THE LABORATORIES OF THE NATIONAL MUSEUM
OF ANTIQUITIES OF SCOTLAND
1980

Edited by
T. Bryce and J. Tate

National Museum of Antiquities of Scotland
Edinburgh 1980
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Introduction

This modest booklet, compiled and edited by members of staff of the Laboratories, is intended to outline and exemplify activities currently in progress.

There are two Laboratories: the Conservation Laboratory and the Research Laboratory, headed respectively by Tom Bryce, Chief Conservation Officer and Jim Tate, Senior Scientific Officer. From 1977 to the end of 1979 the Conservation Laboratory in particular benefited from 12 additional staff provided under the Manpower Services Commission. With these 12 extra pairs of hands, it proved possible to begin to catch up on a great batch of material from rescue excavations funded by the Scottish Development Department (Ancient Monuments). Such material continues to come in, though the additional MSC help is no longer available. Furthermore, increasing standards of Museum display mean that not only are the "normal" aspects of conservation of objects in the collections being attended to, but other aspects, such as possible effects of widely used display materials - as indicated by Helen Dalrymple's note on display materials' testing - are becoming increasingly matters of concern. A diminished number of staff reduces our capability of checking on testing problems that are, in fact, of importance to museum collections everywhere. The National Museum's Conservation Laboratory is not, of course, the only one in Scotland. Even the staff in all of the laboratories put together is insufficient to cope with the amount and range of material for which conservation is needed. In this respect it is pleasant to welcome the development by which an Antiquities' Conservator, funded through the Council for Museums and Galleries in Scotland, will shortly be stationed in the National Museum's Conservation Laboratory. There, using the Laboratory's resources, he will try to serve the conservation needs of the Scottish museums.

The Research Laboratory, with its specialised equipment, is the only one of its kind in Scotland. Because of its nature, we have felt the need to have a body of Honorary Scientific Advisers, composed of individuals with related fields of interest. They are:

D M W Anderson, DSc PhD FRIC
Department of Chemistry, Edinburgh University

M S Baxter, BSc PhD
Department of Chemistry, Glasgow University

Professor K M Creer, MA PhD ScD Cantab, FRAS
Department of Geophysics, Edinburgh University

R B Galloway, BSc PhD F.Inst.P
Department of Physics, Edinburgh University

D. D. Harkness, PhD MRIC CChem
NERC Radiocarbon Laboratory

J M A Lenihan, OBE MSc PhD CEng. FIEEE F.Inst.P FRSE
Department of Clinical Physics and Bio-Engineering, Glasgow University
We welcome their advice and help as the National Museum, through its Research Laboratory, moves into fields where the tread of museum feet have never been heard.

The present volume arises out of a meeting of Honorary Scientific Advisers, of the Laboratories' Sub-Committee of the Board of Trustees, and of Museum staff, held in the Laboratories in November 1979. The contributions presented as talks at that meeting are included here, and a number of selected aspects have been added to give a more rounded view of the work that is undertaken.

Under the Editorship of T. Bryce and J. Tate the production of this informed volume is a mutual effort by temporary and by permanent staff. The cover photographs and those on pages 52, 65, 72, 78 and 80 were taken by Ian Larner, the National Museum's Senior Photographer; the remainder by David Hogg at the Laboratories.

Alexander Fenton
Director
National Museum of Antiquities
of Scotland

March 1980
Research Laboratory:

J.O. Tate, BSc PhD MInstP  - Senior Scientific Officer.
H.E. Dalrymple         - Scientific Officer.

Conservation Laboratory:

T.D. Bryce              - Chief Conservation Officer.
J.M. Macqueen, F.S.A.Scot. - Conservation Officer.
A.W. Quinn             - Conservation Officer.
T. Skinner, BSc         - Assistant Conservation Officer.
R.E. Welander, BA      - Assistant Conservation Officer.
                       (Trainee for Conservation Diploma, Durham University).
A.M. Bojko, MA F.S.A.Scot. - Temporary Assistant Conservation Officer.
D.W. Hogg, BA(Edin)     - Temporary Assistant Conservation Officer.
M.J.M. MacInnes, MA     - Temporary Assistant Conservation Officer.
L.M.K. Nock, MA         - Temporary Assistant Conservation Officer.
J.R. Watt              - Temporary Assistant Conservation Officer.
L. Whitfield           - Temporary Assistant Conservation Officer.
                       (Now at the Department of Clinical Chemistry, Western General Hospital)

Visiting Staff:

E. Mølgaard            - Student from Denmark.
A. Begg, BSc           - Assistant Curator from Lerwick Museum.

Office Staff:

F.M. Dempsey           - Museum Assistant.
C.W. Utterson          - Typist.
Role of the National Museum Conservation Laboratory

Tom Bryce

The Conservation Department of the National Museum of Antiquities of Scotland is concerned with the conservation of archaeological and historical objects of Scottish significance, ranging from the earliest prehistoric times to those objects of a more recent age. It is by far the largest conservation laboratory of its type in Scotland equipped for modern practice to deal with metals, pottery, wood, archaeological textiles, glassware, stone, photography, radiography, replica-making, leatherwork, bone, composite materials etc. A proportion of the objects dealt with come from marine environments and this requires special treatment because of the problems arising from the burial environment. The laboratory occasionally supplies a support service in particular excavations to aid recovery of fragile objects from the ground and by providing urgent treatment to freshly excavated material on-site. Periods of practical training are given at the Granton laboratories to conservation personnel of other Institutions, from time to time and laboratory staff are actively involved in conservation training towards the Durham University Conservation Diploma.

