oxide interface, enough to stimulate the anodic dissolution of iron (11) p.7. It is likely that the effects of sulphate reducing bacteria within the concretion accelerate corrosion both by stimulation of the anodic dissolution of iron and by depolarising the cathodic reaction.

As the conditions within the concretion are acidic and reducing, the iron ion species found is mainly that of the ferrous ion; this will be present mainly as soluble ferrous chloride: chloride ions are taken into the interior as a result of the corrosion current. The sulphate ions present in sea water (11%), (Weier, 7, p.133) are notable by their absence amongst the corrosion
products reported on marine iron in the conservation literature, although sulphate derived from atmospheric sulphur dioxide has been shown to be very corrosive towards iron (Evans, 13, p.108). However, during this process, sulphate is gradually precipitated as a sparingly soluble basic sulphate, and it is possible that in marine environments the activity of sulphate reducing bacteria in the surrounding concretion prevents a fresh supply of sulphate reaching the metal surface. The main cause of the corrosion of marine iron appears therefore to be the chloride ion. The problem facing the conservator is the removal of chloride ion from the object and the ways in which this can be achieved depend on the nature of the chloride containing species present in excavated iron. The nature of these compounds, which result from the further reactions of ferrous chloride, depend on such variables as pH, oxygen concentration and temperature.

Chloride Containing Species in Marine Iron

Although the solution at the metal surface is generally agreed to be a solution of ferrous chloride, the identity of the solid iron corrosion products has been the subject of much discussion (14)(15)(16) in the literature of conservation. Initially it was thought that sodium chloride would be a major component, but this simplistic view has rapidly been dispelled and the absence of this compound explains the lack of success of simple washing procedures for the stabilisation of marine iron. In view of the current flow prevailing in corroding iron this is not surprising as although chloride ions may migrate to the anodic (iron metal) surface, sodium cations would be expected to move in the reverse direction, towards the cathode. Ferric chloride has also been commonly stated to be a major component. However, as Gilberg and Seeley (15) and Turgoose (17), state, ferric chloride is unstable and hydrolyses readily to form FeO.0H. Ferric oxochloride FeOCI was stated by North and Pearson (14) to be the major chloride containing species in marine iron corrosion products, and it was on this assumption that the alkaline sulphite reduction process was proposed.

The Alkaline Sulphite Reduction Treatment of Marine Iron

The original aim of the alkaline sulphite treatment was to promote the release of chloride ions held in ferric oxochloride. Before this method was conceived, only two methods for the treatment of marine iron were widely used; electrolysis in sodium hydroxide or high temperature hydrogen reduction. Both suffered from severe disadvantages: hydrogen reduction alters the metallographic structure of the metal and thus destroys technological evidence, whilst electrolysis, when applied to porous cast iron, or wrought iron with little remaining core often resulted in the destruction of surface detail or disintegration of the object, due to the evolution of hydrogen. Electrolysis was also inefficient as much of the current was wasted in the generation of hydrogen and little was used in removing chloride from the object. As a result treatment times were very long.

North and Pearson (1) demonstrated a rapid and efficient release of chlorides from objects immersed in a solution containing 0.5M Na₂SO₃ and 0.5M NaOH in sealed containers (to prevent oxidation of
Na$_2$SO$_4$ by oxygen) at a temperature of 70°C. They stated that complete conversion of the iron corrosion compounds to magnetite occurred. It was found that when corroded iron objects were placed in hot caustic solution, the corrosion products were transformed to a red flocculent precipitate, said to be Fe$_3$O$_4$, nH$_2$O. The formation of this precipitate could be prevented by the addition of a reducing agent or by imposing an external EMF on the iron as in electrolysis. The efficiency of the method was ascribed to the efficient hydrolysis of FeOCl by the alkaline conditions, and to the production of magnetite Fe$_3$O$_4$ as an end product rather than Fe$_2$O$_3$, nH$_2$O. This magnetite is a relatively dense material and thus the permeability of the corroded layer was increased, allowing better penetration of the alkali and so more efficient chloride ion extraction. North and Pearson also stated that the production of magnetite rather than Fe$_2$O$_3$, nH$_2$O reduced the tendency for chloride ions to be trapped in the crystal lattice of the corrosion products, although the magnetite could absorb chloride ions if these were present at high concentrations.

During the course of treatment, chloride levels in the wash solution were monitored until no further release of chloride was detected. At this stage the objects were "removed and washed, at room temperature, in successively, deionised water (twice) 0.1M Ba(OH)$_2$, deionised water, acetone and then allowed to dry". (1).

Application of the Alkaline Sulphite Process to the Dartmouth Cannonballs.

The total number of objects treated in this project was 123. This included 9 grenades (many incomplete) and two casting sprues. Initially all the objects were individually numbered, however, over the course of treatment many became separated from their numbers. All were measured and weighed before being placed in the hot (60°C) alkaline sulphite solution. However, as many still had a thick covering of concretion the value of these measurements is doubtful. The presence of this concretion on many of the objects also precludes any assessment of their condition before treatment. However it does seem that they varied widely in condition; many after treatment appear almost perfect apart from casting flaws, and on the majority the flash line produced during the sand casting of these objects remains perfectly visible, and many show the broad arrow or phaeon.

Fig.1. Cannonball from H.M.S. Dartmouth showing casting marks and ordnance mark.
The extent of corrosion may be gauged from the photograph of the one cannonball, I hesitate to say sectioned, rather cut up. It does at least serve to show the depth of the corrosion layer.

Fig. 2. Sectioned cannonball, showing depth of corroded layer.

It is interesting to note that the corrosion has penetrated to the very centre of the casting: also numerous fine cracks are apparent through the body of the metal. The centre of the cannonball would be the last part to solidify and because of shrinkage, the metal in this region would be expected to be under stress. This would tend to make it anodic, since the energy required to break the deformed bonds in this region would be less. If a corrosive medium could penetrate to this region (or indeed any electrolyte solution) then it would be expected to corrode preferentially. The porous nature of low grade iron castings and the fine cracks observable in this specimen should allow such penetration. The expansion of corrosion products at the centre and within the cracks can lead to splitting and cracking of such objects in the absence of proper conservation treatment. Exfoliation of the corrosion crust from the surface may also occur, for the same reason, resulting in the loss of all the surface detail and the shape of the object. The photograph below shows the remains of a cannonball which has been air dried. The rough irregular surface indicates the exfoliation of the surface oxide crust, whilst the corrosion associated with the central stressed area and the splitting of the shot along the hairline cracks can also be observed. The elongated cavity at the centre is due to shrinkage as the metal has cooled and solidified.
Fig. 3. Part of an air-dried cannonball.

In general, the process of corrosion in the case of the Dartmouth cannonballs has produced a compact layer of corrosion on the surface similar to that shown in Figure 2. The depth of the layer varies: in some cases it is only of the order of one millimetre thick, in other cases of the order of a centimetre, as in Figure 2. A second type of corrosion is evident in a few cases. Here large pockets of yellow-brown corrosion product occur, which may cover large areas. The variation in the amount of corrosion may be gauged by a comparison of the weights of several cannonballs of the same diameter, although of course some of the variability will be due to difference in their cast weights. The surface of some shot showed only slight pitting with no thick oxide layer, whereas others showed a smooth oxide layer containing the surface detail. The incidence of these forms is indicated in Table 1.
<table>
<thead>
<tr>
<th>Shot No.</th>
<th>Diameter, mm</th>
<th>Weight, gms</th>
<th>% Nominal weight(5)</th>
<th>Surface condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>84</td>
<td>985</td>
<td>36.2</td>
<td>smooth; 5% lost</td>
</tr>
<tr>
<td>15</td>
<td>86</td>
<td>1210</td>
<td>44.5</td>
<td>smooth; 15% lost</td>
</tr>
<tr>
<td>25</td>
<td>86</td>
<td>1050</td>
<td>38.6</td>
<td>pitted</td>
</tr>
<tr>
<td>26</td>
<td>86</td>
<td>1640</td>
<td>60.3</td>
<td>very pitted</td>
</tr>
<tr>
<td>30</td>
<td>86</td>
<td>1845</td>
<td>67.8</td>
<td>smooth; complete</td>
</tr>
<tr>
<td>32</td>
<td>85</td>
<td>960</td>
<td>35.3</td>
<td>smooth; 10% lost</td>
</tr>
<tr>
<td>36</td>
<td>86</td>
<td>1590</td>
<td>58.5</td>
<td>smooth; 5% lost</td>
</tr>
<tr>
<td>39</td>
<td>84</td>
<td>1110</td>
<td>40.8</td>
<td>smooth; complete</td>
</tr>
<tr>
<td>70</td>
<td>85</td>
<td>1000</td>
<td>36.8</td>
<td>smooth; complete</td>
</tr>
<tr>
<td>72</td>
<td>86</td>
<td>1260</td>
<td>46.3</td>
<td>smooth; 5% lost</td>
</tr>
<tr>
<td>74</td>
<td>85</td>
<td>1465</td>
<td>53.9</td>
<td>pitted; 5% lost</td>
</tr>
<tr>
<td>77</td>
<td>85</td>
<td>1810</td>
<td>66.5</td>
<td>smooth; complete</td>
</tr>
<tr>
<td>78</td>
<td>84</td>
<td>1330</td>
<td>48.9</td>
<td>smooth; 5% lost</td>
</tr>
<tr>
<td>80</td>
<td>87</td>
<td>1265</td>
<td>46.5</td>
<td>smooth; complete</td>
</tr>
<tr>
<td>108</td>
<td>86</td>
<td>1665</td>
<td>61.2</td>
<td>smooth; 10% lost</td>
</tr>
<tr>
<td>116</td>
<td>86</td>
<td>1390</td>
<td>51.1</td>
<td>smooth; complete</td>
</tr>
</tbody>
</table>

In fact, the nominal original weight is probably an overestimate. The density of cast iron varies between 7050 and 7700 Kg/m³, (Scholes,18); for a diameter of 86mm this would produce an initial weight of between 2.3 to 2.6 Kg. making a difference of at the most 10% in the figures given above for the percentage of original weight remaining. Figures for other diameter cannon-balls are roughly similar.

Fig 4 Weight distribution of Dartmouth cannon balls as percentage of nominal original weights(5)
However, larger cannonballs have retained a greater proportion of their original weight, averaging 56.1% for 102mm and 52.8 for 86mm cannonballs for example. This represents a large amount of corrosion in any terms. The original weight of an object, and its shape, should be considered when choosing an appropriate conservation method, as to some extent this will determine the structural strength remaining in an object; round objects will tend to be more sound than thin sectioned objects of equal weight; and for objects of similar shape, larger objects will tend to be more sound than small ones. The Dartmouth grenades are a case in point: they are much more extensively corroded than the much thicker sectioned cannonballs, and in some cases virtually no metal remains. A similar situation is reported by Patoharju (19) for cannonballs and grenades from sites in the Baltic.

Unfortunately, as the cannonballs from H.M.S. Dartmouth were placed in the alkaline sulphite bath in many cases without removing the concretion, several grenades, some with fuses, underwent the process along with the round shot. This could have been avoided if all the objects had been X-rayed; however the reasons for not X-raying what probably purported to be 123 cannonballs are easily understood! Removal of the concretion would have been the appropriate action; apart from revealing what lay beneath the concretion, it would have speeded up the process of chloride removal. The removal of concretion without allowing oxidation of the corrosion products presents difficulties of a practical nature, especially if the concretion is very tenacious, a not uncommon situation. The Cavitron, a small ultrasonic probe originally used for cleaning teeth, may provide an answer in such cases, though there is always the danger of damaging the corroded layer underneath.

The alkaline sulphite treatment should ideally be carried out in sealed, oxygen-free containers, as otherwise the sulphite rapidly oxidises to form sulphate. The Dartmouth material was treated in one large high density polyethylene tank with a not particularly closely fitting lid. The hydrocarbons found in marine iron and its associated concretions (North, 6) may account for the relative success of this equipment, as North found a lower oxygen content in NaOH solutions in which deconcreted marine iron had been stored for long periods, due to the formation of a thin surface film. Although North ascribes the formation of these hydrocarbons to the reduction of cementite; by reactions such as:

\[
\text{Fe}_3\text{C} + 2\text{H}^+ + 2e^- \rightarrow 3 \text{Fe} + (-\text{CH}_2\text{)}
\]

\[
\text{Fe}_3\text{C} + 2\text{H}^+ + (-\text{CH}_2\text{)} + 2e^- \rightarrow 3\text{Fe} + (-\text{CH}_2\text{-CH}_2\text{-})\text{etc.}
\]

and indeed distilled such hydrocarbons (mainly C₈, C₉ and C₁₀) from deconcreted specimens, one would expect a good deal of such material to occur in the concretion itself (by diffusion from the source of production) and it may be that the presence in the alkaline sulphite tank of large quantities of concretion and marine iron provided a hydrocarbon layer sufficient to make good the deficiency of the lid. This may all sound a bit far fetched; however the N.M.A.S. conservation and research staff will not easily forget the characteristic smell of marine cannonballs, which North ascribes to these very hydrocarbons. However,
in view of the importance of maintaining reducing conditions (a point which will be made later) an air-tight lid with a controllable vent is an essential piece of equipment.

The removal of chloride ions from the ammunition into the alkaline sulphite solution was monitored using a Corning chloride meter, (originally designed for medical and industrial use), which measures total amounts of chloride in a given sample by electrolysis, and is accurate to ±5ppm within the range 10-400ppm; it is not very useful for determining the absence of chloride and the silver nitrate test (24) was used for that purpose. Alkaline sulphite samples require neutralisation with dilute sulphuric acid (AR grade) and oxidation with hydrogen peroxide prior to measurement of chloride levels by the Corning meter.

Periodically, the alkaline sulphite solution was exchanged for a fresh solution. The cumulative total of chloride ion removed as a function of time is shown in Figure 5 for each of the wash solutions.

Fig. 5. Chloride removal from cast iron in alkaline sulphite solution.
As can be seen, the rate of chloride extraction varies from time to time. This is a common feature of alkaline sulphite chloride extraction and is thought to represent the penetration and release of deep seated pockets of chloride containing compounds in pockets from which the alkaline sulphite solution has previously been excluded due to the impermeable nature of the corrosion layer. Such fluctuations are also found in other methods, such as electrolysis. The time taken to reduce the chloride level in the solution to an acceptably low figure was one year and six months. Presumably if the objects had had their concretion removed the time would have been considerably reduced.

Cannonballs were removed from the alkaline sulphite solution and subjected to a finishing treatment (see below) at the points marked A, B and C in Figure 5. Those removed at point A resulted, not surprisingly, in disaster: the chloride levels remaining were more than sufficient to ensure the renewed onslaught of corrosion. Two cannonballs were removed at point B and finished by boiling in deionised water (for several changes) after precipitation of sulphate with barium hydroxide, followed by drying through a series of acetone baths. These two have survived very well, although both managed to gain a considerable amount of weight during treatment (17.9% and 4.9%).

The remaining cannonballs were removed in batches from point C onwards. The first batch were treated in the following manner:

(a) rinsed in deionised water (30 minutes)
(b) rinsed in 0.1M Ba(OH)₂ (30 minutes)
(c) rinsed in deionised water, cold (30 minutes)
(d) washed several times in boiling deionised water.

This reduced the chloride levels in the wash water to 4ppm Cl⁻. They were then dehydrated in 3 baths of acetone, of 2 months 2 weeks and 2 weeks duration. Finally they were removed, air dried, oven dried at 80°C, and coated with microcrystalline wax dissolved in toluene, which gives a pleasant matt black appearance. The cannonballs treated in this manner consistently lost weight during treatment: the figures were 9.5%, 10.0%, 6.2%, 2.5% and 10.1%.

On humid days in the laboratory it was noticeable that these cannonballs had a tendency to 'bloom': a white deposit would suddenly appear on the surface, despite the wax coating. The reasonable assumption was that this was sodium carbonate (derived from the reaction of carbon dioxide with sodium hydroxide from the alkaline sulphite solution, or sodium sulphate. The method described by North and Pearson for the removal and/or fixation of these salts after the alkaline sulphate treatment certainly seems rather brief. If the removal of chloride ions is a diffusion controlled process, and it requires one and a half years of immersion to achieve elimination, one would expect that removal of the treatment solution (which should also be diffusion controlled) would take a similar length of time. North and Pearson have attempted to avoid this problem by using barium hydroxide to precipitate the potentially harmful sulphate (20), however, the method as described will almost certainly not achieve this aim: precipitation with barium hydroxide should
probably be allowed to occur over a very much longer period than they appear to suggest, although it must be pointed out that they do not mention any time span for the process.

As a result of the problem encountered with this salt crystallisation, the next series of batches were subjected to extensive washing in boiling deonised water prior to an extended precipitation period, followed by further washes in boiling deonised water, in an effort to reduce the amount of alkaline sulphate contamination and to improve the fixation of the material not removed.

The problem here is that as one removes the sulphate one also removes the alkali and rusting of the object may occur, unless steps are taken to prevent this e.g. exclusion of oxygen or the use of another inhibitor. In this particular instance, it was felt that exclusion of oxygen was the better alternative and this was achieved by floating a layer of paraffin wax on the surface of the (warm) wash water after it had been boiled to remove any oxygen it contained. Removal of electrolytes such as sulphate, sulphite, or alkali was monitored by the use of a conductivity bridge. Some typical results are shown below. The conductivity of the deonised water was around 2 μmhos/cm.

![Graph](image)

**Fig 6** Removal of alkaline sulphite solution
It was found that, after precipitation with barium hydroxide solution it was very difficult, if not impossible, to reduce the conductivity of the wash below about $3 \times 10^2 \text{Mhos/cm}$, and washing was discontinued as it was feared that at the low pH reached at this stage (about pH8) the material could be at risk, although efforts were made to exclude oxygen from the solution.

This more rigorous procedure did reduce the incidence of salt crystallisation, but did not completely prevent it, even though the cannonballs were all impregnated with molten wax after dehydration in acetone, rather than having a wax solution brushed on to the surface as before. The long term effects of this problem will have to be evaluated periodically in the future.

However, despite this problem, the alkaline sulphite process could be considered successful. Apart from the cannonballs which were removed before a sufficient extraction of chloride had occurred, all survived the treatment. Storage in a low humidity environment should ensure their long term future. Some of the conserved material appears in the photograph below.

![Completed cannonballs from H.M.S. Dartmouth.](image)

The several grenades however were not so successful. A few of these contained the remains of their charges; a similar material was analysed by Pearson (8) and found to be 42-65\%C, 2.7-3.6\%S, the remainder being iron corrosion products and the potassium nitrate having dissolved away. The corroded state of the shells has so far prevented metallographic analysis. Most of these grenades treated with powder inside have cracked. This is probably due to the thin section of the shell and the general lack of strength and cohesion, rather than any swelling of the contents, which if anything have shrunk away from the shells. Cracking may also have been caused by the evolution of hydrogen reported to occur when marine iron is placed in alkaline sulphite solution (21) although as I was not present at the time of immersion I cannot say whether this did in fact occur. However, if hydrogen
is released then such cracking may well result either because of the pressure built up within cavities or by the process of hydrogen embrittlement if the hydrogen diffuses into the metal.

Fig. 8. Conserved grenades from H.M.S. Dartmouth.

Discussion.

The alkaline sulphite treatment has largely replaced the process of electrolysis as a method for the conservation of marine iron. It has here been successfully applied to some cast iron cannonballs and not so successfully to several grenades. One of the major reasons for discarding the electrolytic process was that the evolution of hydrogen caused the disintegration of porous cast iron objects or the exfoliation of oxide layers. However, it seems that such effects may also occur with alkaline sulphite, though not of so long a duration. The theoretical basis for the alkaline sulphite method has recently been questioned, as it is no longer felt that FeOCl is the major chloride containing species (15),(22). The alkaline sulphite treatment does however still seem to work, and the findings of North and Pearson that the process of chloride removal in the solution are diffusion controlled still stand, as they performed experiments both with FeOCl and with powdered corrosion products. The effect of the reducing agent, sodium sulphite has also been questioned by Gilberg and Seeley (21) who felt it is not a strong enough reducing agent to effect the solid state reduction of ferric compounds found in marine iron to magnetite; and, in the case of iron, from terrestrial sites found no evidence for the formation of magnetite. They explain the success of the alkaline sulphite treatment for marine iron as being primarily due to the reducing conditions prevailing within marine iron which has not been exposed to the air, and the resulting reactions of free ferrous ions under de-aerated conditions at alkaline pH which produce magnetite, a stable, chloride free iron oxide. In oxidised iron corrosion products, chloride ions may be trapped
in species such as \( \Delta FeO.OH \) and \( \beta FeO.OH \) from which it may not be completely removed by washing, but from which continued corrosion may occur. They stress the importance of not allowing the objects to undergo oxidation prior to treatment as this generally precludes successful treatment.