The main responsibility of the Conservation Department is the care of the Museum's existing collections and the conservation of newly acquired or excavated materials which are expected to become part of the collections. Additionally, the laboratory is engaged in conserving considerable amounts of archaeological material from S.D.D. Scottish sites (particularly large quantities of ironwork, waterlogged wood and leather), other specific objects belonging to local museums, and in replica-making for the Museum itself and for other bodies.

In collaboration with the Research Laboratory we conduct investigations into existing treatment methods, frequently modifying them for the successful preservation of particularly difficult objects. Furthermore, both laboratories are engaged in the development of new techniques although this important aspect of the work, at present, is not being fully implemented because of the limitation of time able to be afforded to it. Staff of both laboratories are involved in advising curatorial and display personnel on environmental problems occurring in new displays and even in established exhibition galleries/storage areas (eg permissible relative humidity, light levels etc) and recommending courses of action.

Our facilities presently consist of a fairly large general laboratory (Fig.1), a small room for moulding, casting and electrotyping (Fig. 2), a wet area principally intended for washing or hosing down large dirty objects and doing small scale waterlogged wood conservation by the Acetone/Rosin process, a radiography laboratory which is in the final stage of development (equipped with a 300/150 KV Industrial x-ray unit), a newly acquired isolated laboratory for large-scale waterlogged wood conservation with separate flammable solvent store (Fig. 3), an exterior storeroom holding the laboratory's backlog of waterlogged artifacts (Fig. 4) and finally office, library, photographic and developing facilities shared with the Research Laboratory.
Fig. 1. Largest of the conservation laboratories - general view.

Fig. 2. Casting Laboratory - a silicone rubber mould is being lowered into an acid copper plating solution.
Fig. 3. Newly acquired laboratory premises for treating large waterlogged timbers.

Fig. 4. Storeroom housing backlog of waterlogged wood awaiting treatment.
Although we give the impression of being a fairly large organisation our number of permanent staff is extremely moderate and until recently the laboratory has relied heavily on M.S.C. funding through the S.T.E.P. Programme. The laboratory is dealing with approximately 2,500 conservation requests per year and this necessitates the keeping of an efficient recording and labelling system, especially since, as a National Museum Laboratory, material arrives from such a great variety of sources.
The Research Laboratory

Jim Tate

The most obvious purpose of a scientific laboratory attached to a museum is to broaden historical knowledge by providing information to the curatorial staff on the technical history of the collection. This is bound to result in the laboratory staff examining and analysing objects with the aim of understanding the methods and materials of construction. One aim of such investigations is of course age determination; the ability to carry out any absolute dating process is clearly likely to be an important asset to most museum departments.

The primary function of the Research Laboratory is then to apply advanced scientific techniques of chemical and physical analysis to artifacts from the N.M.A.S. and from museums and archaeological sites throughout Scotland. Some of the techniques are well established, but because of the nature of the objects - or fragments - studied, there is usually some degree of originality necessary in their application.

The majority of techniques which are in use enable us to perform analytical work at two levels. Very often a rapid qualitative analysis is all that is required to identify the principal constituents of an artifact which is, perhaps, half way through a cleaning or conservation process. For example, corroded iron objects often have other metals associated with them which are only apparent once some of the corrosion is removed: the correct identification of such metals is obviously important before any chemical treatment can proceed. Work such as this is usually carried out by wet chemical analysis or by x-ray fluorescence, but both these techniques, with additional human effort, will provide quantitative analyses such as are necessary for typographical classifications. X-ray fluorescence has the great advantage of being virtually non-destructive; surface cleaning may be required but often no sample has to be removed from the object. The other main analytical technique, neutron activation, does however require a sample to be removed and this, together with the rather long turn-round time makes the method unsuitable for rapid 'one-off' analyses.

The laboratory has in the past undertaken a considerable amount of research in order to develop the Thermoluminescence dating technique for pottery and burnt minerals. Further development of this work is intended once the present equipment is satisfactorily proven, although this is unlikely to be possible until the number of research staff can be increased.