In this particular case, the fact that the concretions were not removed before treatment probably aided the success of the project though it also extended the duration. The difficulties associated with the use of alkaline sulphite solution on site for the storage of iron objects are touched upon by Bryce (23), as the solution may damage inlays, organic material, or textile impressions. Perhaps the best solution is to maintain the objects within their concretions in deoxygenated sea water until they can be assessed in the laboratory for example, by X-radiography.

A major problem in the alkaline sulphite treatment, however, is the removal of the solution at the end of the process: at least as much care and consideration should be given to this aspect of the process as to the extraction of chlorides, as the sulphates which may be retained are potentially dangerous to the objects. Another major problem is the evolution of hydrogen, which may cause cracking of highly deteriorated objects or the exfoliation of non coherent scale.

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Identification of Dyes on Museum Textiles

H.E. Dalrymple

Unless causing conservation problems such as fading or running, the colour and hence the dye on a museum textile is often taken for granted: it can however, when analysis is allowed, give important information about the textile's date and place of origin. There is an abundance of historical references to the manufacture and application of dyes from Early Egyptian times up to the present day. They had periods of going in and out of fashion and invariably any new dye was treated with great suspicion, especially when it was imported and competed with a similar coloured, home-produced dye. For example, in 1577, because of the dangers to their own businesses, the English growers of Woad denounced the higher yielding imported Indigo as a "newly invented, harmful, boldely devouring, pernicious, deceitful, eating and corrosive dye" (1). Dye usage was also controlled by discovery and/or invasion of new lands as dyestuffs producing vivid and unusual shades were considered to be valuable trophies with which to return home.

One of the most important discoveries in the history of dyes was in 1856 when William Henry Perkin attempted, quite unsuccessfully, to prepare quinine from allyl-toluidine using sulphuric acid and potassium dichromate. When this did not yield his desired product he repeated the reaction using aniline as his starting material. Again, no quinine, but the black sludge obtained imparted a purple colour in solution. At this stage, he forgot about his quinine and, for some unknown reason thought about using this purple solution to dye silk. He had in fact produced the very first aniline dye which became, commercially, a great success. The dye chemists who, for the previous hundred years or so had concentrated on improving methods of dye application were now hot on the heels of Perkin and his new dye, Mauvien, and so commenced the era of the synthetic dyes which soon almost completely replaced the natural dyes.

Our work on the identification of dyes was started in June, 1980 by Nicole Descoults, a French student, who experimented with the numerous methods available. The main part of her time was devoted to extraction of the dye from the fibre and identification using Thin Layer Chromatography (T.L.C.). Many solvent/eluant combinations were tried but with limited success basically due to the type of stationary phase used. The plates were silica gel 60F254, precoated on aluminium sheets, which afford little separation for natural dyes though they are quite useful for some of the synthetic dyes. Most workers in this field suggest using a polyamide or acetylated cellulose stationary phase but for trial and error tests for suitable solvents these would have made it a rather expensive project. Nicole also experimented with solvent distribution methods: they are now the basis of our methods of identification and are used in conjunction with U.V./visible spectrophotometry.

The work has progressed involving a good deal of research through technical books and papers on the subject and with help from
other workers interested in the identification of dyes such as Judith Hofenk de Graaff of the Central Research Laboratory for Objects of Art and Science, Amsterdam, Doctors Duff and Sinclair of Paisley Technical College and Professor Whiting of Bristol University. The methods used by these people are all similar but Professor Whiting has done more to "refine" them and my work is based very much on his ideas (2).

Emphasis is mainly on the natural dyes and the initial problem in this field is finding a source of these dyestuffs, e.g. Lac, Madder etc., in order to test available methods and to develop new and more accurate ways of identification. Another problem is that the methods of applying dyes varied through the ages and from one country to another. This is most apparent with the dye Indigotin (from Woad or Indigo plant) for which numerous recipes are listed in various books. For most of these recipes, Indigotin was used as a vat dye being first reduced to its leuco form (yellow anion) for application to the textile and then oxidised in light and air to its blue colour. Using concentrated sulphuric acid, Indigotin was rendered water soluble and the dyed fabric did not require the usual long air exposure treatment to re-oxidise the dyestuff. It was easy to apply to the textile but unfortunately it was just as easy to remove it by washing.

What the dyers of the time did not realise was that they were pioneering a class of dyes known as the Sulphonated Dyes, by slightly altering the chemical structure of Indigotin to produce Indigodisulphonic Acid and therefore its method of attachment to the textile. This problem of the dye component being changed in the final product i.e. the dyed textile, has meant that standard samples have to be dyed in the laboratory, using various recipes and mordants: the dyes are extracted from these standards to use as comparisons in the identification methods.

For the solution spectrophotometry we have recently purchased a Pye Unicam SP7-500 U.V./Visible Spectrophotometer which is connected to an existing Philips PM8141 X-Y recorder. It is a double beam, scanning instrument with microprocessor control and its features include signal averaging, derivative mode scanning, baseline correction and a scale range for absorbance of -0.3A to +3.000, all of which can be necessary when dealing with small volumes of very dilute samples. The method is simple and straightforward having just two main requirements: the dye must be extractable from the fibre into a suitable solvent producing a non-turbid solution: secondly, a library of standard reference spectra must be compiled to facilitate reliable positive identifications.

Examples of Dye Identification

Indigotin and Cochineal are the dyes which have been found most frequently in the range of textiles made available for analysis: As an example, they were the two dyes to be positively identified on the Strathmore Carpet (Lab. No. 5726) and it is almost certain that either one or both will be found on multicolour textiles such as samplers and costumes. Indigotin's popularity was because of its excellent light and wash fastness and also because of its availability: over fifty different types of plant contain Indigotin and it can therefore be found on textiles with a range of origins. It had little competition because, depending on the geographical location, there were few alternative blue dyes. Cochineal has been popular in European
countries since the early sixteenth century when introduced by
the Spanish, who imported the dyestuff from South America. It
is interesting that Professor Whiting finds Madder to be the
commonest of red dyes (2) but it should be noted that he is
examining textiles from the Middle East and my samples are from
North European sources. However, I have not identified so many
dyes to be certain that this difference in dye popularity is
completely true.

Indigotin can be removed from the fibre with aqueous pyridene:
extraction of this solution with dichloromethane produces a
blue organic layer which can be run on the spectrophotometer
giving a curve of maximum absorption at 600nm. Green threads
as found on Sampler No. R.I. 18 (Lab. No. 6170) were often
produced by first dyeing with a yellow followed by overdyeing
with blue, usually Indigotin and the presence of the latter can
be detected in the same manner as for 'pure' Indigotin.

Not all blues and greens are Indigotin. The blue colour of a
ribbon on a basket hilt sword, No. 74, from Drummond Castle
could not be extracted using aqueous pyridene: this was the
first indication that the dye was not Indigotin. Chemical spot
tests indicated that it was Prussian Blue, a mineral colour -
ferric ferrous cyanide - discovered by Diesbach in 1704, though
it was not until the middle of the eighteenth century that it
was used on a large scale. Thin layer chromatography on silica
gel, with acetone/acetonylacetone, 90:10, as eluant confirmed
this result.

Another example when tests for Indigotin gave negative results
was Lab. No. 6575, a nineteenth century printed dress. The
samples taken for identification were two green silks, A and
B, and a blue cotton, C. Spot tests and chromatography gave
the following results:

Fibre A An azo blue + a yellow dye.
  B A triphenylmethane dye e.g. Malachite Green.
  C A triphenylmethane dye e.g. an Alkali or
     Soluble Blue.

The presence of these dyes suggests a date of, at the earliest,
the mid 1870's which is a later date than that represented by
the style of the dress.

The identification of yellows, (and associated browns and blacks)
has not been undertaken: these colours are derived from a great
many plants and if they could be distinguished, could furnish
greater detail of the origin of the textiles. However, a number
of the dye components are common to more than one plant and
methods of separation and purification on small samples have to
be developed more fully before these plant sources can be identi-
fied by way of their minor constituents.

This article has outlined the methods which we are now using for
dye analysis on museum textiles, with illustrative examples
from some of the samples examined. Analyses so far have mainly concentrated on identification and characterisation of dyes from textiles currently being worked on in the museum. We aim to extend the work by concentrating on the dyes found in dated samplers in the museum collection. We hope that it will then be possible to compare results from groups of thread of similar type and colour, thereby building up information about the use and distribution of specific dyes at specific periods.

References


Silver Analyses by X-Ray Fluorescence

J. Tate

In the first laboratory booklet the new apparatus for X-ray fluorescence analysis was described for qualitative use. Since then it has been improved by the acquisition of an X-ray tube for primary excitation of fluorescence radiation from the sample in place of a radioactive source. This gives considerably greater ease of use and safety, allowing for more precise analyses. In addition the system has been made quantitative by the use of a fundamental parameters data reduction routine in the microprocessor.

Analysis of silver from the museum collection started using this equipment with a study of a group of 14th century silver groats. Several problems arose from this work, the most serious resulting from the thinness of the coins and the consequent difficulty in making the XRF measurements on the coin edges. For this reason the project was suspended and attention turned to some Viking silver which did not present the same problem. The results of these analyses are reported elsewhere in this booklet and summarised with some more recent measurements at the end of this article.

Coin Analyses.

Analyses of Scottish silver coins are sparse (one of the few examples being Metcalf 1977) and the presence in the laboratories for cleaning of some one hundred and thirty 14th century silver coins from a hoard at Tranent provided a suitable chance to improve the situation. A programme of silver analysis was started at the National Museum of Antiquities of Scotland in the 1970s (McKerrell and Stevenson 1972) and it is intended to extend this work. For the experimental measurement of the major and minor constituents in such coins atomic absorption spectrometry is probably the best technique. However it requires several milligrams of material to be removed from each coin, this specimen being destroyed during the measurement. Most of the coins which had been cleaned were in good condition and sampling by drilling or similar destructive methods was not possible. In this situation X-ray fluorescence analysis was the obvious choice.

In principle analysis by XRF is totally non-destructive but as discussed below some abrasive cleaning of a small area of each coin was found to be necessary. It is difficult to measure accurately the proportion of minor or trace elements due to the weak signals which they emit above the background. In the first batch of coins it proved feasible to measure only the four elements copper, gold, lead and silver. Bismuth and tin probably both occur also but in amounts less than about 0.5%. A second difficulty with XRF is in establishing absolute percentages accurate to better than about one per cent because of the considerable amount of data manipulation and assumption made in the analysis.
Fig. 1. Schematic diagram of X-ray fluorescence apparatus

- Sample
- Light source
- Rh target side-window X-ray tube
- Amplifier, enhancer, N₂ level monit & H.V.
- Si(Li) detector & preamplifier
- Analogue to digital converter
- Disc storage
- X-Y plotter
- Printer
- 8K Canberra series 80 analyser
- Cromemco 64K microprocessor

0-49kV
0-1mA generator & timer
Experimental.

The equipment consists of a rhodium target side window X-ray tube and generator (Link systems) operated at a potential of 38kV and a tube current of 0.5mA. The X-rays from this tube are collimated to give an elliptical spot on the sample approximately 1mm by 2mm. The X-rays are incident at an angle of 45 degrees and fluorescence X-rays emitted perpendicular to the sample detected by a Si(Li) detector. (Supplied by Canberra instruments. It has a resolution of 159eV at 5.9keV and a 1 thou Be window.). In order to locate the exact position of the incident X-ray beam on the sample an optical fibre was arranged so as to shine light down the X-ray collimator, following exactly the same path as the X-rays and producing a spot of light on the object. The apparatus is shown schematically in figure 1.

Each spectrum was recorded for 600s into 2048 channels of an 8192 channel analyser (Canberra series 80). The spectra were then stored on disc by the Cromemco microprocessor. Integrals were obtained from the K peaks for copper and silver and from the L peaks for gold and lead, a linear background being extrapolated in each case, this being displayed on the analyser.

Elemental compositions were calculated from these integrals by a fundamental parameters programme which runs, in BASIC, on the microprocessor. The approach used by the programme is described by Cowell (1977) who kindly supplied a listing of the original programme. As initial input the programme requires the primary excitation spectrum of the X-ray tube and integrals from the spectra of pure elements or known standards. The primary spectrum was measured in a previous experiment with the X-ray beam attenuated through a pinhole in an aluminium block before directly reaching the detector. The X-ray tube and detector were enclosed in a plastic bag filled with helium and after correction for absorption in the usual air path and for non-uniform detector efficiency the resulting continuum was fitted to two cubic polynomials. From this, together with integrals from the characteristic peaks the programme can calculate the excitation spectrum at any energy. Integrals of the peaks from pure metal samples (also needed as initial input) were measured exactly as the samples but at a lower X-ray current.

Standards.

The problem of knowing the overall accuracy of the analyses has already been mentioned. In order to test the system and to be able to compare different groups of measurements, several copper/silver alloy standards were made by melting together known weights of pure metals. The standards were mounted, polished and analysed as if they were unknown. The agreement between the expected and the measured composition is indicated in figure 2. Weighing errors were thought to account for the two samples where the expected and measured compositions differed by more than 1% (number 3 by 1.1% and number 8 by 1.2%).
Fig. 2. Comparison of the composition of copper-silver standards from weight of components before melting (expected) and from XRF of the final alloy (measured).

Surface Enrichment.

The bulk of fluorescence X-rays used in this kind of analysis come from a maximum depth in the metal of about 50 microns for silver and 15 microns for copper (for comparison, the thickness of this paper is approximately 100 microns). Thus for the analysis to truly reflect the bulk composition of the metal it is important that the surface be clean and uncorroded and that no enrichment or depletion of elements has taken place during burial. Initially it was hoped that the cleaning (washing in ammonium thiosulphate solution followed by rinsing, drying and polishing) would have produced a suitable surface and several coins were examined on flat regions of the obverse and reverse. Unfortunately the results so obtained were inconsistent for most of the coins. Fig. 3 illustrates the change in silver percentages in scanning along the centre of one arm of the cross of coin 1. One reason for the variations is that the surface is not absolutely flat - dents and bumps have the effect of altering the incidence and take-off angles away from the values of 45 and 90 degrees assumed by the programme. A second reason is that during burial the less 'noble' elements, in particular copper, corroded more rapidly than the silver, leaving a silver rich surface layer. To study this it was necessary to measure the copper/silver ratio, remove a thin surface layer, remeasure the ratio and repeat the procedure. Once all the corroded layers have been removed a constant copper/silver ratio should result.
Fig. 3. Variation in measured silver composition across the reverse of a coin.

Since abrasion of the faces of the coins was clearly undesirable the coins were mounted flat in a modified microscope stage and positioned so that a flat region of the edge was irradiated by the X-ray beam. A spectrum was recorded, the elemental proportions calculated and the relevant area of the edge then gently abraded with 600 grade emery paper wetted with acetone. The process was repeated until a constant composition was obtained, as indicated in Figure 4.
Fig. 4. Change in composition following surface abrasion.

This procedure was adopted for all the coins analysed and has now become a routine procedure where any metal object is analysed quantitatively. Graphs similar to the above were plotted for gold enrichment in the Bronze Age gold analyses reported elsewhere in this publication.
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<td>0.5</td>
<td>1.0</td>
<td>96.0</td>
</tr>
</tbody>
</table>

Table 1. Elemental composition of some 'silver' groats.

Discussion.

The results for 26 groats presented in Table 1. indicate that compositional differences are small over the periods that these were minted. In order to draw any positive conclusions it is clearly necessary (1) to analyse considerably more coins and (2) to be sure that the experimental uncertainty on each measurement is as small as possible, to know that the differences between coins are real and not due to measurement errors, caused, for example, by inhomogeneities in the alloy.

It was this latter which brought the series of analyses to a temporary halt, particularly the feature illustrated in figure 3, i.e. the discrepancy between the silver content found directly from the face of coins and the final results from the edges. We would expect corrosion effects to make the former too high in silver: in fact a lower value was obtained for coin 1. The experiment illustrated in Figure 4 shows that it is indeed silver which is enriched on the surface and if this occurs at the edges it is hard to see how the situation could differ on the faces, except perhaps by alloy movement as the coins were stamped. An
alternative explanation is that the diameter of the X-ray beam was greater than, or equal to, the thickness of the coin. When this was the case, cleaning away the corrosion surface from the edge would not have been sufficient - a proportion of the spectrum coming from the silver enriched upper and lower faces excited by the edges of the X-ray beam would always remain, thus causing the final analysis to be too high in silver. Since the only way around this problem is either to reduce the size of the incident X-ray beam or else to make the measurements on the face rather than the edge of the coin - neither of which were possible - further coins were not analysed.

The 'Aldcliffe Brooch'

This Pictish pennanular brooch has a body made of a silver-copper alloy with gilded decoration. It was analysed to investigate the nature of the gilding and various other features which are discussed in a forthcoming paper by Dr. Stevenson (Stevenson 1984). The metal of the brooch and its pin were analysed by the techniques described above and shown both to be silver alloyed with copper and tin, there being considerably more tin in the pin than the brooch, perhaps to make it stiffer. However, when a broken end of the pin was examined the central core could be seen to be yellow, and on analysis shown to have a far higher copper content, approaching 30% copper as opposed to 6% at the surface. This is shown in the photograph (Figure 5) where the region depleted in the copper rich phase can be seen to be nearly 0.5mm thick, the pin itself having a cross-section of 3 by 1.5mm. In this case the degree of enrichment seems too great to have occurred naturally during burial, so we must conclude that the pin was deliberately pickled or otherwise treated to give it a silvery finish. Whether this was an early fraud or simply a technique to make a replacement pin match the brooch we do not know.

![Image of the brooch and its cross-section](image_url)

**Fig. 5.** (a) the Pictish brooch from Aldcliffe and (b) cross section of the broken end of the pin showing the copper-rich central core.
Fig 6. Summary of Viking Silver analyses

- Terminal of IL3
- Hoop of IL3
- Pin head possibly from IL3
- Brooch pin (6628)
Viking Silver.

Since the ring money and 'hack silver' analyses reported elsewhere in this publication were completed, three other pieces of Viking silver from Skail have been examined. These were a large penannular ring-brooch from the Museum (Catalogue IL3) and two recently acquired objects, a complete pin from a somewhat smaller brooch and a pin head from a brooch very similar to IL3 or perhaps even belonging to it (Graham Campbell 1984). The analytical results are shown in the histograms of Figure 6 where it may be seen that the compositions are indeed very close, and fall well into the ranges expected for objects from the Skail hoard. The diagrams in Figure 6 illustrate clearly the separation in compositions between silver from the two major Viking hoards of Skail and Burra: we are currently working on other objects from these hoards and elsewhere to see just how many of the pieces show such remarkable differences in minor element composition.

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Country Life Conservation

Colin Hendry

The collections kept by the Scottish Country Life Section of the National Museum of Antiquities of Scotland cover all aspects of rural life. There is an emphasis on agricultural equipment as might be expected but other categories such as domestic furniture, kitchen ware, building materials, light and personal transport, and local trading are also included. Crafts and trades like joinery, plumbing, blacksmithing, leatherworking and saddlery all have their place in the extensive stores. As one can imagine, such a diversity of material requires various methods of conservation. Not only because the objects are collected in extremes of condition - some are near mint while others require total rebuilding - but so many different types of metal, wood and fabric are encountered.

The Country Life Section as such was started in 1959 by Dr. Alexander Penton, now Director of the National Museum, although articles of rural interest had been collected by the Museum for many years previous. However, since 1959 the section has grown by leaps and bounds, annually exhibiting its wares at the Royal Highland Show, Ingliston. Until 1977 the exhibition was housed in a large marquee which was erected only days prior to the show opening. This allowed for only superficial cleaning and repairs to be performed, frequently culminating in a scramble on the night before the first day of the show. These days are fortunately in the past now for the permanent building - the Agricultural Museum enables objects to be treated year round and leaves staff only harpered with display headaches when RHS time comes around in June. The Museum at Ingliston is not merely an exhibition hall. Workshops in the rear of the building facilitate extensive repairs to the largest of objects in the

Fig.1. Conservation - 1974 style, outside and in front of the agricultural museum marquee only days prior to the Royal Highland Show, Ingliston.

A roadscaper being de-rusted.
collections. From the loading bank, objects pass through an entrance fitted with a roller door, high enough for a combine harvester, into a work area with inspection pit and all the paraphernalia of an industrial engineering works. To one side off this work area is situated the timber workshop complete with all that this entails – lathe, bandsaw, circular saw, planer, etc. To take full advantage of these facilities, the Country Life Section increased its staff by employing a joiner and a blacksmith/engineer. Both are now thoroughly established and have proved of great benefit to the upkeep of the collections. Where they have excelled is in the area of extensive repairs as when new staves for a cartwheel are required or a new casting for a farm tractor.

One task in particular carried out recently epitomises just what can be done with such facilities on hand. The Museum was fortunate enough to acquire a Mill van, a caravan used as living quarters by the workers of a travelling threshing mill. The only trouble was it had suffered terribly from years of constant exposure to the elements and was in dire need of a complete renovation. In cases of this sort, one has to balance 'conservation' against 'restoration', always a topic of controversy. However, it was very evident from the start that large areas would have to be renewed and so it was decided to undertake a massive project to return the van to 'good used condition'.