There are four laboratories in the building which are used for research purposes, three of those being radiation classified areas where radioactive sources may be used. There is firstly a conventional chemistry laboratory as described later in this booklet. Neutron activation and x-ray fluorescence analysis take place in a windowless laboratory across the corridor which has a smaller 'hot-lab' off, where the radioactive sources are housed. The hot lab has a fume cupboard and is suitable for experiments involving unsealed radioactive sources and handling the pellets of neutron activated pottery (see below). The equipment for Thermoluminescence dating is used in a further office-sized laboratory which is illuminated only by red or amber lighting. The computer is housed in the library, one of the large offices at the front of the building which is also used as a photographic area. The equipment in these laboratories is illustrated in some of the following sections.
The Research Laboratory was first set up in the mid sixties in the basement of 5/6 Randolph Crescent, separate from the Conservation Laboratory in Shandwick Place. In the past year at Granton new equipment has been purchased and put into operation, enabling more research projects to be dealt with in the future with greater efficiency.
Textiles, because of their organic nature, disappear rapidly from most archaeological contexts, and consequently they are one of the rarer items which come into the laboratory for treatment.

Fortunately the site at Papa Stour, Shetland, excavated by Dr Barbara Crawford of St Andrews University, proved to have conditions favourable to the preservation of organic remains, and yielded leather and wood as well as textiles. The site is a late Mediaeval settlement, the putative house and farm of the Kings of Norway, and the textiles were found in a layer of solid peat, possibly the roofing or walling material of the collapsed dwelling, which accounts for their survival.

On arrival for treatment it was found that the textiles were barely distinguishable from the layer of mud in which they were encased. Samples of the fibres were examined microscopically and found to be wool.

Before any cleaning of the textiles could take place, it was first necessary to test the fabric for colour fastness. No signs of dye-bleeding were detected when the fabric was treated with water, but we found that the dyes bled in alkaline solutions. It was therefore important to keep the washing solution as neutral as possible, and so we used Lissapol which is a non-ionic detergent.

As total immersion in a bath of water would have produced an intolerable strain on the considerably weakened textile fibres, the fragments were placed on a screen of nylon net (nylon monofilament) stretched over a rectangular wooden frame. This provided support for the fabric while at the same time allowing the dirt to drain away. (Fig. 1).

Fig. 1. Fragment of textile prepared for washing.
The textiles were gently sprayed with a 1% solution of Lissapol in warm water and tamped with the fingers to break up the mud coating. When the mud had been removed it was possible to ease out the fragments and straighten them. This was an extremely delicate process as the fibres were fragile and the fabric became impossible to manipulate when too waterlogged. It was therefore necessary to stop frequently and blot away excess water before work could continue.

Most pieces responded favourably to this treatment, but in some cases spraying alone was not sufficient to dislodge the fine particles of mud which were embedded in the fibres. We found that the most effective method of dealing with this problem was to sew a layer of nylon net around the fragments to restrict their mobility and then immerse them in successive baths of Lissapol and warm water until the residue of mud had been removed. Particularly intractable crusts of earth could be removed from the textile when dry by a gentle stream of air (without abrasive powder) from the air-abrasive machine.

Once the textiles had been rinsed to remove all traces of detergent, the final part of the cleaning process was to pick out any remaining fragments of extraneous vegetable matter, such as grass roots, which had not been dislodged by washing.

The textiles were left to dry out naturally, although excess water was removed with the aid of blotting paper. This was fairly successful, the fabric retaining much of its flexibility when dry, but because the wool had lost most of its natural oils through the process of decay over the centuries, a tendency towards brittleness and crumbling was apparent. We counteracted this by applying a 5% (weight/volume) solution of Lanolin in Xylene, which although slightly darkening the fabric, consolidated the fibres, lending them greater flexibility.

Finally, the textiles were mounted onto sheets of thick blotting paper by means of threads tacked over them to hold them in place. In order to allow inspection of both sides of the fabric, windows were cut in the paper and the back was faced with clear polythene which had been pierced in several places to counteract condensation.

The textiles exhibit an interesting variety of weaves together with fragments of possible knitting. They are now awaiting detailed examination by Helen Bennet, the Museum's expert on textiles and costume.
Fig. 2. A completed piece of textile from Papa Stour.
The Acetone/Rosin Treatment of Wood at the National Museum of Antiquities

Tom Bryce

1. Introduction

In recent years many conservators have had to deal with ever-increasing volumes of perishable organic materials, particularly waterlogged wood. This is because of the increase in activity of underwater archaeology and in excavations of wet land sites. The conservator nowadays is expected to preserve specimens which might have been abandoned in past years. Invariably many museums and conservation facilities have a formidable backlog of waterlogged wood in storage awaiting treatment, and where this occurs, too much valuable time is needed for routine maintenance. This Museum is by no means an exception to this rule since we do have a considerable backlog of waterlogged specimens awaiting conservation, although this has arisen from a great number of years and it has been reduced somewhat over the past two years (particularly the processing of small/medium specimens of up to 1 metre long). Successful treatment of large timbers is a far greater problem and this is because of the constraints of capital, space requirements and the possible hazards of using flammable solvents in large quantities over long periods.

It is worth emphasising that no two waterlogged woods respond identically to treatment because of the complexity of the problems involved. Nor do conservators carry out their conservation in the same way. Some conservators will swear by one method for all wooden objects but really the choice of technique depends on many factors eg wood type, the extent of deterioration, the size of the object, the facilities available, and the conditions which the object will be subjected to after treatment. This will partly emphasise the reasons why so much of the published literature is contradictory.