The renovation took three months in early 1981 and began with the removal of all the rotten outside lining boards and waterproofing felt. Some of the main bearers were also affected and had to have the damaged parts removed. New parts were then spliced in after first being red leaded. The remainder of the van was given a thorough clean and sprayed with four coats of 'Wykamol' anti-infestation fluid. After new wall felt was fitted between the internal and external panelling, new lining boards were made and slotted in place by feather and groove attachments. A small area of good original panelling was taken from the sides and used on the back and front which blended in better with the existing timbers at these parts. The outside walls were then finished by painting on three coats of red lead, one undercoat and two gloss finishes in the original plum colour.
Fig. 2. The Mill van as recovered from Dalkeith showing the extent of the deterioration.

Fig. 3. With the outer panelling and felt removed, new main bearers were spliced in after being red leaded. These show up lighter in the photograph.
Attention was now changed to the inside where all the old flaking paint was removed with 'Nitromors' paint stripper, and a couple of lining boards and half a metre of flooring replaced. A new sash for one of the two small windows also had to be made. Painting required two undercoats and two gloss top coats this time in colours brown and green. The roof was in exceptionally good condition and needed only to be brushed down before its roofing felt was treated with two coats of 'Mighty-plate' bitumen finish. The drip-plates at the sides, however, had to be replaced. The door was in two parts like a stable door and a new frame was made for the top half. A new set of steps were made of wood for the door - the original was not available with the van. Other external parts such as the paraffin tank, tool box and tail lamp were cleaned and repainted. The registration plate was re-painted as were the original owner's plate, 'Derry Baird, Dalkeith', and the 'T' for Trailer symbol on the back wall. Three panes of glass were replaced in the small quartered windows and the cast iron stove cleaned and repaired. The original slots and webbing for the beds were intact. One interesting point was kept whilst refurbishing the outer walls - a patch repair had been made to the right hand side at some time during the working life utilising a pair of old doors. One of these unfortunately was too badly worm eaten for restoration but the other was returned into place after surrounding panels had been repaired. After new tyres and tubes had been fitted the van was once again in totally usable condition.

Erratum.
The fourth sentence of page 38 should read:
'Being in working order the internal machinery was found to be still in good condition, perhaps due to an abundance of oil which had continuously issued forth drop by drop into a drip tray for all of its static years in the Museum store.'
Not all large scale restoration can be performed at Inglis for reasons of either lack of time, space or specialised equipment. Such was the case for an 'international' tractor of 1919 vintage. This particular item had been in the collection for many years and after actually being driven into store from its transport, had lain virtually without maintenance treatment until only recently. Being perhaps due to an abundance of oil which continuously issued forth drop by drop into a drip tray for all of its static years in the Museum store. Externally, also, it was in quite reasonable condition. However it was evident that to preserve the tractor, the metal work was to require considerable attention in the not too distant future. The paintwork and 'International Harvester' transfers were found not to be original so their retention was not important. The first stage was to dismantle it down to basic components and this was completed by the Museum's engineer. Soon after this problems arose as to where the rather large and awkward items could be kept until time was found to commence restoration. A complete tractor is invariably easier to store than various wheels, engine, gearbox, rods, axles, cowlings etc! In every nook and cranny of the workshop could be found parts of the unfortunate 1919 International - a pitiful sight indeed. Deliverance from a potentially stagnant position was provided by the apprentices of Oakridge Agricultural College who gladly agreed to help with the arduous work necessary to renovate the tractor. It was decided that sandblasting of all the metal parts which were in sound order would be the most effective method of cleaning. The entire tractor in its many pieces was shipped off to Oakridge where the process was carried out. All paintwork and rust was removed completely and a paint primer administered. The tractor was then part re-assembled before being returned to the Agricultural Museum. At the time of writing, there are still some bearings to be obtained, hopefully from the original manufacturer, but otherwise the 'International' is nearing completion and looking very healthy indeed after its facelift.
The final step will be to apply paint and transfers bringing the tractor back to its former glory. Since our contact with the College is of mutual interest - they receive training on tractors, we have our tractors restored - we shall very likely wish to maintain this relationship and consult them again regarding other machinery in the collection.

Most other machines and objects in the collection are treated within the Museum and these usually follow a regular pattern of conservation. Large agricultural machinery, binders, reapers, ploughs etc are derusted by wire brush, the only really reliable method for such objects. Grease and oil are removed with white spirit and residue cleaned off. Various protective agents for iron have been tried, but we keep coming back to a vegetable oil ('3-in-one') diluted with white spirit. Any wood present on such objects is sprayed with 'Wykamol Plus' if worm is present. Any original markings or paintwork are preserved if at all possible. Leather is rarely encountered but does occasionally crop up as in our 'Phaeton' carriage which has a totally leather hood and the majority of the surrounding body work also leather. British Museum leather dressing was used in this case, totally successfully and is used almost anywhere this material is found. The product is used normally in a well diluted form (sometimes without bees wax) and occasionally in the wax form.

Smaller objects are treated much the same way, at least in the respect of robust objects such as blacksmiths tools which can stand the rigours of the wire brush. More delicate forms of rusted metal are immersed or treated with either 'Plus Gas' or 'Mosalene' prior to removal of corrosion. Wooden objects may again be treated with 'Wykamol Plus' if worm attack is evident. We find generally that good quality smooth wood, only requires a micro-crystalline wax finish. Food and dairy items invariably only receive a wax treatment, to preserve colour of wood, or if worm eaten they will be fumigated rather than risk pigmentation by liquid chemicals. Fumigation is also the fate for basketwork, creels, etc for this is doubtless the least likely method to damage fragile objects.

Particularly unique or delicate objects are usually sent to the Conservation Laboratory for specialised treatment or consolidation, frequently cases being in a bad state of worm damage and in danger of total disintegration. In the Spring of this year the metal working and repairing facility will be moving from Ingliston to Granton beside the Conservation Laboratory so we hope the close proximity of both will improve treatment possibilities. This transfer will of course also provide more working space for the joiner at Ingliston. Many of the larger items at present held in store at one location will be transported to an ample storage building at Granton, thus not only enabling these items to be attended to, but allowing us access to parts of the collection at the original store, which, prior to this clearance, have been denied treatment because of cramped conditions.
The Analysis and Recreation of Bronzes and Brass Mould Residues

I. Barnes

Many stone and pottery moulds show dark stains or discolouration on the surfaces which have been in contact with hot metal during casting. For pottery this is of course often due to the reduction of iron oxide in the clay from (red) haematite to (black) magnetite. However recent analyses of mould and crucible fragments by X-ray fluorescence spectrometry (XRF) indicated that some of these stains are of a metallic nature, that is the composition and colour are consequences of the metal which was cast into the mould. This suggested that it might be possible in some cases to discover the rough composition of the original cast alloy from the stain itself.

With this in mind two lines of investigation were pursued: firstly a survey of moulds from the collection in the Museum, and secondly the experimental casting of known composition bronzes and brasses into clay moulds made in the laboratory with the object of recreating the observed stains.

First of all we analysed moulds from the collection ranging in period from Early Bronze Age to Viking, including both clay and stone examples as listed in Table 1:

<table>
<thead>
<tr>
<th>Period</th>
<th>Stone Moulds</th>
<th>Clay Moulds</th>
<th>Crucibles</th>
<th>Major Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early to Middle Bronze Age</td>
<td>3</td>
<td>10 + 4 Bronze wasters</td>
<td>1</td>
<td>Jarlshof &amp; Traprain</td>
</tr>
<tr>
<td>Late Bronze Age -</td>
<td>-</td>
<td>6</td>
<td>1</td>
<td>Traprain &amp; Newstead</td>
</tr>
<tr>
<td>Roman Iron Age</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post Roman -</td>
<td>2</td>
<td>7</td>
<td>1</td>
<td>Dunadd &amp; Birsay</td>
</tr>
<tr>
<td>Dark Age</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Mould fragments analysed by XRF.

The stone moulds showed significant differences for the early and late examples, notably in the increase in zinc and decrease in tin between the early and late fragments. Lead appeared early, i.e. in the Early Bronze Age moulds, so too did zinc, while the Dark Age moulds showed huge peaks in the XRF spectra due to zinc. Other elements were present in much smaller amounts. Table 2 summarises the number of analyses and the frequency with which each of the four major elements could be detected. It should be noted that these results are for analyses on the casting surfaces: other areas showed only very small or no metallic traces. Examples of the XRF spectra are given in Figures 1 and 2.
Clearly, for stone moulds, one of the many variables which must influence the degree to which a metallic residue is left is the texture and type of rock. The EBA stone moulds were of sandstone and granite, while the Dark Age examples were of soapstone, which may explain some of the differences between the analyses. Other important criteria must be the use which was made of the mould - manufacture of axes or ingots for example - and the number of times that each mould was used.

<table>
<thead>
<tr>
<th>Period</th>
<th>Material</th>
<th>No. of analyses performed on casting surfaces</th>
<th>No. of spectra in which element was detected.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Moulds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBA</td>
<td>stone</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>EBA/MA</td>
<td>clay</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>LBA/RIA</td>
<td>clay</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>PR/DA</td>
<td>stone</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>clay</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>Crucibles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBA/MA</td>
<td>clay</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>LBA/IA</td>
<td>clay</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PR/DA</td>
<td>clay</td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2. Frequency of detection of metal residue in moulds and crucibles.

The majority of moulds analysed were made of clay and these seem to follow the same trends as their stone counterparts. From early to late examples zinc increased, tin decreased and lead remained fairly constant, but unlike the Bronze Age stone moulds they showed hardly any copper.

Certain relevant questions referring to the moulds are:

Were all the clay moulds fired before use?
How many times was a clay mould used?
Was there an inner lining to the mould subsequently lost in burial?
Were the moulds pre-heated?
How have burial conditions effected any metallic residues?

Some of these we attempted to answer by experiment, others seemed to be fairly obvious. For example, the texture of the moulds were generally those of a well fired material, not the kind of material air dried and then used, which our experiments indicated would not have remained in a fit state for re-use and would have been unlikely to remain intact during the first casting. We realise that a degree of bias was introduced here because the moulds selected for the preliminary analysis were those in better condition - badly fired examples may either have disintegrated or
been in too fragile a state to examine.

We experimented with casting known composition bronzes into cold and preheated clay moulds to see how this might effect the metal retention. For most of these there was little control of the melt temperature except by the length of heating in the furnace. However it appeared that the preheated mould retained more copper than its cold counterpart. This would tie in with the results from the Bronze Age stone moulds which we are fairly sure would have been preheated to reduce thermal shock and prolong working life of the mould. In contrast the clay moulds showed little or no copper, possibly because there was no particular reason to preheat them. Together with these clay moulds were four bronze wasters which were analysed; although not directly matching the moulds their presence from the same period (at Traprain) indicates that bronze probably was the material being cast in the clay moulds.

A few of the moulds had a lining of fine clay inside coarser clay, this type of construction presumably being for the casting of finer objects. Clearly in these types of mould there is the possibility of loss of the inner lining, rendering our analyses of little use.

The analyses reported here together with previous measurements demonstrated the large amount of zinc and/or lead associated with, or giving rise to, grey/black staining on many of the clay moulds. The question is then how the zinc in particular had been introduced into the alloy, since zinc metal was not refined until the mid 18th century, due to the fact that it vaporises directly from the solid phase at only 420°C. To investigate this we prepared melts from copper mixed with crushed zinc ore (calamine) and with the zinc ore added to already molten copper. The second method produced some kind of copper/zinc alloy which when cast left a residue of zinc in the mould surface.

The next step seemed to be to see if there was any relation between the amount of zinc apparent in the mould after casting and the composition of the initial alloy. We prepared five copper alloys with zinc composition from 5 to 11% and melted and cast these into five similar moulds. Table 3 lists the alloy compositions and results of qualitative analyses of the moulds. It illustrates that even small quantities of zinc leave large traces in the mould, as does lead, but that copper and tin make almost no impression.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Composition:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Copper</td>
<td>80</td>
<td>81</td>
<td>82</td>
<td>83</td>
<td>84</td>
</tr>
<tr>
<td>% Zinc</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>% Lead</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>% Tin</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Mould Analysis:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper peak</td>
<td>small</td>
<td>small</td>
<td>small</td>
<td>small</td>
<td>small</td>
</tr>
<tr>
<td>Zinc peak</td>
<td>trace</td>
<td>trace</td>
<td>trace</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>Lead peak</td>
<td>very strong</td>
<td>very strong</td>
<td>very strong</td>
<td>very strong</td>
<td>very strong</td>
</tr>
<tr>
<td>Tin peak</td>
<td>strong</td>
<td>strong</td>
<td>strong</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>Colour</td>
<td>dark green/grey</td>
<td>dark green/grey</td>
<td>dark green/grey</td>
<td>black/green</td>
<td>black/green</td>
</tr>
</tbody>
</table>

Table 3. Experimental casting of low zinc alloys.

The final phase was to try and estimate the effect of burial on metallic residues. Three of the experimental moulds were cut in sections and left in air, distilled water, acidic and alkaline solutions. To try and simulate the passage of time the acid and alkali solutions were made considerably stronger than is likely to have occurred naturally.
<table>
<thead>
<tr>
<th>Alloy composition:</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic traces:</td>
<td>Cu Pb Sn</td>
<td>Cu Pb Sn</td>
<td>Cu Pb Sn</td>
</tr>
<tr>
<td>In air</td>
<td>M S W</td>
<td>W S W</td>
<td>W M W</td>
</tr>
<tr>
<td>pH 2</td>
<td>W M M</td>
<td>W M W</td>
<td>W M W</td>
</tr>
<tr>
<td>Distilled water</td>
<td>M S W</td>
<td>W S W</td>
<td>W M W</td>
</tr>
<tr>
<td>pH 9</td>
<td>W M S</td>
<td>W M W</td>
<td>W M W</td>
</tr>
</tbody>
</table>

**Key:**
- W = Weak
- M = Medium
- S = Strong
- A = 80%Cu, 10%Pb, 10%Sn
- B = 70%Cu, 20%Pb, 10%Sn
- C = 85%Cu, 5%Pb, 10%Sn.

Table 4. Metallic traces left on mould surfaces after 50 days.

Both acid and alkali solutions attack the copper and tin traces but have less effect on lead, while there was little or no change following immersion in distilled water.

In conclusion this work has shed some light on the factors which influence the amount and type of metallic stain remaining on the casting surfaces of ancient moulds, although it was only possible to complete a comparatively small survey. Unfortunately it has also demonstrated that there is no easy way to go from the metals detected in the mould to those which must have been present in the cast alloy. The situation is quite different of course for metallic remains in crucible fragments, or fragments of metal remaining caught in cracks in the mould from which one can reasonably deduce the metals used. However the work has provided some initial information which we feel might usefully be extended by concentrating on a particular site where several different types of artefact are known to have been produced. It might then be possible to use the results in conjunction with further experimental casting experiments to gain more information about the mould and casting technology for specific types of artefact, especially if associated crucible fragments were available.
1. Introduction

I have been employed as the Antiquities Conservator with the Council for Museums & Galleries in Scotland (C.M.G.S.) since August 1980.

C.M.G.S. promotes the non-national museums and galleries in Scotland and provides advice, services and financial assistance to help them maintain and improve standards. The type of museum covered by the service are very varied, and include Local Authority Museums, City District Museums, University Museums and Independent Museums. C.M.G.S. is supported by funds from the Scottish Education Department, by Members' subscription and by fees and charges.

My job as Antiquities Conservator is to provide a conservation service to such museums (although each year a proportion of my time is allocated to the National Museum of Antiquities (N.M.A.S.) in return for the provision of facilities). Specialist conservation reports are prepared for each museum to establish their conservation requirements and priorities and to enable the museums to plan and fund their conservation programmes on a long-term basis i.e. perhaps running over a number of financial years. Such long-term planning allows both the museums and C.M.G.S. to coordinate individual financial restraints, time-limits and any other commitments into the conservation programmes. All conservation work and reports are charged to members at an hourly rate, but are normally grant-aided by C.M.G.S. Such grants are hoped to encourage the conservation of museum collections.

Grant-aid is also available for the provision of environmental monitoring and control equipment (i.e. to record and control temperature, relative humidity, light and air-pollution levels) and for the improvement of storage and display facilities. These provide a vital back-up to my conservation work and have in fact proved to be an important aspect of the job, acting in many cases as a form of 'preventative or passive conservation' for collections that are too vast to be conserved in the foreseeable future. C.M.G.S. must also be assured that specimens which have undergone conservation treatment will be returned to suitable display or storage conditions and not conditions which will result in the renewed damage or deterioration of specimens.
2. Conservation Problems

Since the Conservation Unit was set up, I have surveyed about 25 museums, conserved over 160 antiquities and answered numerous queries from across Scotland. Hundreds of antiquities await conservation treatment and selection has to be carried out on a priority basis, allocating conservation time to as many museums as possible each financial year.

The surveys are geared towards individual requirements and may be concerned with conservation problems in only one part of a museum's collection, to the examination of all aspects of a museum's storage and display requirements. Surveys are even carried out at the planning stage with premises proposed for museum development, meeting the architect to discuss conservation and environmental requirements so that they can be incorporated.

As we deal with very varied types of museums, naturally the collections and their problems are also very varied. Materials of all kinds may be present in any one museum, e.g. archaeological, historical, folk-life, scientific instruments or ethnographic specimens. The quality and scope of these collections has proved extremely impressive. Some of the museums dealt with have all their collections on display, whilst at the opposite extreme others have their collections entirely packed up in semi-permanent storage, perhaps due to major structural work being carried out on museum premises. Both have their resultant problems but naturally the types of problems being dealt with in each instance will differ. Collections on display may well be damaged due to over-intense light levels, with objects faded and degraded, whilst in storage the major problem encountered has been dampness and resultant mould growth. By carrying out environmental surveys of the display and storage areas, problems can be pinpointed and remedied wherever possible. Portable monitors are used on the surveys which have the advantage of giving a quick accurate spot-reading.

Fig.1. Casella Whirling Hygrometer

Fig.2. Weston Portable Photometer.
Obviously for a more accurate impression of the conditions in a museum, constant long-term readings should be taken on recording instruments. C.M.G.S. lends out recording thermohygrometers to museums and this service has proved extremely useful for curators who are not familiar with and have never had access to such equipment, and proves to them the importance and usefulness of environmental records.

Having measured and recorded conditions, a workable remedy must be found for problems. I very quickly learnt that sophisticated solutions were often not very practicable, either due to the limitations of the present economic climate.

In some museums temperature control or the use of silica-gel may help control humidity problems. At a more sophisticated level though humidifying and dehumidifying equipment may be required. Light control is effected by attention to both daylight and artificial light levels. Museums are guided to lower light-intensity and ultra-violet (U.V.) levels to within the suggested safe-limits.

Another important form of "preventative or passive conservation" is good house-keeping in the museum storerooms. Obviously overcrowding and bad packing are two of the worst faults. Shortage of space for storage and lack of storage units and containers are very common. C.M.G.S. provides advice and details to museums on methods of collection storage, storage units and storage containers.

As antiquities must be transported across Scotland from museums to the C.M.G.S. conservation unit based at N.M.A.S.'s laboratories at Granton, then good packing in transit is an important consideration and an area where advice often seems necessary. Objects come in various shapes and sizes and each has its own transit problems.

Even though the conservation unit is physically separated from the museum whose objects are being conserved, C.M.G.S. tries to follow the work through, so that we know where the completed objects are returning, and can provide back-up services as and where necessary.

3. Acknowledgements

I would like to thank the staff of N.M.A.S. for advice, whilst the facilities at the N.M.A.S. laboratories have enabled me to provide a full conservation service to client museums.
The Feasibility of Dating Vitrified Forts
by Thermoluminescence

J. Tate and F. Placido*

Introduction

Mackie (1976) has listed some 70 currently known prehistoric fortified sites in Scotland which include structures where the rock has been melted and fused together. Many of these masses of fused rock are substantial, consisting of standing or fallen blocks of wall with dimensions of several feet. The technology involved in heating such masses of stone to sufficiently high temperatures to cause vitrification has been the subject of much speculation and experiment. With the exception of recent work by Ralston these have been summarized by Nisbet (1974), who has also reviewed the geological data (1975).

Excavations have shown that the fused remains appear to have been timber laced walls (e.g. Mackie (1969)), and that the vitrification took place at the end of the period of use of the structures, probably as part of their destruction.

Several C-14 dates have been obtained, the pre calibration ages being tabulated by Mackie (1976), these being from organic remains associated with periods both before and after destruction. The age range is large - from about 900 to 200 bc (with one at 1200 bc), while more recent work (Alcock 1976 and Longley 1982) has revealed dates as late as 650 ad. They thus span one of the periods where there appear to be several large 'wiggles' in the C-14 calibration curve, that is in the relation between tree ring dates and C-14 dates for the same material.