2. Decay of Wood in Wet Environments

When wood has been submerged in water for a long period, it will deteriorate to an extent that is determined by the burial environment, the burial time and the wood species. Chemical effects, fungi, bacteria, wood boring creatures such as Teredo and Limnoria in sea water, all play a role in the breakdown of wood. The cellulose molecules become degraded causing a corresponding increase in the average diameter of the submicroscopic capillaries. As decay proceeds, the structure will become increasingly composed of the more stable lignin substances. Water is contained in wood as free water in the cell cavities and also in a weak chemical manner by bonding with hydroxyl groups formed as a result of the degradation of the cellulose.

The most striking property of archaeological waterlogged wood is its behaviour when dried in air without any prior treatment. Apart from loss of weight no change takes place until the free water in the cell cavities has gone and the chemically bound water in the cell walls starts to disappear. As this happens the wood will begin to twist, crack and warp. Shrinkage is normally greatest in the tangential direction and least longitudinally.

Deterioration of wood results in a great loss of mechanical strength of the wood and it is the water within the weakened cellulose structure which
provides strength for waterlogged wooden objects to withstand their own weight and keep their form. The moisture content of the wood is a useful guide in determining the extent of deterioration. It is important to note that with progressing degradation, the permeability and porosity of the wood increases, while the strength and the specific gravity decreases.

The National Museum of Antiquities of Scotland has had for a long time an urgent need for a suitable location to treat large timbers because of the necessary isolation and the safety requirements which the Health and Safety Inspectorate demand nowadays. We have acquired such a building (68 sq. metres), for a few years at least, fairly close to our main laboratories. This has allowed us to scale up our wet-wood programme using acetone/rosin so that we can treat our backlog of timbers of up to 8ft. long as well as cope with the current flow of small objects from Scottish archaeological sites.

![Image](image.png)

Fig. 1. General view of empty Acetone/Rosin impregnation tank showing copper heating pipes.
Fig. 2. Large Acetone/Rosin impregnation tank in use.

Fig. 3. Lid of outer tank being removed - stirrer rods have been dismantled.
Fig. 4. The Acetone/Rosin tank must have a fitting lid. This general view shows the asbestos cement lid fitted over the flange of the stainless steel tank.

Fig. 5. The asbestos cement lid is being lifted to inspect the solution - face masks must be worn.
Fig. 6. A Dräger Detector is being used to monitor the level of acetone vapour above the saturated acetone/rosin solution.

Fig. 7. Close-up of the Churchill Thermocirculator - tubes are insulated to minimise heat loss.
The basic principle involved in this method is to remove the bulk of the impurities within the wood with a dilute mineral acid, to dehydrate the water using successive baths of acetone, and finally to totally impregnate the wood with a saturated solution of rosin (colophony) in acetone at 52°C so that the cavity system of the wood will be filled, and collapse of the wood will be impossible.

Initially the wood is cleaned with a soft brush to remove mud, peat etc. and normally photographed at this stage. Fragmentary objects are drawn so that the pieces may be properly identified later on and any tagging is done with Teflon tape. This tape will withstand treatment with acids, alkalis, organic solvents and heat well in excess of 100°C. Delicate objects are splinted if necessary and any bagging of objects is done with perforated polypropylene sacking.

With composite artifacts of wood and iron, especially those excavated in salt water, the iron will corrode rapidly, mask much of the wood with iron corrosion and the wood will be filled with randomly distributed iron corrosion products. The removal of iron corrosion and calcareous deposits is a great problem. It can be slowly removed by careful mechanical cleaning (chipping etc) and by chemical means (eg 10% ammonium citrate etc).

Impurities within the wood will greatly hinder impregnation of any consolidant eg resin acid substances, extraneous organic matter, insoluble sulphides, gallates and tannates. The wood is thus treated with 3% technical grade hydrochloric acid to remove the bulk of the impurities. The presence of sulphides is easily recognised by the evolution of hydrogen sulphide during acid treatment. The result of acid treatment is quite remarkable and can change the appearance of an inky black waterlogged specimen to its natural colour in only a few days' immersion. The duration of acid treatment depends on the condition of the wood, the burial environment and the wood species. The acid contained in the wood must of course be thoroughly flushed out. This is done in continuously running tap water, the removal being checked by several pH readings taken from standing solutions of deionised water.

Unfortunately conservation treatments for wooden artifacts are not compatible with treatment methods for metals, and it is not always possible to separate metal components from wooden artifacts so that they may be treated separately. Wood/iron composites cannot of course be treated with dilute hydrochloric acid because of the harmful effect on the iron component but nevertheless the ironwork may be cleaned mechanically, treated for chlorides, and the entire objects conserved quite safely and effectively by Acetone/ Rosin as though they were all wooden objects.

Dehydration with acetone is the next major step. Acetone is chosen because of its miscibility with water, its ability to dissolve a reasonable amount of consolidant, its surface tension rating, and its relatively low cost. Dehydration is carried out by using successive baths of acetone to remove the free water within the wood and this is best followed by specific gravity measurements (S.G. Acetone 0.79). These acetone baths may be used several times for different batches of wood until they become too contaminated with water to be worthwhile using again.