A possible alternative dating method is that of thermoluminescence (TL). The TL method allows one to obtain an estimate of the time since the last stage of vitrification took place, or the last significant heating event. The age thus obtained must refer to the date of destruction, in contrast to the C-14 dates from occupation levels, or from charcoal associated with the construction.

Thermoluminescence

Natural radioactivity causes the continuous build up of energy within mineral crystals, albeit at a very slow rate. The energy is actually in the form of electrons excited from their normal positions in the valence band being trapped at lattice defects or impurities. The length of time which an electron will remain trapped depends on the characteristics of the trap site itself and on the lattice temperature. Raising the temperature to several hundred degrees centigrade causes the release of those electrons which would, at normal temperatures remain for thousands of years. The release of such electrons results in the emission of brief bursts of light, thermoluminescence, the magnitude depending on the amount of trapped energy released. Following the
'zeroing' effect of such heating, the amount of trapped energy again builds up, and can be determined by measuring the thermoluminescence during controlled heating of a small sample in suitable apparatus in the laboratory. The time since the previous heating event can be found if the TL sensitivity and the flux of natural radioactivity can both be measured. The TL method has been well proven for pottery dating and authenticity as well as the dating of volcanic activity and burnt stones (current fields have been surveyed by Wintle (1980)).

Aspects of TL Relevant to Vitrified Fort Dating

One problem encountered in pottery dating, that of sample size should not occur here since the vitrified masses are in many cases so large; there should be no problem in obtaining several samples for dating from each site, allowing comparative ages to be obtained to help answer the question of whether or not the vitrification was extended over an extensive period. (Although it is recognised that dates obtained from physically separate blocks may have to be considered as completely distinct measurements; it may not be possible to compare the dates as directly as for pottery sherds which come from a relatively small area within one site.).

Several other advantages arise from the large amounts of vitrified material available. First for the TL measurements themselves it should be possible to extract just the sample we want - i.e. a particular rock type from a well defined position within a large block.

The second particularly interesting aspect from a TL point of view is the problem of dosimetry. In contrast to buried pottery, and to some extent burnt stones, the TL measurements will be made on samples extracted from large matrices of similar material. In some cases it should be possible to choose samples from positions where the material is apparently homogeneous for quite large distances (i.e. for all, or for a significant proportion of the gamma dose), and moreover, covered with a vitreous layer. It seems likely that there will therefore be little effect from water saturation (unusual in North Britain!), and it may be that there is appreciable radon build up. Initially we hope to take samples with a 2" core drill (as used for concrete), using the core for the TL measurements, and measuring the gamma dose both by inserting the probe of a Nuclear Enterprise P5R6 scintillation counter and with phosphors. Complementary measurements will be made by neutron activation analysis which will also reveal the uranium/thorium ratio, and with standard TL measurements from cored samples should also provide information regarding the magnitude and extent of the heating event which caused vitrification. This information will be obtained from high temperature TL measurements as for fire damaged concrete (Placido 1981), extended to higher temperatures by use of special filters (Valladas 1978) and also on quartz rich samples by investigating the predose response as a function of previous heating temperature.
Preliminary Experimental Work

Clearly the main question is whether the vitreous material or heated rocks have suitable TL characteristics. Some preliminary work was carried out at Oxford in the 1960s (Aitken, personal communication), but so far as we know the only other TL work has been by Wright (1979 a,b) who carried out some dating of Swedish vitrified fort material, and Carpenter and Ryan (1975) who have indicated their intention to investigate some Irish vitrified material.

We have therefore undertaken some preliminary experiments with rock from Craigmarloch Wood (Renfrewshire) and Sheep Hill (Dumbartonshire), where we tried both crushing pieces of rock completely surrounded by glassy vitrification, and performing measurements on the vitreous material itself (in both cases using fine grain samples). Both phases seem to emit TL signals, although the sensitivity of the vitreous phase was very low (for measurements made on one preparation of this phase). For Craigmarloch Wood the rock sample was mainly feldspathic, but no anomalous fading was apparent over a period of two weeks. This is certainly a short period, but hopefully any rapid initial fading would have shown up. In fact subsequent glows revealed only a small predose effect on the high temperature peak.

Anomalous fading of the thermoluminescence signal is a well known problem in some feldspars and when present makes the material undateable with present techniques. The ability to select samples which appear to contain the more suitable rock types from within the large vitrified structures greatly increases the chances of being able to avoid this problem. It also means that it may be possible to attempt dating using different mineral species independently and by combining results from more than one species, thereby exploiting their different dosimetric properties.

More detailed experimental work has just commenced with a research fellowship financed by the Science and Engineering Research Council.

References


Wintle, A. "Thermoluminescence Dating: A Review of Recent Applications to Non-Pottery Materials". Archaeometry 22 (2) 113-122.


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Polychrome Panel of Madonna and Child -
An Interim Report
Beatrice Teissier

1. Description and Condition

The carved polychrome wooden panel (43cms x 38cms) of a Madonna and Child is said to come from Mary of Guise's House, Blyth's Close, Edinburgh. The panel was thought to be of early 16th century manufacture but there is evidence that much of it may be of an earlier date.

The Madonna and Child are enthroned within an arch supported by two ornamental columns in a fenestrated gothic style. These rest on a plinth consisting of an ornamental foliate design. The two columns are framed by two further ornamental columns in the same style, with two low niches, one on each side, resting on boxes adjacent to the plinth.

The pieces are affixed to two rough boards and the whole is contained within a simple frame of a later date.

The paint work is in a bad condition, being cracked and chipped and in a number of places revealing a gesso ground. Large worm holes are evident on the face of the Madonna and the body of the Child. The panel shows evidence of having been very inexpertly cleaned at one time, with different paint layers having been exposed at random, down to the bare wood in a number of places. Otherwise, the structure of the piece is sound except for a vertical crack running down the middle of the panel from the top of the arch down to the top of the Madonna's head. The rough back boards have numerous worm holes.

2. Work Done

(i) Back Boards

The worm holes, although seemingly dormant, were treated with Wykamol Plus, which was carefully injected with a hypodermic syringe.

(ii) Front

The surface dust and dirt was carefully removed with a soft brush. The whole was gently washed with a 1% ⅓ solution of Lissapol in deionised water, applied with swabs. This initial cleaning simply revealed the overall dullness of the polychrome. The figures of the Madonna and Child were a dull brownish black colour, except for the areas where gesso or wood were exposed, and where patches of the paint showed through. The sky and the ground behind the Madonna were dark buff combined with a dark red colour. The ornamental work was partially covered with a mixture of buff and dark orange
paint. Traces of white plaster were visible within some of the crevices of the ornamentation. A bright speck in the left hand fenestration proved to be the remains of gilding (see analyses). The left-hand niche was partially painted dark blue, in which several small dark blue glass-like fragments were embedded. Dark blue and red glass-like fragments were also embedded in the upper ground of the arch.

Fig.1. Polychrome panel after initial cleaning.

Fig.2. Rear View of Panel.
Before further cleaning proceeded it was decided to run an XRF analysis on the polychrome to attempt identification of the visible pigments. Paint sections from nine points on the panel were taken, mounted and photomicrographs made. These and some additional paint sections were then taken by Joyce Townsend of the Glasgow Museums. Both reports can be seen in the appendix.

Before work on the removal of the paint layers could be undertaken, it was necessary to consolidate the piece. This was done by running PVA emulsion into the small thin cracks and into the larger cracks with a small paint brush.

The dirty brown colour which covered the robes of the Madonna proved to be a waxy layer lying on top of a varnish. Several solvents (methanol, acetone, xylene, toluene, petroleum spirit, pyridene, isopropanol and butanol) were carefully applied with swabs but found to be ineffective. Methylene chloride only removed surface dirt. The only effective method of removing this layer was found to be by the careful use of a scalpel. A little of this work has now been done and a layer of dark blue paint (Prussian Blue, see Analysis) with which the mantle of the Madonna had at one time been painted, has been exposed.

The tentative removal of the same waxy/varnish layer from other parts of the panel revealed an aquamarine blue on the two bases beside the plinth, a light sky blue in the right hand side niche, and a silvery/gold metallic line (possibly the ground of one time gilding) on the Madonna's throne.

3. Radiography

The whole panel was X-rayed. The structure of the panel and a number of unsuspected iron nails holding the object together are clearly seen below.

Fig.3. Radiograph of the panel.
4. Wood Identification

Small sections of the wood were taken by Theo Skinner, mounted on slides and examined under a microscope. The back panels and the more modern frame were found to be spruce. The figure of the Madonna and Child were found to be made of cherry.

5. Analyses

As mentioned above, both X-ray fluorescence and optical microscopy examinations were made on samples from several areas. These examinations are given in detail in the appendix where it is shown that several phases of overpainting and 'restoration' must have occurred since the panel was initially made.

6. Conclusion

The panel was exhibited in the Museum's recent "Medieval Art Exhibition" after undergoing only minor cleaning and repair, adequate for its safety and display. For the purpose of exhibition it was decided to inpaint eight small areas of exposed gesso. A thin layer of pliantex (diluted with gerk-lene) was applied to the bare gesso before the temporary application of gouache colour. Modern pigments were used to avoid possible confusion at a future date. Careful recording also took place. Additionally, the capital of the inner left pillar was re-stuck with P.V.A. emulsion adhesive.

It is hoped that eventually the panel will be fully restored. When we first received the panel we were only considering very basic conservation but it soon became clear that much more complex work was necessary. The ethics involved in taking paint layers down, layer by layer, and their interpretation was of prime consideration. Polychrome conservation has never been within the scope of this laboratory although the Museum has several such works within its collections. The work done so far was done after consultation with conservators experienced in this field and it is hoped that as soon as circumstances permit, a full restoration be carried out under the supervision of an experienced polychrome conservator. I am particularly grateful to Mrs. Broderick of the Victoria and Albert Museum for her time and for her valuable advice.

Reference

Appendix - Pigment Analyses

A. X-ray Fluorescence

After the panel had been initially lightly cleaned several areas were examined by X-ray fluorescence spectroscopy (XRF) to see whether any useful information could be obtained regarding the extent and type of the pigmented regions. Being non-destructive it was possible to record a fairly large number of spectra, nearly all of which showed substantial amounts of lead. The presence of one or more lead layers made it difficult to extract much useful information from the spectra which, where there is a dense layer, result mainly from the upper surface. For this reason paint sections were taken, the detailed description of which are given in section B.

The features which XRF did show up were:

Much of the surface was covered with dirty white material which appeared to be a form of plaster (or white-wash?).

The white ground showed calcium and strontium, i.e. as plaster or gypsum.

Reds were red lead, sometimes with traces of mercury.

Crimson was mercuric sulphide.

Blues showed some copper (as on parts of the Virgin's robes) but both cobalt and arsenic in the dark blue of the niche in the left-hand column.

The browns of the upper part were iron oxides.

The niches and parts of the arch had been sprinkled with fragments of blue and red glass.

A gold spec on the fenestration of the left-hand pillar was fairly pure gold.

Silvery gold areas on the throne and upper parts of the panel were indeed silver, but with little or no gold.
B. Optical Microscopy and Microchemical Tests  
(Joyce Townsend, Conservation Scientist, Glasgow Art Gallery)

Virgin's Robe

The original layer was executed in an organic pigment and was probably paler and more pink than the subsequent layers. Then this area (with others) was covered by a thick, coarse-grained layer of red lead, which seems to act as a ground, and repainted with pure vermillion. The present vermillion layer at the surface is still another addition, over a white ground. The dark layer over the red lead is puzzling; it could be shading, as a dirt layer over the ground seems unlikely.

Virgin's Mantle

There is no evidence of a repaint with red lead here. The original blue looks like indigo, with the later, darker, blues consisting of Prussian Blue. This pigment was discovered in 1704 or 1710 and was not available commercially until ca 1724, so these layers are definitely not original.

Virgin's Veil

No pigment was found in the sample from the veil, only ground and dirt.

Sky and underside of capital

The overpaints make these samples confusing. One sample has pale organic pigment in the lowest layer, while the others begin with a pale blue layer of indigo over the ground. The pink is possibly a stray overlap, not an intentional layer. Some layers are missing from samples taken below the capital, understandably.
One sample contained smalt in a low layer, presumably associated with the indigo. It is not easy to see smalt in the sections: it could be present in the dark layer below the indigo to give shading, but a more likely usage would have been to sprinkle it on top of the indigo, with very little medium. The pigment particles are pretty coarse, even for smalt.

Smalt was available in the early 16th to 19th centuries, and became very scarce in the 19th century, so it could reasonably pre-date the Prussian blue layers. Its absence in the sections is reasonable if it is in the layer below the indigo, as large, low-relief particles would not show up here.

Base of Throne

There are no complete sections from this area. Gold is certainly present, overlying red bole and a gypsum ground (like the earliest ground of the Virgin's robe) which appear to be original. The area was also repainted in red lead.

Sides of Throne

Again, no section shows all the layers. One shows two ground layers over red lead and Prussian blue, the other shows traces of vermilion and brown ochre with a white ground-like layer. This is probably the present surface layer, and is similar to the sky. No evidence is available for the original colour, but if it was gilding it may be detectable during cleaning.

Carved Pillars, Arch etc.

These areas have not been treated with red lead. The original ground is gypsum and the blue areas, originally indigo (with no evidence of smalt, though it was not easily seen elsewhere) have been repainted twice with Prussian blue (darker than the indigo, in bulk). The top repaint was applied without a ground. The layer structure seems identical to that of the sky.

The red areas consist of vermilion over a ground, with lead white present. This could be original, since vermilion is such a bright, intense pigment that even a damaged layer remains colourful. The other, less likely, possibility is that it is contemporaneous with the first Prussian blue layer, which was also applied over a ground.

Conclusions

The earliest layers then consist of an original ground of gypsum, with the Virgin wearing a pinkish robe (organic pigment) and a (now faded?) mantle of indigo, and seated on a partially or completely gilded throne; sky of indigo possibly shaded with smalt; pillars, arches etc executed in indigo and possibly vermilion. The white pigment mixed with the indigo is not lead
white, and may be a gypsum filler.

The presence of smalt is consistent with the age of the piece, or could be taken as slender support for its late Medieval date, although caution must be exercised since smalt could be conclusively identified in only one section. The gypsum ground suggests that the technique owed more to Italy than to northern Europe.

Some time after 1704, more likely after 1724, the Sky, Virgin's Mantle, Background Pillars etc were given another ground, and repainted in Prussian blue. Possibly the indigo was then faded; in sections it looks lighter than the Prussian blue. Later, after appreciable dirt had accumulated, the same areas were extensively retouched with Prussian blue. No additional ground was applied, and the Virgin's Throne was also restored. Her robe was not treated until, later, the Sky, Virgin's Robe and some or all of her throne were given a thick coating of red lead mixed with a white pigment (spot-tests cannot show if this is lead white, too) which is a ground layer, to judge by its thickness and coarseness. Perhaps the panel was cleaned before this drastic treatment, as no dirt layer separates the red lead and the Prussian blue. A finer, white layer was applied over this, followed by pure vermilion. The orange-red shade remains strikingly visible, even beneath a layer of dirt. Though the panel is very dirty, the resulting top layer is not nearly as obvious in sections as the dirt layer separating the two Prussian blues, which might indicate quite a time-lag between restorations.

The Virgin's Robe had another two layers (ground and vermilion) applied subsequently. There is no sign of a dirt layer separating these from the first vermilion layer.
Bronze Age Gold Analyses

C. Mortimer

Introduction

This article summarises recent work on the analysis of Bronze Age gold work which has been carried out as part of an undergraduate dissertation for the Archaeological Sciences degree course at Bradford University. Full details of the experimental method and results are written up in this dissertation.

The National Museum of Antiquities of Scotland has a wide range of types represented in its collection of Bronze Age goldwork. This collection has recently been enlarged by the nine pieces of the Easter Ross hoard, comprising three cup-ended ornaments (or dress fasteners), five bracelets and a circular strip of corrugated sheet gold. In common with most of the gold artefacts some of the hoard was 'discovered' rather than excavated and details of its circumstances are scarce, although excavation was carried out in the area. The principle aim of this work was to determine the major element composition of the Easter Ross gold together with other comparable pieces in the collection.

Most of the Museum's gold has been analysed by Hartmann (1983 and Taylor 1980). Optical emission spectroscopy (OES) was used involving the clipping of a small (c.3 mg) sample from an unobtrusive area. The silver content was determined by gravimetric analysis and also in some cases by specific gravity measurements. Both these methods have some disadvantages, in particular specific gravity measurements are inaccurate for non-binary alloys and this has led to the lower precision of silver values (as opposed to copper, gold and tin) quoted by Hartmann.

The X-ray fluorescence technique of analysis has the major advantage of being non-destructive, and this was felt to be of prime importance, outweighing the disadvantage of lower sensitivity for some elements.

Calibration

Before the analyses were undertaken the absolute accuracy of the system was examined by the use of various known composition gold/copper/silver alloy standards. Some of these were made in the laboratory, while three were borrowed from the British Museum Research Laboratory (these were kindly provided by Drs. Hughes and Cowell, the standards being used in Oddy and Blackshaw 1974). Our own standards were made by melting together known weights of the pure metals in graphite crucibles, followed by slow cooling. The resulting alloys were mounted in plastic and polished flat for analysis.
Fluorescence spectra were recorded using the equipment described elsewhere in this publication, the spectral intensities for each of the three elements being used as input for the fundamental parameters analysis programme FUNBAT. There was some overlap of the copper K-alpha line with one of the gold L lines, but this was a small effect and it was found sufficient to simply extrapolate a linear background from the minimum between those peaks rather than 'strip' a normalized pure gold spectrum in each case. The comparison of weight percentages against XRF calculated percentages are given in Table 1 (for measurements at 38KV, 0.1mA):

<table>
<thead>
<tr>
<th>Standard</th>
<th>Copper</th>
<th>Silver</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>XRF %</td>
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<tr>
<td>1</td>
<td>4.95</td>
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<td>2</td>
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<td>7</td>
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</table>

Table 1. Comparison of standard composition by weight of pure metals used and from the XRF results.

This shows good agreement between weight based percentages and XRF analysis and suggests that the calibration (which is based on spectra from pure metals) is satisfactory, certainly to ± 0.5% Cu, ± 1% Ag below 20% Cu and 25% Ag.

Analyses

Two difficulties with real artefacts as opposed to polished standards were those of positioning flat area reproducibly before the detector, and determining any surface enrichment of the gold. This latter is a result of the removal of the more chemically active elements in the alloy (in this case copper and silver) by soil acids during burial. Since the fluorescence X-rays come from only the top few microns, XRF is strictly only for surface analyses (see for example Cowell 1977). Simple analysis from the surface was not felt to be sufficient so a sequence of analysis followed by gentle abrasion of an area about 3mm x 2mm using a scalpel was adopted. This was continued until a constant composition was obtained which could reasonably be felt to represent the bulk composition. A similar procedure had already been demonstrated on copper/silver alloys, but using 600 grade emery paper wetted with acetone. On the relatively soft gold objects it was found more satisfactory to lightly draw a scalpel blade across the area.

The change in composition between the surface and final analysis after abrasion is shown in Fig. 1, for the copper values. As may be seen, while some artefacts showed considerable surface
depletion of copper, others showed little or none, indicating how important the assessment of this effect is even for comparative analyses of different artefacts. The effect could also be seen by examination of the surface using a Scanning Electron Microscope in the area where the OES sample had been taken. Unfortunately these areas could not be utilised for the XRF analyses since in all cases they lay on the inside curve of the objects and so could not be presented to the detector in the correct orientation.

Graphs of the change in composition with number of abrasions showed increase in copper and silver similar to that observed by Letchmann (1970) in experimentally etched samples. In all cases the visible effect of the abrasions was easily removed by light polishing and cleaning.

The results obtained for the artefacts also analysed by OES are given in Table 2. Here the OES results have been adjusted to include the silver - the OES results published in Taylor (1980) are expressed in a somewhat different way. It should be noted that the XRF percentages are computed assuming copper, gold and silver are the only elements present. The OES results show small amounts of tin, but this was below the limits of detection for the routine XRF analyses (surprisingly even for Eq122 where the OES indicated 0.5%).

<table>
<thead>
<tr>
<th>Artefact No.</th>
<th>Type</th>
<th>Post-abrasion XRF Results</th>
<th>OES Results (Adjusted to include Ag)</th>
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<tr>
<td></td>
<td></td>
<td>% Ag</td>
<td>% Cu</td>
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<td>FE 4</td>
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<tr>
<td>122</td>
<td>5</td>
<td>15.6</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Type 1 = Penannular bracelet with expanded terminals.
2 = Penannular bracelet with plain terminals.
3 = Cup-ended ornament (or dress fastener).
4 = 'hair ring' or 'lock ring'.
5 = Small penannular ring.

Table 2. Comparison of OES (Hartmann 1980) and the present XRF results.
The inspection of Table 2 shows, for the silver content, reasonable agreement for 9 objects (within 1%), 6 with differences between 1 and 2% and 4 where the results differ by more than 2%. The uncertainties in the OES measurements are not stated, although some of the silver values are only approximate (e.g. 10-15% for FE72, or ca 8% for FE6). To investigate the XRF experimental errors on actual objects, ER3 and EQ120 were analysed (without abrasion) on four different areas. The consistency of these was good, for example for ER3 the average and standard deviations were:

\[ 5.1 \pm 0.2\% \text{ Cu} \quad 81.5 \pm 0.4\% \text{ Au} \quad 13.4 \pm 0.2\% \text{ Ag}. \]

Since these were for unabraded surface analyses, inhomogeneity does not seem to be an acceptable reason for those results which differ significantly from the Stuggart values (with the possible exception of FE4), so for FE6 and FE57 in particular some contamination of the OES sample must be concluded.

As a further check, specific gravity measurements were made (in chloroform) on 16 of the objects and the composition calculated from the graphs of Oddy and Blackshaw (1974) assuming 5% copper. Although not particularly accurate as has already been mentioned, the values so obtained were not significantly different from the XRF compositions.

The Easter Ross Hoard

About 15 years ago several pieces of Bronze Age goldwork were ploughed up and being thought of little value by the farmer remained unrecognised until 1979, by which time only 2 pieces remained. A team from the Museum retrieved seven more gold objects from the same area although little in the way of associated structures or features could be located, mainly due to plough damage to the thin soil layer above the bedrock.

The nine pieces were analysed as above, yielding the percentage compositions of Table 3.

<table>
<thead>
<tr>
<th>Museum No.</th>
<th>Description</th>
<th>Cu %</th>
<th>Au %</th>
<th>Ag %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER1</td>
<td>Cup ended ornament</td>
<td>6.8</td>
<td>80.6</td>
<td>12.6</td>
</tr>
<tr>
<td>2</td>
<td>Armlet</td>
<td>6.8</td>
<td>80.1</td>
<td>13.1</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>5.5</td>
<td>80.9</td>
<td>13.6</td>
</tr>
<tr>
<td>4</td>
<td>Corrugated band</td>
<td>4.6</td>
<td>80.6</td>
<td>14.8</td>
</tr>
<tr>
<td>5</td>
<td>Cup ended ornament</td>
<td>6.1</td>
<td>76.0</td>
<td>17.9</td>
</tr>
<tr>
<td>6</td>
<td>Armlet</td>
<td>5.7</td>
<td>75.9</td>
<td>18.4</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>5.5</td>
<td>76.5</td>
<td>18.0</td>
</tr>
<tr>
<td>8</td>
<td>Cup ended ornament</td>
<td>5.8</td>
<td>79.2</td>
<td>15.0</td>
</tr>
<tr>
<td>9</td>
<td>Armlet</td>
<td>7.8</td>
<td>75.2</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table 3. Composition of the Easter Ross Gold Hoard.

The complete set of results are plotted on the triangular diagram of Fig.1. This is a direct plot, of the data, no scaling or conversion of the axes being necessary since only 3 elements are assumed present in the XRF analyses. There does in fact
Figure 1.
Triangular Plot of Bronze Age Gold Artefacts.

Key
- □ Armlets, expanded terminals and plain
- ○ Cup-ended ornaments
- ◇ Corrugated strip
- + Small ring
- △ 'Hair ring'

Solid symbols denote Easter Ross artefacts.
seem to be some separation into two groups, mainly in the silver content, but there is no obvious correlation with the artefact type. It is interesting that the higher silver content "group" only includes items from the Easter Ross Hoard, although the number of data points is too small to regard these results as statistically significant.

In conclusion nineteen Bronze Age gold artefacts have been analysed by XRF and the results compared with previous OES measurements, showing in general good agreement between these two independent methods except in four cases, in two of which the OES values are felt to be incorrect. In addition the 9 artefacts from the Easter Ross Hoard have also been analysed and have been found to be generally similar to the other pieces, with the possible exception of 4 which have a somewhat higher silver content.

References


Furniture, Insect Pests and Fumigation

Tom Bryce

Introduction

Over a number of years the National Museum of Antiquities of Scotland has been building up its furniture collection and today that collection is quite a substantial one covering all periods of interest in Scotland. However the problems for the Museum and for the Conservation Laboratory have been enormous. Being forced to move our furniture from store to store regularly over the past few years, chronic lack of space for display and storage, general shortage of conservation staff in relation to all our fields of interest (no conservator on staff is specifically trained in furniture conservation) are the reasons why the Museum's priorities have been directed elsewhere.

Fig.1. Our severely overcrowded furniture store.

Problems

The majority of furniture is either totally or partially composed of wooden components, very often jointed and glued together. Wood surfaces are often painted, varnished, inlaid, stained, veneered, and frequently furniture is upholstered and has metallic attachments. From a conservation point of view furniture is a very complex material to deal with and a great number of job skills are required.

The main forms of deterioration are due to unacceptable environmental conditions, attack by insects and wood rotting fungi, mechanical breakdown, mishandling of specimens and chemical damage.

Environment

Wood is of course a hygroscopic material and must be maintained in
favourable conditions. But as mentioned previously furniture collections are composite, usually including much metal-work so this must be taken into account also. If wood-work is subjected to relative humidity levels which are unacceptably low, shrinkage will occur and warping and splitting will take place. Unacceptably high relative humidity causes expansion of the wood and there is the possibility of mould growth on the wood itself and on certain glues traditionally used in furniture making. Though extremely overcrowded, our furniture store is now environmentally controlled and humidified to 55% R.H. at 19°C. This however is a relatively new occurrence and there have been problems in past years, mainly because of low relative humidity over the winter months, as a direct result of indoor heating.

Fig. 2. Illustrates warping and damage to veneer caused by poor environmental conditions.

Furniture should also be regarded as vulnerable to deterioration by excessive lighting. In particular objects should not be placed directly in front of windows unless screened by blinds to cut out ultra-violet light and also prevent damage by heat from the sun. Artificial light should only be present at a relatively modest level and thought should be given to the possibility of needing U/V filters over fluorescent tubes.

Insect Pests

The type of insect pest is of course dependent on what part of the world an attack takes place. In this country the main pests are the wood boring beetles which can damage furniture to such an extent that all the structural strength is lost and can render some specimens so aesthetically displeasing that they become valueless. The term "boring beetle" is rather misleading since the damage is actually done by the grubs or larvae of the beetles as they tunnel through the wood and the surface "worm-holes" are actually the exit or flight holes by which the beetles emerge.
The four beetles of immediate interest are the common Furniture Beetle (*Anobium punctatum*), Powder-Post Beetle (*Lyctus brunneus*), Death-Watch Beetle (*Xestobium rufovillosum*), and House Longhorn Beetle (*Hylotrupes bajulus*). Other insects certainly do damage such as those of the Weevil family and many lesser known varieties which mainly inhabit lumber yards. However, to the conservator, they are normally much less important. All of this is alarming enough, but we can consider ourselves lucky in this country that we don't have to deal with furniture damaged by termites (*Isotera*) which can literally devour furniture and structural timbers.

![Fig. 3. Furniture Beetle (*Anobium punctatum*)](image1)

![Fig. 4. Powder-Post Beetle (*Lyctus brunneus*)](image2)
Within the National Museum, as far as known, insect attack has been limited to that of Furniture Beetle though Powder-Post Beetle is suspected as being present within our country life store. Being a collector of nautical items many wooden objects have evidence of previous damage on the sea-bed from Shipworm (Toredo navalis) and Gribble (Limmoria lignorum).
(A) **Furniture Beetle** (*Anobium punctatum*)

This is the most common of the wood-boring beetles and is not only found in antique furniture or timber of the home but also is present in nature where it inhabits dead branches of trees. Furniture Beetle is found in both hardwoods and softwoods.

Life begins from eggs, the hatching larvae eventually changing into pupae and finally the adult beetles are formed. Such insects go through a remarkable course of development known as metamorphosis.

![Diagram of Life Cycle of Common Furniture Beetle](image)

Fig. 9. Life cycle of Common Furniture Beetle
(i) **Egg**

The eggs are white in colour, oval in shape and take approximately 4 weeks to hatch. About 20-40 eggs are laid in rough wood or in cracks so consequently they are seldom seen. They are very small but can be observed without magnification.

(ii) **Larvae (grub or caterpillar)**

On hatching, grubs which are creamish white in colour immediately bore into the wood for nourishment and shelter, making their own separate tunnels. Their rate of progress depends on the wood species, age of the wood, moisture content and temperature. Normally they burrow for 1-2 years. In good conditions they can obtain adulthood in 1 year but if conditions are poor (e.g. low moisture content) they will take 2 or 3 years. Wood is digested and excreted in the form of oval shaped pellets.

![Figure 10. Furniture Beetle grub](image)

(iii) **Pupa (Chrysalis)**

At the end of the feeding and growing stage each grub goes to near the wood surface, excavates a cell, changes into a pupa and becomes quiescent. It no longer eats and for 2-3 weeks lies in a mummy-like form then gradually assumes the form of an adult beetle.
(iv) **Adult**

Each beetle releases itself from the pupal cell by biting a round hole (average size 1/16") through the thin film of wood, crawls out, and at that point is capable of flying. The colour can vary between reddish brown and dark brown. There are parallel rows of small pits in the wing cases and the size of the adult is 1/10"-1/5". Its head is concealed from above by a hooded thorax. Very soon after emerging adult beetles mate and the female lays her eggs within a few days. The adult beetles soon dies after the eggs are laid. Within a short time another generation of grubs will begin their destructive life underground.

**B. Powder-Post Beetle (Lycus brunneus)**

There are actually 4 main types but the above is the most common. The adult insect is distinguished from the Furniture Beetle and the Death Watch Beetle because it is long, slim and does not possess the characteristic hood. The grubs of Furniture Beetle and Death Watch Beetle live by digesting cellulose but the grubs of the Powder-Post Beetle need starch, so it is mainly found in the sapwood of hardwoods as long as this essential foodstuff remains. It is never found in softwoods such as pine.

Powder-Post grubs tend to destroy wood in layers rather than the grubs tunnelling separately. The beetles themselves are brown in colour and measure 1/5"-1/4". They normally breed from eggs to adults within 6-12 months. The female beetle generally lays 100-150 eggs which hatch in approximately 3 weeks (May-September). The boredust of the larvae (creamish white in colour) tends to be fine and floury in nature. The exit holes are approximately 1/16" and round.

**C. Death Watch Beetle (Kestobium rufovillosum)**

This is a major pest in inaccessible structural timbers in historic buildings and churches. Its principal home is in oak and other hardwoods, and only occasionally attacks softwoods, and even then, it is because of the close proximity to hardwoods. They practically never attack sound and dry timber since they prefer a reasonable degree of moisture.

Death-Watch Beetle breed from eggs (approx. 50-60) to adults in 3-11 years. They go through the same transformation as the Furniture Beetle but they remain in the pupal cell for several months before emerging as adults between March and June. The well known tapping sound is thought to be caused by the insects knocking their heads against the wood as a form of mating call. Death-Watch Beetle is identified from the large exit holes (1/8") and the bun-shaped bore dust. The larvae tunnel separately like the Furniture Beetle. The adults can vary in colour from reddish to black and are generally 1/4"-1/3" long.
(D) **House Longhorn Beetle (Hylotrupes bajulus)**

This insect has established itself all over the world and is well known for its attack on the sapwood of softwoods especially in roof tops and in attics. Similar to Powder-Post Beetle, it is difficult to detect since the larvae tend to digest the wood in layers and leave a veneer of wood on top. The exit holes (1/4"-3/8") are not round and even but instead are slightly oval and usually full of powdery dust and short compact cylindrical pellets are evident.

The life cycle is generally 3-11 years. Approximately 100-200 eggs are laid. The larvae tend to be a shiny, creamish colour and are known to be fast eaters. The adults (2/5"-4/5") emerge from July to September.

(E) **Shipworm (Toredo navalis)**

The larvae of this creature swim about freely until they are developed. They then attach themselves to submerged timber and begin to bore into it, growing all the time. This can reduce wood lying on the sea-bed to a honeycombed structure (holes vary from 1/5"-1" wide). Shipworm is worm-like in appearance but with hard, boring jaws.

(F) **Gribble (Limnoria lignorum)**

This little sea creature is about 1/8" long and has been described in the past as being like a wood louse. Despite its size it is capable of great structural damage. It only attacks wood to a small depth but wave action removes damaged areas and allows the process to start all over again.

Once an insect attack is noticed in a piece of furniture the normal procedure is to isolate it even if this means giving it a temporary cover of polythene sheeting. It is of course much better to completely isolate an infected object in a separate room. In any case an outbreak should have urgent attention because infected objects can very quickly become riddled with woodworm holes. One specimen can cause the re-infection of an entire storeroom. It is important that regular inspection be carried out on furniture collections particularly on susceptible items such as plywood backboards, wickerwork, sapwood areas ( rich in starch), basketry etc. This is particularly important between Spring and Autumn, which is the emerging period of the adult beetles.

![Fig.11. Here we see that unvarnished areas are particularly susceptible to woodworm attack.](image-url)
Fig. 12. An object composed of 2 separate ash components—note how the attack is much greater on the quick grown wood than the slower grown wood.

Fig. 13. Cross-sections of above.
Discovery of worm holes doesn't always mean that an attack is in progress because it could have happened many years previously. However it is not always easy to decide whether an attack is a fresh one or not. As a general guide if the holes are freshly made the edges will be sharp and wood dust will remain just inside the holes. The presence of wood dust itself doesn't always mean there are active workings. However an object which has not been moved for some time with fresh boredust on top of ordinary dust is a definite sign of active attack. If in doubt one should not take any chances. The procedure should be to isolate the specimen, identify it if possible, remove and destroy the powder, treat and re-inspect over the life span of the beetle.

Fig.14. Oak/larch bureau which has been recently fumigated.
Fig. 15. Rear view and close-up of worm attack at rear of bureau. Note the extensive attack on the larch in comparison to the oak.

Whilst stating above what should be done in every museum, I have to admit that this has seldom been possible in our own situation. This is because of the severe lack of storage space, lack of staff to do the work and insecure tenancy arrangements of past and present stores. Although this situation still exists it has been recognised that this form of preventative conservation must have high priority and indeed an organised programme of fumigation, has begun.

Fig. 16. Here we see an isolated case of larvae making an exit hole through a thin lead sheet.

**Woodworm – Remedial Action**

If woodworm were merely to be found on the surface of wood, killing them would be a relatively easy matter. In practice, accessibility is the real problem and protection is limited to the depth of penetration of particular reagents. Eggs themselves, laid on wood surfaces are even more resistant. Of the utmost importance at this point is to stress that all insecticides and fumigants are poisons, some much worse than others, but they must all be treated and handled with the utmost care. The protection required in their use varies enormously and before one contemplates using any of them one should familiarise oneself with all the manufacturers literature, the standard books of reference, and if in any doubt contact the Health & Safety Executive.
It would seem useful to mention the main methods of woodworm eradication used in the past and today. Over the past 20 years or so, the Conservation Laboratory has had considerable experience in treating woodworm but of course not all methods used in the past would be a first choice today. Although woodworm can be killed by merely raising the temperature to 82°C or above, this is of no use to the conservator faced with a problem specimen of furniture. The main categories are as follows:

1. Fumigation

This can be regarded as the application of toxic reagents into an enclosed space. There are numerous methods by which this may be done, many of them requiring very specialised equipment and experienced operators.

Toxic gas has the advantage that it permeates the woodworm tunnels efficiently so it is useful for complex structures, large amounts of furniture, thick members, or where upholstery is present (could be damaged by liquid insecticides). The major disadvantage by gas is that no lasting protection is provided as with liquid insecticides which leave residual poison within the wood, taking effect for many years.

(a) Hydrogen Cyanide (Zyklon)

This is a deadly poison requiring special apparatus and experienced personnel. Its use is very much restricted nowadays. A recent paper by Hans-Gert Backman (Studies in Conservation, 26(1981), 111-118 recommends that fumigation with Hydrogen Cyanide should be done only at low relative humidity (below 30%) for fear of the formation of metal cyanides when metals are present.

(b) Methyl Bromide (Haltox)

A highly poisonous substance again requiring special apparatus and experienced personnel which is currently used by a number of museums. Usually a lachrymator (e.g. chloropicrin) is incorporated as a safety measure.

There is some concern amongst conservators that methyl bromide may not be suitable for objects containing feathers, rubber, leather or upholstery containing horse-hair. The effect of the gas though is thought to be minimal.

(c) Ethylene Oxide (Etox)

A highly dangerous reagent requiring very stringent precautions and special apparatus. It is usually marketed as a mixture with equal quantities of methyl formate (Etoxiat) or as a mixture of 90% Ethylene Oxide and 10% Carbon Dioxide.

(d) Hydrogen Phosphide (Phostoxin)

Highly poisonous fumigant requiring special apparatus.
(e) (i) Carbon Disulphide (BP46°C)

Carbon Disulphide is a clear liquid with a low vapour pressure and an unpleasant smell. It is a poison which evaporates readily and is capable of forming explosive mixtures in air. It is a reliable insecticide which is safe to use with painted and varnished furniture and in the past has been used on worm eaten panel paintings. It can be used at normal temperature and pressure by making a small area or container gas-tight. It has generally only been used on a small scale because of the dangers and always done in isolation from people and from naked lights. The required amount of liquid is simply placed above worm-infested furniture in an air-tight system, the liquid volatilises and the heavy vapour drops down over the objects. Fumigation generally takes 3-4 weeks.

The Conservation Laboratory in its previous premises frequently employed this method for small items of furniture.

(ii) Carbon Disulphide / Carbon Tetrachloride (1 part / 4 parts)

The principle and application is the same as above except that this mixture has the advantage of being non-flammable. However objects with fugitive colours cannot be done in this way. Because the mixture is not as toxic as an equal volume of Carbon Disulphide, the fumigation procedure takes longer.

(f) Paradichlorobenzene

The white crystals of paradichlorobenzene are simply placed at strategic points in and around furniture (not in direct contact) in a gas-tight system. Again this method has generally been used only on a small scale because of the dangers. Its main use is for moth attack but can be used to eradicate woodworm.

The Conservation Laboratory have for many years used this reagent but in recent years this has been seldom and in a very restricted way.

(g) Fumite - The Vapour Fumigant

This product works on the principle of killing adult beetles at the time of mating and larvae from the eggs are also susceptible to attack before they tunnel into the wood. The active ingredient is Lindane.
The insecticide is contained in generators which can be purchased in various sizes. The generators are lit by the operator who swiftly vacates the fumigation area which is made gas-tight. The area then becomes filled with a cloud of insecticide. The fumigation period is only 4 hours but it is recommended to leave it overnight.

The laboratory, using this method under approval from the Health & Safety Executive, recently fumigated an entire storeroom of furniture and numerous buildings containing holdings of country-life material. This is seen as the beginning of an organised fumigation policy. Of course this treatment will certainly not have eradicated all the woodworm but it is hoped that the number of emerging and breeding adult insects have been significantly reduced as a result of the treatment.

2. Irradiation

It has been reported by Norman Hickin in "Conservation of Wood in Painting and the Decorative Arts" (p19-22) that woodworm can be destroyed by irradiation using a cobalt source. More than 72,000 Rontgens were required to be totally effective. It could prove possible that conservators like ourselves with access to powerful radiography units may be able to use the facility for treating modest sized, worm-infested furniture specimens. However, current literature seems to suggest that this is unlikely to be a success.

3. Liquid Insecticides

These are of the oil-borne or organic solvent type where the poison is carried into wood. The most common of those used are the organo-chlorine compounds (hydrocarbons containing chlorine) such as DDT, Dieldrin, Gamma - BHC, pentachlorophenol chloronaphthalene etc. and also the organo-phosphorous compounds. Within recent years there has been considerable public resistance to the use of many insecticides such as Dieldrin, which is fairly restricted in its use nowadays.