The impregnating material is a solution of rosin (colophony) in acetone.
At room temperature the solubility of this solution is only 40% by weight but at 52°C the solubility is 67% by weight. Fortunately the vapour pressure of acetone above a saturated acetone/rosin solution at 52°C is lower than the vapour pressure for the pure solvent at room temperature. Nevertheless acetone is still a highly flammable solvent and all stages of the procedure must be carried out with great care, particularly when dealing with large quantities.

The impregnation is carried out using a 67% W acetone/rosin solution maintained at 52°C, bearing in mind that the quantity of acetone present in the wood from the dehydration will alter the specific gravity of the acetone/rosin solution, and this must be compensated for by the addition of more rosin. The acetone/rosin solution is monitored regularly by specific gravity measurements (a 67% W solution has a specific gravity of approximately 0.94 although the specific gravity of the rosin can vary slightly from batch to batch). Partly carbonised objects should never be put into the main impregnation tank because they will blacken the solution and ruin it for further use.

The acetone/rosin solutions are contained in stainless steel tanks and heated by pumping hot water from thermocirculators (electrical circuits protected) through copper piping fitted around the inside of the tanks.

Each impregnation tank is insulated by being contained within a slightly larger tank of plywood complete with lid, and by means of several inches of vermiculite below and around the stainless steel tank. Good fitting asbestos cement lids with neoprene rubber seals are necessary to avoid loss of acetone from the acetone/rosin solution within the stainless steel tanks. The acetone/rosin solutions are kept agitated at all times by stirrer rods, the electric motors being mounted externally on the lid of the outer wooden tanks.

The impregnation time depends on the wood species, the extent of deterioration and the thickness of the objects under treatment. In one extreme, one can have sound, dense waterlogged woods such as oak or lignum vitae which will require much longer for total penetration than soft, spongy waterlogged woods which are fairly easily impregnated. On removal of objects from the rosin bath, excess rosin is drained and swabbed off as much as possible without any use of solvent. The objects are placed within humidity cabinets to keep the objects as near 55% relative humidity as possible, until they have stabilised ie until all acetone has evaporated. The excess rosin is then swab-cleaned with minimal amounts of acetone to reveal the natural appearance of the wood.
4. **Advantages of Acetone/Rosin**

   a. Suitable for the treatment of most woods. Good dimensional stability in these cases.

   b. The final appearance of treated artifacts is a natural one with good weight properties. This is a particular advantage with fine detail on woodwork and for showing up details of the method of manufacture.

   c. Rosin is a natural product (residue from distillation process from pine trees). It is not hygroscopic.

   d. Objects consisting of several pieces may be assembled using normal adhesives (eg H.M.G.) and gap-filled if necessary. Sometimes it is necessary to dowel fragments together when there is not enough mechanical strength to support them. If wood is used as the dowelling material it should also be impregnated with rosin before being used, because of possible expansion or contraction due to R.H. changes.

5. **Disadvantages of Acetone/Rosin**

   a. The fact that one is dealing with a flammable solvent, special precautions are needed particularly with large quantities of acetone.

   b. The cleaning of excess rosin is messy and takes time and care to remove.

   c. Not suitable for some woods with particular difficulties (eg where preservation of bark is important, rosin is too brittle a substance to be effective since even the slightest shrinkage of the wood will leave the bark virtually unattached to the wood beneath it).
Display Materials Testing
Helen Dalrymple

To determine any long detrimental effects of the materials of a showcase on museum objects, environmental conditions have to be created to increase these effects in order that they may show up in a relatively short space of time. In general the best way of artificially speeding up such chemical reactions is by increasing the temperature.

For the tests reported here conical flasks with screw tops were used as containers and various combinations of materials added. Where a high humidity was required, 2-3 drops of deionised water were put in the flasks also. They were kept at a temperature of 60°C to give, in a few months, a comparison of effects which could occur over several years in the museum. Pieces of pure silver and lead were used to represent museum objects. Initially pH indicators were used to detect any acid fumes given out by various woods. The flasks containing lead were purged with carbon dioxide to enhance corrosion conditions, the remainder sealed in a normal air atmosphere.

The majority of tests have given negative results, to date, but in a few cases some degree of corrosion has occurred. (Only the adverse effects noted in the tests are stated in the results: any material mentioned without a result may be assumed to have shown no effect.).

Wood – Chipboard, Plywood, Mahogany, Pine, Sundeala and Obichi were examined.

- Chipboard – initially gave highly acidic fumes which gradually decreased over a period of two months.
- Plywood – fairly acidic fumes which did not diminish.
- Pine – fairly acidic fumes which did not diminish.
- Sundeala – slightly less acidic than the previous two.

Mahogany has been proved in the past to be an ideal wood for museum showcases and because of this, and the apparent lack of it in new cases, it was decided for the present to leave it out of further tests.

Sundeala, Obichi and Chipboard were examined more carefully since they appear to be in greatest use in our own museum.