The liquid insecticides kill by direct contact and leave a persistent or semi-persistent poison in the wood. These reagents are generally applied by syringe, pipette, brush or spray. The work is best done between Spring and late Summer. This is because the beetles are emerging throughout that period and newly hatched grubs are near the surface. The fluids are expected to kill larvae, pupae and emerging adults. The toxic residue is expected to kill surviving insects from deep within, when they go into an infected area. In application one should strive to make sure that all surfaces are covered so that adult beetles cannot emerge through untreated surfaces. Particular attention should be paid to injecting the worm holes. One must always watch out for staining, softening of paint or varnish or other such damage.
It would seem appropriate to mention some of the common proprietary brands of liquid insecticides and state in brief those which we have used ourselves and any observations we have made.

a. Wykamol Plus

This is an organic solvent based insecticide containing Gamma HCH, bis(tri-n-butyltin) oxide and orthophenyl phenol. It is colourless, non-staining and harmless to varnish or French polished surfaces. This insecticide has been in regular use here for several years. No problems have been encountered.

b. Wy kemulsion 70

Unlike the above, this insecticide is non-flammable and is composed of an emulsified organic solvent preservative containing chloronaphthalenes, gamma BHC, organotin compounds and orthophenyl phenol. Some conservators have expressed doubts as to its ability in penetrating adequately but in any case the presence of water makes it unsuitable for application to furniture. Its main use is in the treatment of roof timbers.

c. Rentokil Woodworm Fluid

This insecticide is composed of Lindane as the active ingredient although formerly Dieldrin was also included. The Museum for many years used this material on a fairly large scale to treat mainly country-life agricultural objects but some furniture was also done. Treated objects tend to remain oily for a substantial period.

d. Xylamon Woodworm Killer - BV - Special

This product is based on chloronaphthalene.

e. Xylamon - LX - Hardening - N

This has been used by us occasionally over many years. It is useful for treating badly worm-eaten wood and consolidating it (normally applied by syringe, wiping away excess to avoid staining). Our experience has been that it imparts a darker colour than normally desired but otherwise effective.

f. Cuprano1 Standard Woodworm Killer

This insecticide is based on metallic naphthenates and was used by the laboratory in the early 1960s.

Conclusion

The Museum's overcrowded collection of furniture will soon be moved to new, good quality storage premises at Customs House, Leith, where full relative humidity control will be implemented. A custom-built fumigation chamber (internal measure-
ments 20' x 8' x 8') has been purchased and will be sited at the rear of the premises (see figs. 17 & 18 below). After much thought and advice from relevant bodies the reagent methyl bromide was chosen as the most suitable and practical fumigant for our purposes. Ethylene Oxide was ruled out as a possibility because of the increased hazards and costs involved, and since its use is likely to be restricted even further in the foreseeable future as a result of proposed legislation.

Fig. 17. Overall view of interior of methyl bromide fumigation chamber.

Fig. 18. Control end of chamber.
Conservation of an Animal Skin Buoy

Fiona Macalister

1. Description

An animal skin had been inflated and stretched around a circular wooden platform. String had then been wound round, binding the skin to the wood. The string and the wooden handle had been tarred to make them watertight. A crude wooden handle had been attached to the wooden platform with wooden pegs.

2. Condition

The animal skin was very dry and brittle and intensely folded (Fig.1.), but was still intact except for a small split, approximately 2cms in length. The circular wooden top and handle were in good condition and had been coated with pitch or tar. The skin, also, had vertical stripes of tar. The rope attached to the handle did not require any treatment. It was hoped that it would prove possible to restore the buoy to its original condition.

Fig.1. Animal skin buoy before conservation.

3. Treatment

1. Softening the Skin

The following solution was prepared:-

5% v/v ASAK 520S (Bayon) – a leather lubricant
1% v/v Tego B – a fungicide
94% water

The tar was tested for fastness using a cotton bud.
dipped in the solution, which was quickly pressed against the tar, and when none was removed the testing was continued for one minute. The solution proved to be safe to use.

The Buoy was placed in a drum containing the lubricating solution and was weighted down with a glass sheet, because it tended to float to the surface. Care was taken not to soak the wooden top and handle, nor the rope.

The Buoy was left for a total of ten days in the solution, but was examined daily. After two days the skin had become a little more supple but the folds and creases could not be opened out. It was decided to add \( \frac{1}{\sqrt{2}} \) glycerine to the solution. The solution had been prepared using cold water but a little warm water was added with the glycerine, to help the various constituents to dissolve and to help the solution penetrate the skin. It had already been found however that the solution entered the buoy through the split in the skin. This would have speeded up the process of lubrication. Each time the buoy was examined the liquid was carefully poured out of the buoy, through the split, and the skin was manipulated. Gradually the skin became more supple, except in the areas where the pitch was thickest.

After ten days the suppleness had increased greatly. The weight of the solution inside the buoy had forced the folds to open out. Once the liquid had been removed, however, it was impossible to open out all the folds at the same time.

ii. Reshaping and Drying the Skin

In order to retain its shape the buoy had to dry while inflated. A meteorological balloon, with a diameter of approximately 63cms was carefully fed into the body of the buoy, through the split, after having drained out most of the solution. The balloon was inflated very carefully, by no means to its full extent. As the balloon expanded it filled the body of the buoy and forced open the folds and creases. Three screw clips were placed over the lip of the balloon to stop air escaping.

While it was drying the buoy was suspended by a rope. The excess Bayon was removed with paper towels and the skin partially dried using a hair dryer. The skin was then allowed to dry naturally but was examined frequently to make sure that no splitting had occurred.

When the skin was dry the screw clips were released and a little air removed from the balloon using a small vacuum pump. It was realised that it would not be possible to remove the balloon without making the split
in the side much larger so the balloon was left in situ, partially inflated. The neck of the balloon was cut off and the hole in the skin repaired.

Fig. 2. Buoy after conservation.

iii. Repairing the Split

Fine nylon tissue of neutral pH (weight: 12gm²) was placed across the hole, inside the split in the buoy. A number of layers were applied using Pliantex diluted with Genklene and coloured with powder pigments to bring the level up to the surface.

iv. Filling the Gap

While the buoy was drying it was noticed that the wooden handle was beginning to come away slightly from the circular wooden platform. This may have been due to drying out of the wood after it had been partially submerged in the solution for a short time during treatment, or it may have been due to the weight of the skin pulling downwards, while the object was suspended.

The gap was filled with Sylmasta, a white epoxy putty. This was pushed into place with a wooden cocktail stick. The hardened putty was painted with acrylic paints.

3. Fibre Identification

It did not prove possible to identify the skin but the rope was analysed and was found to be sisal. Whole mount slides were made of the fibres and were examined at magnifications of X100, X250 and X400. Compare figs. 3 and 4, where the latter
is a photomicrograph of a reference slide of sisal.

Fig. 3. Photomicrograph of fibre taken from the rope, magnification X250.

Fig. 4. Photomicrograph of reference slide of sisal, magnification X250

4. Reference

Throughout the treatment reference was made to the following article:

The meteorological balloon was supplied by Phillips Rubber Ltd; Manchester.

This work was carried out while I was an Assistant Conservation Officer at the National Museum Laboratories, during the first year of my training for the Diploma in Archaeological Conservation at Durham University. I would like to thank everyone at the laboratories for their continued help and advice.
Analyses of Massive Bronze Armlets

J. Tate  I. Barnes  A. MacSween

The analysis of massive bronze armlets by X-ray fluorescence spectroscopy was started as part of a student project (by I.B.) with work on the examples in the Museum collection. The project was suggested by Mr. Trevor Cowie of the pre-history section, the hope being that compositional analysis and any information about manufacturing technique might help to define the chronological sequence of the objects. The work was of particular interest because a newly discovered armlet, from Braes of Doune (NW of Stirling) had been sent to the Museum in 1982 and subsequently declared as treasure trove. This brought the total number of known examples to twenty-two. Of these, five have been lost since discovery although one still exists as a cast in the Museum. Four of the armlets are in the British Museum, one in Perth Museum, three at Inverary Castle, one in Dunrobin Castle, one in the museum of the Irish Academy and the remainder in our own Museum.

Massive armlets of the type studied are only known from North Britain, with the exception of the one presumed export in Ireland (see the distribution map of fig.1). They are thought to date from first and second centuries AD. The armlets are described in detail in Macgregor (Simpson (1968) and Macgregor (1976)), Smith (1880) and Brailsford (1975). The recent find is to be published by Cowie (1983). A stylistic comparison and tentative chronology of the armlets is suggested by Macgregor (1976): in this note we will simply summarise the experimental results so far. The armlets examined were of either the 'folded' or 'oval' type: in the former possible development from coiled spiral armlets can be seen in that the objects are not symmetric, the two 'ends' of the pattern are visible. In the oval type these ends are not visible and, the shape has two planes of symmetry.

Method of Analysis

X-ray fluorescence is in itself a non-destructive analytical technique, but for correct determination of the composition of ancient alloys it is often necessary to remove a layer of surface corrosion or patina at the spot being examined. The method for doing this was similar to that described for silver objects elsewhere in these articles, namely the sequence of gentle abrasion followed by analysis until no significant change in composition could be detected. The area analysed corresponded to an elliptical spot about 2mm by 1.5mm although a somewhat larger area (about 4mm by 2mm) generally had to be cleaned due to difficulty in repositioning the objects between analyses - mainly because we endeavoured to utilize a previously flattened surface as the area for analysis, meaning that the armlets had to be held in rather awkward orientations.

Fluorescence spectra were obtained in the normal way, recorded on disc and percentage composition of the major elements determined using the fundamental parameters programme FUNBAT. The input data for FUNBAT are the total number of counts in each fluorescence peak. To obtain this was straightforward for the copper K, lead L and tin K lines used, where a linear background could
Fig. 1. Distribution map of massive bronze and spiral snake armlets. The recent find from the Braes of Doune is ringed.
be estimated under each peak. However for zinc the principal peak overlaps one of the peaks from copper, and this had to be removed before the value for zinc could be estimated. The technique used was to 'strip' from the spectrum the peaks obtained from pure copper, normalized to the same intensity as the copper peak from the armlet, thereby revealing the zinc peak. It was found most satisfactory to calculate the normalization factor simply from the height of the copper peak.

Most of the armlets examined showed evidence of mending and repair, in most cases assumed to have been done at manufacture to cover up casting flaws or after early damage, since on pieces which still had their patina this covered both mend and surrounding metal equally. The final analyses were made on areas away from such mends although several more qualitative analyses were made on areas where metal had been joined or filled. In some of these cases quite different compositions were obtained for the repaired areas as might be expected: it was not felt to be worthwhile performing full quantitative analyses. In Table 1 the compositions are calculated assuming only the four elements shown were present in the alloy: in fact small amounts of iron were present (less than about 0.2%) but these were not included in the analyses.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ref No.</th>
<th>Museum Number</th>
<th>Type</th>
<th>Copper %</th>
<th>Zinc %</th>
<th>Lead %</th>
<th>Tin %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aboyne</td>
<td>231</td>
<td>FA21</td>
<td>Oval</td>
<td>88.9</td>
<td>0.7</td>
<td>5.1</td>
<td>5.3</td>
</tr>
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<td>Aboyne</td>
<td>232</td>
<td>FA20</td>
<td>&quot;</td>
<td>88.6</td>
<td>7.3</td>
<td>0.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Aboyne</td>
<td>233</td>
<td>FA22</td>
<td>&quot;</td>
<td>87.4</td>
<td>0.5</td>
<td>0.7</td>
<td>11.4</td>
</tr>
<tr>
<td>Auchenzabdie</td>
<td>235</td>
<td>FA15</td>
<td>&quot;</td>
<td>87.0</td>
<td>0.9</td>
<td>3.3</td>
<td>8.8</td>
</tr>
<tr>
<td>Belhelvie</td>
<td>236</td>
<td>FA16</td>
<td>&quot;</td>
<td>86.5</td>
<td>4.4</td>
<td>2.2</td>
<td>6.9</td>
</tr>
<tr>
<td>Burnannoch</td>
<td>238</td>
<td>FA18</td>
<td>Folded</td>
<td>87.7</td>
<td>3.5</td>
<td>0.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Seafield</td>
<td>244</td>
<td>FA19</td>
<td>&quot;</td>
<td>82.7</td>
<td>14.2</td>
<td>0.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Stanhope</td>
<td>245</td>
<td>FA25</td>
<td>Oval</td>
<td>87.0</td>
<td>9.5</td>
<td>0.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Stichill</td>
<td>246</td>
<td>FA17</td>
<td>&quot;</td>
<td>85.1</td>
<td>2.4</td>
<td>3.6</td>
<td>8.9</td>
</tr>
<tr>
<td>Perth</td>
<td>250</td>
<td>139</td>
<td>&quot;</td>
<td>89.9</td>
<td>0.5</td>
<td>6.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Braes of Doune</td>
<td></td>
<td></td>
<td>Folded</td>
<td>81.9</td>
<td>12.5</td>
<td>1.1</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 1. Percentage composition from XRF analyses.

Eight of the eleven armlets analysed showed surfaces considerably enriched in tin and lead in the patina: in three of these cases zinc was low in the patina, but two in fact had higher zinc levels than was found in the bulk metal, although one of these had been heavily cleaned at some time in the past. The newly discovered armlet, from Braes of Doune, has a surface which appears to have been chemically cleaned quite recently, perhaps when it was found. It has no patina but a rough surface with casting holes and flaws showing up clearly (Fig. 2).

An example of the considerable change in tin content between surface and bulk metal is given in Fig. 3. This shows the results of a number of surface analyses in different areas (marked with
Fig. 2. The armlet from Braes of Doune.

BUNRANNOCH ARMLET FA18

ANALYSIS NUMBER

○ VARIOUS AREAS ON SURFACE
□ MIDDLE BOSS
◊ BOTTOM TERMINAL
★ TERMINAL HATCHING
■ R.H. TERMINAL
× CENTRAL BOSS

Fig. 3. Percentage tin of FA18 before and after abrasion on different areas.
circles) and then the results from four separate sequences of analysis, abrasion analysis etc, as indicated, for the Bunrannoch armlet.

Discussion

The two pairs of armlets in the British Museum have recently been analysed and these results are shown in Table 2, together with the earlier analyses for the armlet from Stanhope and two of those from Aboyne. These last three were performed at the end of the 19th century and the Stanhope analysis clearly differs from the values we obtained. It is not clear which of the Aboyne armlets were analysed: however Smith's figures agree quite well with ours for FA20 and FA21 respectively. The British Museum armlets were analysed by atomic absorption spectroscopy, which has the advantage of better detection limits for some elements than XRF but the disadvantage that a sample has to be removed.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ref. Number</th>
<th>Museum Type</th>
<th>Copper</th>
<th>Zinc</th>
<th>Lead</th>
<th>Tin</th>
<th>Iron</th>
<th>Nickel</th>
<th>Silver</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Castle Newe 239</td>
<td>1946 4-2,1 Oval</td>
<td>88.1</td>
<td>2.51</td>
<td>0.12</td>
<td>8.85</td>
<td>0.11</td>
<td>0.03</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>a Castle Newe 240</td>
<td>1946 4-2,2</td>
<td>88.6</td>
<td>2.53</td>
<td>0.13</td>
<td>8.6</td>
<td>0.11</td>
<td>0.02</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>a Pitkeloney 242</td>
<td>38 7-14 3a Fold</td>
<td>83.4</td>
<td>14.0</td>
<td>0.14</td>
<td>2.3</td>
<td>0.23</td>
<td>0.02</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>a Pitkeloney 243</td>
<td>28 7-14 3b</td>
<td>86.6</td>
<td>9.0</td>
<td>0.14</td>
<td>3.2</td>
<td>0.16</td>
<td>0.02</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>b Stanhope 245</td>
<td>FA25 Oval</td>
<td>90.69</td>
<td>-</td>
<td>-</td>
<td>9.29</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>c Aboyne</td>
<td>&quot;</td>
<td>88.2</td>
<td>9.1</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>c Aboyne</td>
<td>&quot;</td>
<td>86.5</td>
<td>1.4</td>
<td>4.4</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Other analyses of Massive Armlets.
(a) Tite & Cowell (1975)
(b) Macadam, in Smith (1880)
(c) Church (1865).

One of the aims of this work was to see whether the various armlets show any compositional changes which could help to resolve their chronology. Macgregor (Simpson 1968) has proposed a tentative sequence based mainly on stylistic judgements. In this she sets the oval examples (Castle Newe, Belhelvie, Stanhope) first, followed by a period of overlap with the folded type. The analyses do not yield much information either to support or contradict this. The zinc content is not lower for these than for some supposed later; in fact the armlet from Perth and two of those from Aboyne are all very low in zinc, these all being of Smith's Folded type.

The results for the three pairs (Castle Newe, Pitkeloney and Aboyne FA20 and FA21) indicate that in fact no particular alloy composition was aimed at, probably any available scrap was simply melted down and re-used. The manufacturing technique is also of interest and some clues can be gained from microscopic examination of the areas analysed. For the Aboyne 'pair' the alloy has an 'as cast' structure while the other Aboyne armlet shows a structure indicative of working and annealing. Of course since such examination was limited to the small area cleaned for the XRF analysis these conclusions must be rather tentative. The Castle Newe and Pitkeloney armlets seem to have been worked and annealed (Tite & Cowell 1975), while that from Perth appears to have been cast directly. It has not been possible
to examine the remaining examples.

Different alloy compositions from repairs and mends has already been mentioned; the Perth armlet is broken into three sections and we were able to analyse two of these. The composition shown in Table 1 is for the central portion, the smaller terminal had the composition 88.7% copper, 0.04% zinc, 8.1% lead and 3.1% tin. The difference in lead (2%) may be due to segregation on casting - or it could be from the mould being filled with two slightly different melts, subsequently breaking where they joined.

We would like to thank Dr. M. Hughes of the British Museum Research Laboratory for sending the BM report, and the authors for allowing us to quote their results. We are also very grateful to the Duke of Argyll for lending the three armlets from Aboyne for study and to Alison Reid for arranging the loan of the armlet from Perth Museum.

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REPORT ON THE CONSERVATION OF THE ORKNEY HOOD

Marjory Findlay

In 1981 the woollen textile on display in the National Museum of Antiquities of Scotland, known as The Orkney Hood, came to the textile conservation unit for full conservation treatment. Since it was considered to be unique, every effort was made to analyse all aspects of the object prior to conservation.

Consultation was sought with, and help generously given by, Miss A.S. Henshall, Dr. Helen Bennett, Dr. Michael Ryder, Dr. J.P. Wild, Miss Penelope Walton, Dr. Elisabeth Munksgaard, Miss Elizabeth Crowfoot, Miss Mary Cahill and Laurence Flanagan. Further research will continue.

Fibre and dye analysis was made by Mrs. Helen Dalrymple of the National Museum Research Laboratory, and Scanning Electron Microscope Photographs were taken by Dr. Alan O'Berg of the Royal Scottish Museum. The remaining photographs were taken by Ian Larner and Doreen Moyes of the National Museum.

The hood had been displayed on a stand in the museum for a considerable time. No records of find conditions or past treatment appear to exist apart from the fact that it was dug up from a bog in 1867 in St. Andrew's Parish, Orkney. It was closely examined by Miss Henshall and her findings reported in Early Textiles Found in Scotland: I Locally Made; PSAS 1951-2. She considers that it may possibly belong to the Viking Age or even earlier, due to its technique and the use of tablet weaving that incorporates a fringe to make an edging. At the same time, fibres had been taken for sampling by Dr. Ryder and the results of his examinations appear in The Evolution of Scottish Breeds of Sheep; Scottish Studies 12, Part II (1968). A range of fibre diameter from 10μ - 114μ is shown for the nine yarns he examined, which are described as hairy medium; he suggest that the practice of plucking a fleece leaves many kemp fibres in the skin, and this may account for the small proportion of these coarse hairs actually found in many examples of ancient textiles. The seven yarns submitted to Helen Dalrymple gave fibre diameter results that range from 15.8μ to 162.7μ, the finest being generally found in the tablet woven bands.

Fig.1. Shows range of fibre diameters, fine and coarse (X100 magnification)
The brown colouration of the yarns was due to the presence of pigment in the fibres and also possibly to environmental staining. No dyes were found to be present. The inside of the garment was deeper in tone than the outside.

When first seen on its stand, the hood presented a somewhat unconvincing appearance. A break in the fabric up the back was very probably artificial and had been haphazardly sewn together by a cotton thread dyed with Anthracene brown (Seuberlich, invented 1877). No chemical damage was noted in the fibre surfaces as viewed under the microscope.

The hood has the general appearance of those known as cucullus, a hooded shoulder cape; from the peak at the crown to the lower edge of the tablet band at the back it measures approximately 49.4 cm (19½") around the shoulders it is 95.3 cm (37½") and the length of the fringe is 28-30.3 cm (11"-12"). The greatest width of material measures approximately 51.5 cm (21½"). No selvedge could be detected.

The weave is a warp chevron 2/2 herringbone twill in stripes that vary from 18-88 threads in each. Both warp and weft yarns are Z twist and the material is considered to have been worked on a warp-weighted loom. It contains a gore, reaching about 2/3 the width of the cloth, which is similar to other gores in
The first stage in conservation was to subtract 1 gram of wool for future C14 dating before any conservation was undertaken, in order to have a sample as "untouched" as possible for testing. This was achieved from loose fragments of yarns and one or two loose strands of the fringe.

Visual examination showed a good deal of scattered debris among the yarns of the weave but a generally sound physical condition. Some of the strands of the fringe, however, were very frail and ready to part. It seems that the hood was very probably made up from a piece of material of the following shape:

1 fabric of hood  2 narrow tablet band  3 broad tablet band  4 sites for holes  5 fringe

Fig. 5. Plan of Hood.
There is a wedge-shaped piece of fabric incorporated on either side of the face opening at approximately jaw level (whether as insertion or applique is hard to determine); the top and bottom edges of these have been embroidered with chain stitches in dark brown and yellow wool. The stitching has been extended, presumably to meet around the back of the head, although traces only remain. This would constitute some definition to the head area. The greatest puzzle lies in the sites of at least eight pairs of holes at more or less regular intervals, that are placed equally on either side of the face opening in the broad tablet band. When made up, the right hand band was overlapped by the left, and so the holes with their short leather thongs (some of which remain in situ) lay hidden. Their positioning suggests that they held the hood to something else, or were tied around some object to the hood. No explanation has emerged and the textile maintains its quixotic mystery.

Fig. 6. Bands showing remains of thongs and holes for thongs and overcast of one band to the other.
The former Finds Researcher at the York Archaeological Trust, Dominic Twiddle, now Director of the Trust, has said that the Trust has some lengths of leather thonging, with a similar brood and narrow end as those of the hood, which are knotted to each other in the same manner as the thongs of the hood are knotted to themselves.

The thongs were photographed and their individual sites carefully plotted before they were removed. A silk cord of suitable diameter was threaded through each hole to make sure its site was retained during the washing process.

Conservation treatment throughout was at room temperature. The textile was placed on a coarse nylon screen for support and remained on this throughout the wet cleaning process. A preliminary soak in de-ionized water for one hour helped to relax the fabric. A sample of water from each wash/soak operation was retained. The pH measurement registered about 6.5 throughout (Whatman pH papers), the same as for the de-ionized water alone. This suggested that some former wet treatment had been given. Nevertheless the fabric felt brittle and dehydrated to the touch. Felting that might accrue from mechanical washing action or detergent solution was not considered a particular hazard in this case; nor was shrinkage.

It was at one time the practice at the National Museum to apply a lanolin solution to such woollen textiles, but in this case no confirmation could be obtained. The SEM photographs show a great deal of detritus present, which may be significant, for after some ten days a mould growth appeared in the first sample that was retained (the soak in de-ionized water alone) and was identified by T. Skinner of the Conservation Laboratory as penicillium. The colour of this sample was a fairly pronounced yellow/brown and quite clear before the appearance of the mould. This suggests that the detritus was conducive to the growth of the mould. As treatment continued the samples became progressively free of colour, with no mould growth.

The first soak was followed by a 50% glycerin and de-ionized water application worked into the fibres gently by means of a round-ended glass rod and left in situ for one hour. The textile was rinsed in de-ionized water and an application of 50% glycerin and 1% Syneronic + CMC non-ionic detergent solution was applied to all surfaces with a small sponge and worked through the fibres thoroughly. The textile was left for half an hour, then washed through with the sponge technique, and rinsed. (Glycerin was used as a fibre lubricant and soil release agent in the initial stages of the wet treatment only).

The detergent solution only was applied by sponge and the textile left for half an hour, after which it was thoroughly rinsed with a gentle continuous flow of de-ionized water into and out of the wash tank, until no detergent remained. It was dried off on towelling and left overnight.

The textile itself was supported entirely by stitching to a toning fine net while opened out, except for the tablet woven bands
which were considered sufficiently strong to need no support. All loose threads were secured by stitching with fine strands of specially dyed silk yarn. The hood was then assembled into its final 3-dimensional form over a duplicated hood shape of specially dyed fine wool, incorporated for overall support. Care was taken to match the weave and yarns of the original when joining the back. The fringe strands were reinforced by fine silk thread "woven" up the length of the weakest, and all were given added support by being stitched to the band with silk thread.

It could be seen after conservation that the wet cleaning had removed most of the debris from among the weave yarns and the SEM photographs show that comparatively little detritus still remains on the fibres.

![Fig.7. SEM photograph of fibre before conservation X250](image1)

![Fig.7A. SEM photograph of fibre before conservation X1,000](image2)

![Fig.8. SEM photograph of fibre after conservation X250.](image3)

![Fig.8A. SEM photograph of fibre after conservation X1,000.](image4)

The leather thongs were individually treated with Pliantine Special G - a choice from three lubricants tried - but the pair at one site (No.7) were left untreated for future comparison.
The amphoteric nature of wool causes it to be both acid and alkali sensitive, although greater damage is caused at pH values over 7. The sulphur-containing cystine cross links of wool are one of its most important characteristics, reflected in its physical properties. The earliest stages in the weathering of wool are said to be the most important because it is then that the easily accessible cystine links are either destroyed or stabilized; and the most important effect of the destruction of these links is that the fibres become more alkali and acid soluble. As the cystine links are removed the mechanical properties of wool are weakened. It has been shown that atmospheric attack over a long period will sever these links by oxidation or hydrolysis, but also that little weight loss or change in appearance can go hand in hand with the removal of the cystine disulphide groups.

\[
\begin{align*}
\text{HN} & \quad \text{NH} & \quad \text{HN} & \quad \text{NH} \\
\text{HC} - \text{CH}_2\text{S-S-CH}_2\text{CH} & \quad \text{HC} - \text{CH}_2\text{SO}_3\text{H} & \quad \text{HO}_3\text{S-CH}_2\text{CH} \\
\text{OC} & \quad \text{CO} & \quad \text{OC} & \quad \text{CO} \\
\text{photochemical} & \quad \text{oxidation} & \\
\end{align*}
\]

Yarn and fabric structure affects the rate of weathering and coarse wool is known to recover less well than fine from tests of elongation and strength.

The matrix of wool consists of 2/3 the whole fibre and, being non-crystalline, is accessible to water. The three most important effects of water in the water/keratin system are that it acts as a cross-link between the keratin chains in the \( \alpha \)-keratin network; it acts as a swelling agent to reduce interaction between the chains, and as a plasticiser of the keratin structure.

If undamaged, the thin non-protein membrane that covers the overlapping cuticular scales of the wool fibre surface act as a water repellent. One of the most important ways of determining the amount of chemical damage that may have taken place in wool fibres is to measure the amount of "work" that is required to stretch a fibre up to 30%. After 30% it rarely recovers.

It is often not possible to take sufficient samples from a museum object to determine damage or strength loss and in the case of the Orkney Hood such determinations were confined to visual examination. One can assume that the conditions of the past have proved not too harmful, and that the wet cleaning of the conservation treatment will have benefitted the textile.
Fig. 9. Orkney Hood after Treatment

Fig. 10. Rear View after Conservation.

References


Radiography in Conservation
Tom Bryce

To the conservator, radiography is one of the most important versatile non-destructive inspection techniques available today. Quite simply a radiograph is formed by passing X-rays or gamma rays through an object onto photographic film, which when developed, forms a permanent record. X-rays themselves are a form of electromagnetic energy which are of very short wavelength, much shorter than that of visible light.

Several years ago the Conservation Laboratory was able to purchase X-ray equipment and set up a small laboratory, through special government funding. The equipment purchased and seen below is a Pantak 300 KV/12mA Constant Potential Industrial X-ray Unit with Twin Tank HT Generators and incorporating an End-Grounded 150KV/20mA Tubeshield and Dual Focus Insert.

Fig.1. General view of the X-ray Equipment.
One of the fundamental duties of the conservator is to provide as much technological information as possible. Unlike industrial or medical applications the conservator uses X-rays on historical and archaeological objects in order to obtain an understanding of the methods of manufacture, observe hidden detail, interpret the condition of objects including internal defects, cracks, casting flaws etc and to spot the presence of different materials by their different densities. As well as being a research tool, radiography can also be a time saver. For example, numerous archaeological objects (particularly ironwork) can often be X-rayed fairly swiftly to assess the merits of conservation, frequently reducing the workload. Occasionally, objects of great interest are found when one least expects it. Fig. 2 shows a totally encrusted marine iron object from H.M.S. Dartmouth which was suspected as being of little consequence. However radiography (Fig.3) revealed that beneath the massive layers of corrosion/concretion was a complete iron knife in a sheath.

Fig. 2. Totally encrusted iron object.

Fig. 3. X-ray of object in Fig. 2. (print)
Non-Dispersive XRF Analyses of Viking Silver from Orkney*

N. White and J. Tate

Introduction.

The series of analyses around which this study has been based are part of a larger silver analysis programme being undertaken by the National Museum of Antiquities of Scotland. Previous work has included the analysis of Anglo-Saxon coinage by McKerrell and Stevenson (1972), and Scottish medieval silver coinage is also being examined (see this publication).

The material examined in this study is taken from two Viking hoards which were unearthed in the Orkneys during the mid-nineteenth century. The two hoards of Burray and Skaill are by far the largest of the Viking hoards so far discovered in Scotland (Graham-Campbell 1976).

Previous studies of the Scottish hoards have tended to concentrate on typological classifications, and studies of the numismatic contents of the hoards, even though in the majority of cases the coins only represent a small fraction by weight of the hoard.

In this work we have decided to examine the non-numismatic objects from these two hoards by means of a compositional analysis of a batch of material.

In carrying out the analyses there were three main objectives in mind. Firstly, to ascertain the range of fineness of the material in terms of its silver content using a non-destructive technique. Secondly, it was envisaged that a quantitative analysis of the material would reveal any compositional differences that might exist between the two hoards. The final aim of the study is somewhat more general than the first two, in that it involves the interpretation of the analytical results within the framework of our knowledge of the Viking period. It is hoped that it may be possible to shed some light on the origin of the material in the hoards, and provide a better indication as to the context of the hoards in the Viking age archaeology of Scotland.

The islands of Orkney were first settled by Vikings from Norway around the beginning of the ninth century A.D. The nature of the settlement is now fairly well understood as the result of several excavations of both settlement sites and grave sites. The economy seems to have been primarily orientated around farming. However the presence of the silver hoards (five in total from Orkney) as well as the Earl’s palace complex at Birsay indicates another aspect to the Viking economy, namely the acquisition by individuals or families of portable wealth in the form of silver.

The two hoards differ somewhat from each other in character; the Burray hoard consists of thirty arm-rings, known as ring money.
because of their supposed use as a form of pre-monetary currency. In addition to these rings there is one intertwined necklet and 108 pieces of hack-silver, plus three Anglo-Saxon coins. In contrast the hoard from Skall is far richer in nature. The hoard consists of almost 7 kilos of silver composed of 9 thistle brooches, 14 necklets of twisted silver, 27 examples of ring money plus an assortment of small ingots and pieces of hack-silver. In addition some 18 whole or fragmentary coins were found, 16 of which were Arabic dirhems.

For the purposes of this study it was decided that the objects to be analysed from the two hoards should be as closely compatible as possible in terms of form and possible function; it was for this reason that the arm-rings were chosen as the objects to be analysed. The ring-money has the additional advantage that each individual piece is a totally discreet manufactured object, while many of the brooches and neck-rings are formed from several composite parts.

Technique and Method.

The analyses were performed with the equipment which is described elsewhere in this publication.

The elemental integrals used in the calculation of the percentage composition were found from each spectrum by extrapolating a linear background beneath the region of each peak. The spectra, each of 2047 channels, were first smoothed (using a three-point smoothing function) and backgrounds for the K-alpha peaks of copper and silver and the lead L peak estimated (taking the average of four values for the background on either side). The zinc K-alpha peak lies between the copper K-alpha and K-beta lines, so a spectrum of pure copper, normalised to the integral of the copper peak, was first stripped from this region of the spectrum and the zinc integral then estimated. For gold the problem is overlap with the zinc K-beta line. Rather than strip off the zinc peaks it was thought to be more reliable to use the integral of the second pair of (unresolved) L lines and reduce the value by the contribution from the weak L lines of lead in this region (this being generally a 5 to 10% reduction in the gold value, but becoming a considerably higher fraction in low gold, high lead spectra). The lead and bismuth L peaks were not sufficiently resolved to do other than obtain an approximate value by integrating the region of the bismuth peak after stripping a standard lead spectrum, normalised to the intensity of the lead peak. For all these integrals the stripped spectra were examined on the display of the analyser so that the validity of the background extrapolation could be checked.

The integrals for each spectrum were converted to percentage composition using a fundamental parameters programme in the Cromemco microprocessor, again this is discussed elsewhere in this publication.

Internal accuracy depends on the composition due to the nature of the interference between peaks, but typical values estimated from uncertainties in definition of the peak and background are:
copper $\pm$ 0.1%, zinc $\pm$ 0.4%, gold $\pm$ 0.1%, lead $\pm$ 0.1%, bismuth $\pm$ 0.2%, silver $\pm$ 0.2% (these are for a perfectly flat, homogenous alloy sample). Minimum detectable limits likewise depend upon the alloy, but typically for the counting period of 200s used are copper 0.3%, zinc 0.1%, gold 0.1%, lead 0.05%, (bismuth 0.3%), and silver 0.1%. No tin was observed, although the lower limit of this would be somewhat higher than for silver due to overlap with the silver K-beta peak.

Although the material being studied is commonly referred to as silver the objects are in fact an alloyed material whose main constituents are silver, copper and zinc with in addition varying small quantities of lead, gold and bismuth. These objects have been buried for a period of some 1000 years during which time the nature of the surface metal has been altered by the presence of weak acidic solutions in the soil. The copper, being the baser of the two main constituents, has been leached out of the surface leaving a thin layer preferentially enriched in silver.

The implications of this is that a straightforward surface analysis will produce results that are too high in silver. (The fluorescence X-rays for copper come predominantly from a depth of 10 to 40 microns depending on the alloy.). To overcome this difficulty it was decided that it would be necessary to carry out a series of controlled abrasions on the surface of the metal in order to be sure of obtaining analytical results which were representative of the internal composition, unaffected by any surface effects.

To ascertain the extent of these surface effects a series of trial experiments were carried out on one of the pieces of hack-silver. Examination of a polished and etched cross-section of the piece by optical and scanning electron microscopy revealed a surface layer approximately 150 to 200 microns in depth displaying an almost total absence of the copper-rich phase which is present in the rest of the material.

Subsequent to this examination the second half of the piece was treated in the following manner to ascertain the amount of abrasion required to obtain a satisfactory result. A small area of about 2mm square was carefully abraded using 600 grade silicon-carbide paper wetted with acetone. XRF analyses were carried out after each series of abrasions until the results corresponded with the known internal composition.

Obviously this method has to be somewhat adapted for complete objects, where the internal composition is unknown prior to analysis. In this case after each analysis the percentage of silver was recorded and plotted against the number of abrasions. When the silver content remained at a relatively constant level this was taken as the internal composition of the metal. This is the same technique as was used for the silver coins and examples are illustrated in that article.

One further problem was created by the need to remove the object from the equipment for each abrasion. It is essential that the surface being analysed should be replaced each time in exactly the
same position in relation to both the X-ray beam and the detector. This required the construction of a sample holder which could hold the sample in a precise location in front of the detector, with the surface to be analysed in a vertical plane, and could then be removed to allow the previously vertical surface to be held in a perfect horizontal plane for the abrasion process.

Results.

On the basis of the results obtained from the series of analyses from the two hoards of Burray and Skaill it is possible to separate the two hoards on several counts. There are several distinct differences between the alloy compositions of the two hoards (Table 1). The material from Burray (IL 236 to IL 266) represents silver which has been alloyed with brass as is shown by the fairly high zinc content, as high as 13.8%. The Skaill material however is very low in zinc and would appear to have been alloyed primarily with pure copper. In addition the Burray material on the whole has a larger amount of alloy material in the composition resulting in a far lower average silver content than for the Skaill material. The average silver content for the Burray material is 65 ± 13% in contrast with the Skaill average of 89 ± 5%. In addition to the two hoards being separated on the basis of their major alloy composition they can also be separated on the basis of their lead content, the average lead content for Burray is 2.1% ± 0.6% compared with the value for Skaill of 0.9 ± 0.2%.

It was hoped that it would be possible to further separate the hoards on the basis of their trace elements, in particular gold and bismuth. The Skaill material does tend to have a higher gold content but there seems to be very little distinction between the hoards in terms of the bismuth content. However it must be borne in mind that the bismuth values determined by XRF in this way are very approximate and really serve only to indicate the presence or absence of bismuth. Gold and bismuth are potentially the most useful elements in attempting to establish where the silver has originated from both because the two main sources of silver available to the Vikings at the time, namely from raids on Western Europe and by trade with the Arabic world, are well separated by these two elements and because neither element is much affected by cupellation processes (McKerrell and Stevenson 1972). However, since both are present only in small quantities the errors associated with determining these quantities are quite high. Additionally, the integrals required for the quantitative analysis for these elements have to be derived by a stripping process due to interference from other elements. Clearly this stripping process works most satisfactorily in the case of zinc where the percentages present are somewhat higher, rather than with the trace elements where the statistical uncertainties are already greater.

How far can the results obtained be correlated with the archaeological context of the two hoards? We have already seen that of the two hoards that from Skaill is far richer in nature containing very fine brooches and neck-rings displaying some very skilled workmanship. This ties in well with the analyses, which show that the material from Skaill is fairly fine silver. The Burray hoard however does not contain the fine objects which are present in the Skaill material, and the analyses show that the silver content is also far lower, many pieces containing less than 55% silver. Tentatively one might interpret the Burray material as being the hoard of a merchant or trader; whereas the Skaill hoard displaying far more wealth may well be the hoard of a member of the
<table>
<thead>
<tr>
<th>No.</th>
<th>Spectrum</th>
<th>Museum No.</th>
<th>Cu (%)</th>
<th>Zn (%)</th>
<th>Au (%)</th>
<th>Pb (%)</th>
<th>Bi (%)</th>
<th>Ag (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VO16B</td>
<td>IL236</td>
<td>38.2</td>
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<td>0.6</td>
<td>2.2</td>
<td>nd</td>
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<td>IL237</td>
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<td>0.1</td>
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<td>nd</td>
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<td>0.2</td>
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<td>nd</td>
<td>68.8</td>
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<td>IL247</td>
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<td>1.2</td>
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<td>IL253</td>
<td>7.9</td>
<td>7.5</td>
<td>nd</td>
<td>1.1</td>
<td>0.2</td>
<td>83.3</td>
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<td>VO33B</td>
<td>IL253</td>
<td>7.9</td>
<td>7.5</td>
<td>nd</td>
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<td>0.2</td>
<td>83.3</td>
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<td>2.3</td>
<td>0.1</td>
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<td>VO35B</td>
<td>IL255</td>
<td>31.4</td>
<td>2.8</td>
<td>nd</td>
<td>2.1</td>
<td>nd</td>
<td>63.6</td>
</tr>
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<td>VO36B</td>
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<td>2.0</td>
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<td>IL258</td>
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<td>2.1</td>
<td>nd</td>
<td>68.3</td>
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<td>IL259</td>
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<td>8.1</td>
<td>0.3</td>
<td>2.0</td>
<td>0.1</td>
<td>60.5</td>
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<tr>
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<td>VO40B</td>
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<td>2.3</td>
<td>0.1</td>
<td>87.3</td>
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<td>IL261</td>
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<td>1.7</td>
<td>0.1</td>
<td>65.4</td>
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<tr>
<td>26</td>
<td>VO42B</td>
<td>IL262</td>
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<td>2.0</td>
<td>0.1</td>
<td>57.7</td>
</tr>
<tr>
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<td>IL263</td>
<td>46.1</td>
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<td>nd</td>
<td>3.0</td>
<td>nd</td>
<td>39.7</td>
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<td>2.2</td>
<td>0.1</td>
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<td>IL265</td>
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<td>3.4</td>
<td>nd</td>
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<td>0.1</td>
<td>64.7</td>
</tr>
</tbody>
</table>

nd - not detected.

Fig. 1. Major element composition of selected pieces of ring money from the Burray and Skaill Hoards, as determined by XRF analysis.
Aristocracy on Orkney.

References


*A slightly fuller version of this article is published in the Proceedings of the 22nd Symposium on Archaeology, University of Bradford, 1983, pp. 245-253.
The costume is the Perth Glovers' Dance Dress, hat and stockings from Perth Museum and Art Gallery and is illustrated in Plate 1. The conservator, Margaret Roberts of the Council for Museums and Galleries in Scotland requested analysis to confirm the date attributed to it and to help in the selection of cleaning methods. Nineteen samples identified as silks mainly, were taken from various areas of the costume.