Sundeala and Obichi with Silver

The relative humidity was initially set at 70% by the addition of a few drops of water. In the flask containing Obichi, this changed to zero over one month whereas the humidity in the Sundeala flask remained constant. The Obichi was slightly swollen and soft to touch indicating absorption of the moisture. The silver from the Sundeala flask became badly tarnished compared with little tarnishing of the silver in the Obichi flask.

Chipboard

Because of the acidic fumes given off by chipboard, and because of its frequent use in the museum's showcases, it was decided to look at its effect when painted. Pieces of pure lead were washed in dilute acetic acid and weighed
before use: one of two pieces of silver in each flask was lacquered in the same way as a conserved object.

As in previous tests, carbon dioxide was added to flasks containing lead and three drops of deionised water were added to half of the flasks to give high humidities.

The Chipboard was coated with two types of paint - Dulux Silthane Silk and Leyland Vinyl Matt. The contents of the flasks were examined periodically for tarnishing on the silver and the production of lead carbonate on the lead. Because of the small size of the lead pieces this would have been difficult to detect and only a vague visual assessment could have been made, therefore the lead was washed in dilute acetic acid and weighed each time to detect weight loss. Loss of weight is caused by the corrosion product, but not the lead, dissolving in the acid. The various weight losses of the lead are shown in Table 1.

During this time, flasks were prepared containing coin envelopes with silver and lead.

The unlacquered silver showed more tarnishing than the lacquered pieces in all flasks including the blanks, this being more marked in the flasks containing Chipboard with Dulux, (both high and low humidity). The coin envelopes did eventually cause some tarnishing of the silver which was probably due to fumes given off by the adhesive being affected by the heat of the oven; this effect is unlikely to become apparent in their normal use.

<table>
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<th>Flask Contents</th>
<th>2 weeks</th>
<th>4 weeks</th>
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<th>21 weeks</th>
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<td>0.8</td>
<td>0.9</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>&quot;Wet&quot; Blank</td>
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<td>0.8</td>
<td>1.0</td>
<td>1.8</td>
<td>1.9</td>
</tr>
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<td>0.7</td>
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</tr>
<tr>
<td>&quot;Dry&quot; Chip.+ Dulux</td>
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<td>0.9</td>
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<td>-</td>
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<td>0.7(15 wks)</td>
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</tr>
<tr>
<td>&quot;Wet&quot; Envelope</td>
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<td>-</td>
<td>0.5(10 wks)</td>
<td>1.9(15 wks)</td>
<td>2.0(19 wks)</td>
</tr>
</tbody>
</table>

Table 1

The high weight loss for "wet" Chipboard and Dulux (the "wet" referring to high humidity) became noticeable after fifteen weeks, when it jumped, over a period of two weeks, from 0.7% to 10.3% with no apparent change in conditions.

Compared with the relatively high values of the Dulux/Chipboard combination, the Leyland Vinyl Matt/Chipboard appears to give quite good results with the paint giving a good seal round the wood. The rather large difference in weight losses does suggest that paints should be checked before being brought into extensive use in the museum.
Again, the effect of heat on the coin envelope adhesive is the probable cause of the last result listed in Table 1.

Conclusions

The results show that if Chipboard has to be used, a paint such as Leyland Vinyl Matt is necessary to reduce its corroding effect. Obviously, a paint such as the Dulux used here, should be avoided, since it either does not form a good seal over the surface of the Chipboard or may itself give off corrosive vapours.

Although the Chipboard used eventually stopped producing acidic fumes, this does not mean that all Chipboard will behave in this way. Both Chipboard and Plywood are made up of "waste" wood bonded together with an adhesive, therefore their composition will vary as will their effects. Plywood and pine also both give off potentially harmful acidic fumes. Obichi appears to be an excellent wood to use in showcases having no tarnishing effect on silver, unlike the Sundeala. Finally silver itself should be kept lacquered to minimise tarnishing when exhibited with these display materials.
Moulding and Casting. Two Objects from Birsay

David Hogg

Introduction

Two principal moulding materials are in use in the Museum laboratories, the choice being dictated by the soundness and porosity of the original artifact to be reproduced. The description which follows is intended to show how each of these materials is used. The subsequent casting procedure in polyester resin is largely the same in all cases.

The Original and Pre-Moulding Treatment

Prior to moulding, a careful examination of the artifact is carried out to anticipate any problems which may occur. The surface is examined for flaking, cleaving, porosity, corrosion etc. Even in the case of fragile objects, impressions may be made if the risk of damage can be greatly reduced by precautionary consolidation and/or lacquering without obscuring fine detail on the original. In most cases, a very fine separation layer is applied to the surface of the artifact to protect it from the moulding material, and to reduce the movement of air from cavities within the object which might otherwise disrupt the contact between the object and the moulding agent. Obviously, any protective layers must be removable after moulding, and have no adverse effects on the condition and appearance of the object.

The first object (Fig. 1) is a seal tooth, 7cm long, with engraved runes, fashioned to the appearance of a fish, with drilled 'eyes', the 'mouth' being formed by the natural opening at the root. The runes were emphasised in black. The tooth had two deep cracks; one running the entire length of the top, the other from the tail to mid-way along the unengraved side. (Because of the anisotropic nature of both bone and ivory, such warping and cracking is not uncommon.) The widest surface separation was a little under 2mm and was caused by the larger of the two cracks. This afforded a view of the interior, which appeared largely sound with only a slight tendency towards brittleness. The object was otherwise in good condition with a high polish, although with soil and fine grit along the cracks and around the eyes and mouth. This was removed by local brushing with alcohol, since it did not yield to dry brushing. Before an impression mould was made, the interior of the tooth was consolidated and the cracks filled to prevent penetration by the moulding material. The consolidant, cellulose amyl acetate, was slowly injected by syringe through the larger crack and left to harden off. In the case of the cracks, Plasticine would have served as a temporary stopping against the moulding material, but it was decided that the object should be further strengthened by filling them with an adhesive which would remain after moulding. An epoxy putty was inserted along the cracks, care being taken to avoid applying any to the polished surface of the tooth. The putty was tinted after moulding to a close colour-match with the original.

The second object, a 'toggle' in the shape of a closed S (Fig. 2) is 12cm long. The top surface showed signs of previous flaking with two small laminated segments partially detached. This surface had a very light intermittent polish. A deep crack some 3cm long ran along one of the outside curves and had resulted in a slight deformation in shape - a maximum movement of about 2.5mm. The bottom was irregular, honey-combed and fairly brittle. Soil was trapped in the many crevices and hollows. This was removed by mechanical picking with wooden probes and light, rapid washing with alcohol swabs. After cleaning, the toggle was consolidated by immersion in cellulose amyl acetate under low vacuum. This method allowed air to be drawn slowly from the interior of the object, the air being replaced by the consolidant in which the object was totally immersed.
Much better impregnation was achieved than is possible with manual application via surface brushing. Excess consolidant was swabbed from the surface and the object air-dried. The two flaking areas on the top surface were then repositioned with cellulose nitrate adhesive under light pressure and allowed to set. The large crack was filled with repeated thin applications of this adhesive until the infill was almost level with the surface, the gap being closed as much as the object's flexibility would allow with very light clamping. At this stage both objects were ready for moulding.

Fig. 1. Birsay Seal Tooth and Replica (upper).

Fig. 2. Birsay Toggle set in Plasticine ready for moulding.
Moulding

As stated above, the choice between moulding agents is governed by the nature and condition of the original. Although many materials may be used to obtain a negative impression of an object (some hot-melt, others cold-curing), the two used in the Museum Laboratories are a synthetic silicone rubber and rubber latex, both of which are cold-curing.

The superior material, silicone rubber, is available in various grades, ranging in viscosity from very liquid to a stiff paste, all curing to give a strong, flexible mould - the thinner variants being better suited to the recording of very fine detail. The material used in the Laboratories is a liquid cured by use of an organic peroxide catalyst and since there is no loss of material via evaporation while curing, it is, and remains, very stable dimensionally. The shrinkage rate of silicone rubbers is very low - probably not much more than 1% on average. The mould gives excellent rendering of detail and casts may be taken repeatedly without appreciable loss of definition. The curing time depends, of course, on the amount of catalyst present - 2% V curing in about 30 minutes at normal room temperature. The flexible and relatively long working life means that the base and catalyst may be mixed together thoroughly but not over-hurriedly - so that air bubbles need not be trapped in the mixture from where they may disfigure the surface of the mould. However, the combination of curing-time and fluidity has the disadvantage that the silicone rubber can be used only on objects with a sound, closed surface where there is no danger of it penetrating beneath. Such an occurrence would be extremely damaging to the original! The seal tooth, however, was ideally suited to the use of this material. The further disadvantage should be mentioned - silicone rubber is very expensive!

The toggle was too open and porous for silicone rubber, so the second method, vulcanised rubber latex, was used instead. Several layers are applied, each being allowed to dry before the application of the next. The latex dries very quickly by evaporation of water (and a little ammonia) and does not enter small capillaries etc to any great extent. Providing deeper cracks, crevices and undercuts are carefully stopped so as to register an impression but afford no deep penetration the original object will come to no harm. Unfortunately, the latex is subject to dimensional changes at all times, and records detail less finely than silicone rubber. Also, the completed mould is rather flaccid and requires a supportive, containing, mother-mould. The mould shrinks and deteriorates under the action of ultra-violet light and subsequent castings show an increased loss of finer detail.

The Birsay objects were set up similarly for moulding. Firstly, the 'eyes' and 'mouth' of the tooth were filled with Plasticine to within 1mm of the surface. This would record the exact position and top details of these features whilst stopping-off the interior. Each object was then coated with a thin protective film of silicone wax release agent (dissolved in n-hexane). (A prior test had shown that the black in the runes of the tooth would not be affected by the solvent.) Each object was to be moulded in two pieces. Therefore, each was set firmly in a level bed of Plasticine with half its surface exposed for moulding in such a way that major cracks in the original would match with joint lines in the finished replica. It was ensured that the Plasticine/artifact contact was complete to prevent seepage of moulding material.