Plate 1. Early illustration of Perth Glovers' Dance Dress.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample Area</th>
<th>Colour</th>
<th>Lab. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Petal lining</td>
<td>Green</td>
<td>6799</td>
</tr>
<tr>
<td>2</td>
<td>Bodice of dress</td>
<td>Green</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>Petals</td>
<td>Green</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>Skirt lining</td>
<td>Light Brown</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>Skirt fabric</td>
<td>Cream</td>
<td>&quot;</td>
</tr>
<tr>
<td>6</td>
<td>Dress Ribbon</td>
<td>Purple</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>Dress Ribbon</td>
<td>Deep Pink</td>
<td>&quot;</td>
</tr>
<tr>
<td>8</td>
<td>Dress Sewing Thread</td>
<td>Green</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
<td>Dress Sewing Thread</td>
<td>Green(thought to be modern)</td>
<td>&quot;</td>
</tr>
<tr>
<td>10</td>
<td>Hose</td>
<td>Deep Pink</td>
<td>&quot;</td>
</tr>
<tr>
<td>11</td>
<td>Hat Crown</td>
<td>Red</td>
<td>&quot;</td>
</tr>
<tr>
<td>12</td>
<td>Hat Crown</td>
<td>Blue</td>
<td>&quot;</td>
</tr>
<tr>
<td>13</td>
<td>Hat Brim</td>
<td>Deep Pink</td>
<td>&quot;</td>
</tr>
<tr>
<td>14</td>
<td>Hat Brim Thread</td>
<td>Deep Pink</td>
<td>&quot;</td>
</tr>
<tr>
<td>15</td>
<td>Metal thread</td>
<td>'Gold'</td>
<td>6808</td>
</tr>
<tr>
<td>16</td>
<td>Hat Brim</td>
<td>Green</td>
<td>6989</td>
</tr>
<tr>
<td>17</td>
<td>Petal Lining(stiffened)</td>
<td>Green</td>
<td>7020</td>
</tr>
<tr>
<td>18</td>
<td>Petal interlining</td>
<td>&quot;</td>
<td>7020</td>
</tr>
<tr>
<td>19</td>
<td>Neck opening</td>
<td>Black</td>
<td>7022</td>
</tr>
</tbody>
</table>

Samples 15-19 were sent to the laboratory at a later date than the first 14 samples and were looked at separately.

Numbers 1, 2 and 3 were of similar shade and were taken as a group: the fibres were heated with 1:1 pyridine at 50°C for thirty minutes and gave green solution with the fibres themselves becoming a darker green. The fibres were removed from the solutions which were shaken with equal volumes of dichloromethane but the lower organic layers remained colourless. The same fibres were heated with acidified methanol resulting in yellow solutions and blue fibres. The blue fibres were again subjected to pyridene at 50°C and this resulted in blue solutions, the colours of which were extracted by dichloromethane. The dichloromethane solutions gave peaks of maximum absorption at $\sim 600$ nm when scanned in the U.V./visible spectrophotometer: this is indicative of Indigotin. The normal method used to produce a green was to dye the fibre yellow and to then over-dye with Indigotin: when produced in this way the Indigotin can be detected with the first pyridene extraction. However, it is possible, but was not the common practice, to create a green by dying first with Indigotin and then with the yellow. Standards were made in the laboratory using the two procedures and when the identification methods were applied it was found that if Indigotin is applied under a yellow it does not give positive results when tested for in the manner recommended by Whiting (1), and that the normal tests have to be applied in reverse order, i.e. acidified methanol extraction followed by aqueous pyridene extraction, to remove the Indigotin from the fibres. It can therefore be concluded that sample numbers 1, 2 and 3 were first dyed with Indigotin and then overdyed with a yellow, the identification of which has not been possible.
The only blue thread was number 12 and was suspected to be Indigotin since this dye had already been found on the costume and was one of very few blue dyes available before the 1850's. However, although a blue solution was obtained with aqueous pyridene the colour was not extractable into dichloromethane. A fresh sample was treated with dilute sodium hydroxide and this gave a green fibre in a green solution: when this was neutralised with dilute hydrochloric acid a pale blue solution was obtained. A standard of Indigodisulphonic Acid, when treated with the same reagents, behaved in an identical manner and both sample number 12 and this standard gave similar U.V./visible absorption spectra, indicating that the blue colour had been produced using the sulphonated form of Indigotin.

Samples 7, 10 and 13 were the next group to emerge when the red/pink fibres were examined. The colours were extracted with acidified methanol: the solutions were diluted with water and most of the methanol removed before adding an equal volume of diethyl ether. This solvent would extract any Madder or Kermes from the aqueous solution but negligible colour was detected in the organic layer indicating a negative result for them. The aqueous layer was then shaken with pentan-3-one which took up some of the colour of the solutions. Absorption curves were indicative of Cochineal. The intensity of absorption was measured in each sample and the distribution coefficient of the dye in pentan-3-one and aqueous solution was calculated, (organic solvent/aqueous solution ratio), the results of which are set out in Table 1.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wavelength of maximum absorption in pentan-3-one</th>
<th>Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>494.4 nm</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>494.4 nm</td>
<td>0.4</td>
</tr>
<tr>
<td>13</td>
<td>494.4 nm</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 1.

The ratios were all less than 0.8 which is a positive indication that the dye used was Cochineal rather than Lac which can give a similar absorption curve but which is much more soluble in the organic solvent thus giving a higher distribution ratio (1). Cochineal and Lac can also be confused in very old textiles due to the degradation of the component acid groups.

Another red sample, number 11, from the hat crown was not as straightforward. Initial tests gave similar results to those of number 6, a purple fibre, but the absorption curves differed. Number 6 had an absorption maximum at 545 nm and the curve indicated a lichen dye but did not match, exactly, any of our standard spectra of some of the many species of lichen: a more definite identification other than it is some type of lichen dye can not be made for number 6. A sample of number 11 was heated with a few drops of hydrochloric acid for half-a-minute and the dye was taken up in methanol. The absorption curve of this solution was then compared with those of standards prepared in the same way: the main peak at 463 nm and the shoulder at 516 nm matched those of Brazilwood.
The remaining pink thread, number 14, from the hat, gave an absorption curve in acidified methanol similar to that of Cochineal, exhibiting a peak at 495 nm. However, the absorption curve of the pentan-3-one extract differed, in a number of ways, from the Cochineal standards which had been dyed in the laboratory using various mordants. The peak of Cochineal at 494 nm was, for number 14, a secondary peak at 500 nm: the main, but very broad peak for the unknown was at 403 nm. There were two shoulders, one at 529 nm and one at 476 nm. An extraction with diethyl ether gave proof that the dye was not Madder or Kermes and the spectra did not resemble those of lichen dyes. Only one of the laboratory standards showed a peak at 403 nm and that was Alkanet, however this was secondary to a curve having a double peak at 518 nm and 488 nm. Sample 14 was limited in size and the resulting solutions were very dilute hence there was a lack of resolution of the peaks. Taking this into account it could be feasible that the threads were dyed with both Cochineal and Alkanet to produce the desired shade of reddish pink.

Samples 8 and 9 were green sewing threads, the latter having a very strong colour and suspected to be rather modern. Number 8 was found to be a single green i.e. not composed of a blue plus a yellow, and the colour was not extractable into the usual solvents applied for dye analysis: it was not identified. A blue colour was extracted from number 9 leaving a yellow fibre: this blue was soluble in acidified methanol but not the aqueous pyridine normally used to extract Indigotin from fibres. When the solution was scanned on the spectrophotometer it gave a peak at 609 nm matching the peak produced by Indigodisulphonic Acid in aqueous solution.

Sample numbers 4 and 5 were beige coloured, one darker than the other and both were tested for the presence of a dye such as Cochineal, which was sometimes used with an iron mordant to produce such colours: all tests were negative. These colours could be produced using one of a number of materials ranging from, for example, the Cochineal mentioned to cold tea.

This first collection of fourteen samples were all examined under the microscope and all were identified as silk except number 1 which was linen.

The other five samples were sent to the laboratory with more particular requests, than simply dye identification, to gain even more knowledge relating to the make-up of the costume.

The only metal thread from the dress (number 15) had a gold colour: X-ray fluorescence was used to identify the metal(s) present and it was found to be almost pure copper. A sample which was mounted and examined under the microscope showed the presence of a pattern stamped out along the length of the thread with copper corrosion products evident in the indented areas. (plate 2).
Sample number 16 was a green silk from the hat brim sent to complete the analysis of the hat. The warp and weft were different shades of green but were both found to be dyed with Indigodisulphonic Acid plus a yellow.

Samples 17 and 18 were stiffened linings from the petals. The first part of this request was to identify the dye on number 17 which proved to be Indigotin and a yellow. The main priority in the request was to identify the stiffening agent before conservation treatment commenced. Using the standard potassium iodide/iodine test, a blue/black colour formed indicating the presence of starch. Obviously due to the solubility of starch wet cleaning should be avoided and it should also be noted that starch decomposes on application of heat.

The final sample was a fragment found at the neck opening and fibre and dye identification were requested. The fibre was found to be silk but there was insufficient sample for a dye identification.

Conclusion

The results are summarized in Table 2.

It is obviously necessary that care be taken when conserving an object but by first identifying the material, or composition the choice of conservation methods can be made with more understanding and without any doubt that harm could accidentally come to the object. Cochineal is light fast but on washing the colour could bleed or, at the very least, become duller and more blue. The colouring matter of Brazilwood is soluble in water, weak alkalis
and acids but is insoluble in some organic solvents. Indigotin is wash and light fast but the sulphonated form, Indigodisulphonic acid is very water soluble and will even 'bleed' from fibres in a humid atmosphere, in fact just above the level of humidity normally recommended for the storage and display of textiles.

The costume is dated to the seventeenth century but these results do not entirely confirm this. All of the dyes found were in use at that time except Indigodisulphonic Acid. It is known that the costume was brought out of storage and worn at a celebration in the middle of the nineteenth century and it was suspected that some alterations had been carried out at this time. The crown of the hat in particular was not in keeping with the expected style for a seventeenth century costume. It can be seen from the results that this must indeed be the case with the hat being added to or even totally replaced using material dyed with the nineteenth century Indigodisulphonic Acid. It is also interesting to note that this is the only part of the entire costume which has Brazilwood whereas all other reds and pinks are Cochineal. The results for sample numbers 13, 14 and 16 indicate that the hat brim could possibly be original and in keeping with the rest of the costume. On close examination of the skirt it was evident that the petals had been turned inside out, probably at the same time as the hat alterations: one of the sewing threads (number 9) was found to be dyed with Indigodisulphonic Acid which confirms this theory.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Indigotin (under a yellow) Linen</td>
</tr>
<tr>
<td>2</td>
<td>Indigotin (under a yellow) Silk</td>
</tr>
<tr>
<td>3</td>
<td>Indigotin (under a yellow)</td>
</tr>
<tr>
<td>4</td>
<td>No dye identified</td>
</tr>
<tr>
<td>5</td>
<td>No dye identified</td>
</tr>
<tr>
<td>6</td>
<td>Lichen or similar</td>
</tr>
<tr>
<td>7</td>
<td>Cochineal</td>
</tr>
<tr>
<td>8</td>
<td>No dye identified</td>
</tr>
<tr>
<td>9</td>
<td>Indigodisulphonic Acid (plus a yellow)</td>
</tr>
<tr>
<td>10</td>
<td>Cochineal</td>
</tr>
<tr>
<td>11</td>
<td>Brazilwood</td>
</tr>
<tr>
<td>12</td>
<td>Indigodisulphonic Acid</td>
</tr>
<tr>
<td>13</td>
<td>Cochineal</td>
</tr>
<tr>
<td>14</td>
<td>Cochineal (plus, possibly (Alkanet))</td>
</tr>
<tr>
<td>15</td>
<td>Copper strip with pattern</td>
</tr>
<tr>
<td>16</td>
<td>Indigodisulphonic Acid (plus a yellow)</td>
</tr>
<tr>
<td>17</td>
<td>Indigotin (plus a yellow) Stiffened with starch</td>
</tr>
<tr>
<td>18</td>
<td>No dye identified</td>
</tr>
<tr>
<td>19</td>
<td>Stiffened with starch</td>
</tr>
</tbody>
</table>

Table 2 Summary of Identifications.
Reference

The History and Conservation of the Swords at Drummond Castle

Celia Kyriacou

Introduction

For the last 9 months I have been the conservator for the Drummond Castle weapon collection, working under the aegis of the National Museum of Antiquities of Scotland. This collection of over 400 items consists of swords, scabbards, dirks, guns, targes and other miscellania associated with weaponry and military dress.

The major part of my work has involved the cleaning, consolidation and repair of swords and scabbards for eventual display in the Keep at Drummond Castle. This experience has led me to formulate a regime of treatment which is described below. However before this, I will attempt to place some of the Drummond Castle swords in their historical context.

Historical Perspective

There are several early swords in the collection, two of which are shown here. The first, Figure 1, is a claymore, the Scottish equivalent of the long, two-handed European sword. This, two-edged weapon was developed late in the 15th century and became common in the Highlands and in Ireland where it was carried by large numbers of Scots mercenaries during the Anglo-Irish wars (Wallace, 1970). Figure 2 shows a rapier, a light civilian sword which first appeared in Europe during the early 16th century. The thin pointed blade stimulated a new style of fighting,
"fencing", based on the thrust of attack and the defensive parry. (Wilkinson-Latham, 1977). The hilt bars and plates thus eventu-
ally became cup-shaped providing greater protection for the hand, as in this fine example from Drummond Castle probably dating to
the 17th century.

Most of the swords from the Drummond Castle collection are bas-
ket hilts. This broad and powerful type of sword developed in
Britain during the 16th and 17th centuries, from the European
broadsword with its wide, two-edged blade that tapered to a point.
The characteristic basket was formed by the arms of the guard
being bent back and attached to the pommel. At first this was
achieved by inserting the arms into holes, and later a groove,
in the middle of the spherical pommel. One variation was to
have eyes in the arms through which screws were inserted into
the pommel to provide additional strength. Figure 3 shows an
early 17th century basket hilt from the Drummond Castle collec-
tion with this type of guard attachment.

The basket-hilted broadsword and the one-edged backsword were
particularly popular in Scotland during the 17th and 18th centur-
ies. This stimulated great originality and skill in the manu-
facture of the basket guard especially in Glasgow and Stirling.
The Highland clans favoured certain distinctive styles, for
example, the beak-nosed, ribbon hilt shown in Fig. 4. This style
was common during the last quarter of the 17th century and the
early 18th century.

Fig. 3. Basket hilt with arms
screwed into pommel
(after treatment)

Fig. 4. Beak-nosed ribbon hilt
(after treatment)
Throughout the 18th century many Scottish basket hilts were decorated with pierced designs on the guard plates. Fig. 5 shows an early example with the wide blade associated with Highland basket hilts. After the 1745 Uprising, the bearing of arms was prohibited in Scotland and only the newly-formed "loyalist" regiments could carry swords. Individuality in the manufacture of the basket hilt declined as certain designs became standard military issue. Figure 6 illustrates a mid 18th century standard cavalry broadsword with the new type of guard attachment developed by Walter Allan of Stirling during the second quarter of the 18th century. This involved the arms being welded to a ring upon which the pommel rested (Wallace, 1970). The more elaborate brass basket hilt in Figure 7 was most likely an officer's regimental sword.

Fig. 5. Early 18th century pierced basket hilt (after treatment).

Fig. 6. Standard cavalry basket hilt (after treatment).

Fig. 7. Regimental brass, pierced basket hilt (after treatment).
Many sword blades were imported into Scotland from Germany during the 17th and 18th centuries because of the superior quality of the steel. The name "Andrea Ferrara" was almost always engraved on these blades and was intended to indicate high quality to the Scottish buyers because of the esteem in which they held this name; supposedly that of a legendary swordsmith (Wallace, 1970). The hilt grips of superior swords were covered with shagreen (shark-skin) and bound with wire during the 18th century. Both of these features are predominant among the Drummond Castle basket hilts providing further evidence of their 18th century derivation.

Red material hilt liners with doeskin interiors were customary on standard military issue, Scottish basket hilts from the late 18th century. Most of the Drummond Castle swords have liners, some of which must have been later additions to earlier swords. The majority of the scabbards are unrelated to the swords and consist of thick dark hide with steel mounts at the middle and both ends. There are several with brass or silver-plated mounts but generally the uniformity indicates standard military issue.

Conservation

There are certain factors which have determined my approach to the conservation of these swords and scabbards. The great numbers and limited time for completion of the project make speed essential. The conservation methods of cleaning and stabilisation may have to be supplemented with restorative measures to bring the objects up to display standard.

The variety of materials from which these swords are made label them composite artefacts. These materials can be grouped into 3 categories, metals, textiles and leather. The composite nature of an object necessitates a treatment for each material which will not be deleterious to the others. Unless this is possible, the surrounding areas should be protected or the treatment suitably contained in its intended area. The difficulties of containment eliminate any electrochemical, electrolytic or chemical stripping methods for the removal of rust from the steel blades and hilts. In addition the unexcavated state of the swords and hence the lack of any substantial layers of corrosion, reinforce mechanical cleaning methods as being the most suitable and effective.

Fig. 8. Initial state of basket hilt (before treatment).
When the swords arrive, the rusted metalwork is usually covered with a thick layer of discoloured lanolin and the hilt covers are disfigured with dirt and grease, as shown in Figure 8. The lanolin is removed with Genklene, 1, 1, 1-trichloroethane, a non-flammable grease solvent which is less toxic than toluene. Plus gas A, a rust solvent, is then applied to the rust, allowed to soak in and gently rubbed with fine Grade 000 steel wool. Increasingly abrasive methods may be used to remove more stubborn rust, from working with a metal pick or scalpel and the rust solvent, to using a glass bristle brush and ultimately the air-abrasive unit with glass beads. This treatment is intended for the complete removal of active red rust but leaves the blackened, pitted areas that were once sites of active corrosion. To remove these would require much time spent in extensive abrasion and subsequent polishing. This surface is stable provided the metalwork is protected from moisture by waxing or lacquering.

The steel is dried with acetone after polishing with Solvol Autosol, an abrasive paste. Ideally the metalwork should be dried in an oven for several hours to remove all moisture before lacquering but because of the sword's size and composite nature, acetone is a better alternative. Two coats of Incralac 30% v/v in toluene are applied with a brush, allowing the first coat to dry before application of the second. Finally a small amount of Renaissance Microcrystalline wax is applied to the lacquered metal surface and polished with a lintless cloth. This is primarily a protective measure for the lacquer because the swords, being returned to temporary storage, may be moved without professional supervision. It has the additional bonus of giving the lacquer a more subtle, less glossy appearance.

One treatment involved the rejoining of a broken piece from the backguard to the basket hilt. It was the site of an old break that had been previously brazed together. An attempt to dowel the piece in place proved impossible when limited access prevented a drill hole for the dowel at the appropriate angle. The solution was to solder the joins using a soft lead/tin solder. This produced a secure and potentially reversible restoration which can be seen in Figures 9 and 10.

Fig. 9. Close-up of soldered join in backguard.
Fig. 10. Basket hilt with soldered join and re-stitched doeskin lining (left of grip).

The tarnish on brass hilts is removed with 50% v/v ammonia solution and I.M.S. Afterwards they are polished with Duraglit for silver, dried with acetone and lacquered. Incralac, an acrylic lacquer, is particularly appropriate because it contains benzotriazole, a corrosion inhibitor for brass and bronze. Gentle application of Duraglit is sufficient for cleaning the silver-plated metalwork.

The textiles which may be found on the Drummond Castle swords comprise the red woollen felt hilt liners bound with blue silk ribbon and the red wool, or silk pommel fringes. Their condition varies from general dirt and disfigurement to structural damage caused by moths. Light brushing and vacuuming is followed by swabbing with Genkleene using lintless cloths. The blue and red dyes are stable in this dry-cleaning solvent. Most of the liners have been sewn in place and cannot be removed therefore protection with polythene is important during treatment of the metalwork.

Leather is found on the basket hilts in the form of sharkskin bound over a wooden grip. This area is most susceptible to
woodworm attack and an extreme example is illustrated in Figure 11.

Treatment with Wykamol precedes cleaning with white spirit and eventual waxing. The doeskin linings of the hilt covers are cleaned by rubbing in Draftclean, a pulverised rubber, which is then vacuumed up. This mildly abrasive action has the additional advantage of softening the collagen fibres of the skin thus increasing the suppleness. Stubborn dirt is removed with white spirit. The seams of these liners are areas of weakness and subject to splitting. Small splits are adhered with nylon gossamer tissue (12 g/m²) and Pliantex as in Figure 12).

![Image 11](image11.png)  ![Image 12](image12.png)

Fig.11. Woodworm attack in Basket hilt grip.  
Fig.12. Small split in doeskin seam adhered with nylon gossamer tissue and Pliantex.

Large splits generally need the greater strength provided by re-stitching and the old stitch holes are used wherever possible. An example of this is shown in Figure 10.

The scabbard leather is degreased with white spirit, then Pliantine Special G, diluted to 60% v/v in white spirit, is brushed on. Several coats are needed to ensure the penetration of this leather dressing. The consolidant/adhesive Pliantex, diluted in Genklene, is applied to the cracks, abrasions and areas of red rot caused by acid attack. Microcrystalline wax is then used sparingly to polish the leather.

The swords are primarily conserved using simple mechanical techniques. The order of work is important for example the cleaning of metalwork should be completed before treating the textiles
unileather. A well planned approach facilitates the control and isolation of each treatment of the different materials.

I would like to thank Tom Bryce and David Hogg for their helpful advice on conserving the Drummond Castle weapons.

References