The mould from the tooth was made as follows. A wall of Plasticine was built round the tooth's platform to form a basin slightly higher than the highest point on the object's surface. (Fig. 3.) The catalysed silicone rubber was brushed thickly over the tooth, making certain that no air pockets resulted. The rest of rubber was then poured slowly into the Plasticine basin until
covering the high point of the tooth by several millimetres. This was left for several hours to cure completely. The Plasticine was then removed (Fig. 4). The silicone rubber surface surrounding the tooth was coated with Lacomit resist. A Plasticine wall was made around this and the process repeated to give the second mould and allowed to cure. Only after this was the object separated from the completed moulds.

Fig. 3. Seal tooth set in plasticine ready for moulding.

Fig. 4. Seal tooth in half mould.
The toggle, set in its Plasticine base (Fig. 2) required no containing wall. The clear latex was painted and stippled over object and Plasticine with a soft brush. It is necessary to work quickly but avoid making air pockets and bubbles. As soon as the first coat was dry (the latex becomes semi-opaque at this stage), a second coat was applied. After a third coat, a stiff paste of latex and wood-flour was applied on top. This was smoothed off with liquid latex and left to dry overnight. (From the second latex coat onwards, drying may be accelerated by the use of gentle heat - eg with hair-dryer.). A mother mould was then prepared. Firstly, a separation layer was applied over the latex/wood-flour by covering it with a layer of scrim onto which thick wax polish was rubbed. Coarse-chopped strand fibre-glass layers were applied in overlapping strips and stippled with catalysed polyester resin, making good contact with the contours of the latex/wood-flour beneath. When dry, the whole was turned over, the Plasticine removed (making sure that the toggle remained in its half-mould), the latex painted with Lacomit resin, and slight separations between object and mould filled with silicone wax release agent. The moulding process was repeated. The mother moulds were then removed and the latex moulds gently peeled away from the toggle, avoiding tears in the latex. The wax release agent was removed from the bone object with n-hexane.

Casting

Polyester and epoxy resins provide very durable casts. They also make possible light-weight, strong reproductions of very large objects.

Before casting, batches of polyester resin were pigmented with dispersion dyes and tested for colour alongside the Birsay artifacts. The tooth had two obvious colour areas and dyed resins were prepared accordingly. The toggle appeared generally uniform in colour, the top surface being only slightly lighter than the rest. On closer inspection, the colour surface was seen to consist of many different hues, but this fact was disregarded for the moment and, again, two batches of resin were mixed, one fractionally lighter than the other. Local variations were simulated on the finished replica. Portions of these stock resins were decanted, and then catalysed as they were required.

In each case, the resin for the first coat was diluted slightly with unpigmented resin and its hue altered fractionally with dye. Since the resin is semi-transparent on application, opacity being achieved after two or three coats, this helped modulate the perceived surface and obviate excessive evenness of colour. The resin was brush-stippled over the area of the mould presented by the object and allowed to cure between coats.

For the toggle, various sands and some powdered graphite were added to the second and third coats to imitate a graininess in the original; and in the case of the tooth, several unsuccessful attempts were needed before the two different colours merged in a way similar to the original.

Fibreglass reinforcement was added after the third coats; one layer of fine surface matt followed by two of chopped strand, each layer consisting of several overlapping pieces carefully trimmed to the impression boundary. On curing, the casts were removed from their moulds and trimmed where necessary.

The two parts of the cast tooth were filled with an epoxy adhesive and then assembled with the same material. The eyes, mouth and cavity behind them were drilled out later with dental burrs. The runes were painted and the cast glazed with a little oil colour in dammar varnish/turpentine to replicate colour variations and the degree of gloss on the original.
The toggle was assembled using the same adhesive. Filling, for additional strength and appropriate weight, was done by injection of a weighed amount of liquid epoxy resin. The replica was rotated while the resin cured, to reinforce all surfaces and to distribute weight evenly. The case was finished off with a little oil-colour in a medium containing a silicate matting agent to dull down the resin's lustre.
Conservation of Two Roman Wheels with Iron Tyres

From the Roman Fort at Newstead

Mary Macqueen

The Roman Fort at Newstead is about a mile from Melrose and is near the River Tweed. The earliest reference to the site was made in 1743 by the Rev. Adam Milne, and the first notable find from the site was an Altar, discovered in 1783, now in the National Museum. In 1904 the Council of the Society of Antiquaries decided that the site was worth investigating and Mr. James Curle, W.S. was asked to excavate it. He lived about 2 miles from the site and so for the next five years from the 13th of February 1905 until 19th of May 1909, continuous excavations were carried out. Further work has since been done on the site.

The wheels came from Pit 23 and consist of an iron tyre, a wooden felloe, a wooden hub with iron nave bands and ten wooden spokes. They are 3ft in diameter with the felloe a single piece of ash bent, through artificial softening, to present one joint held in place with an iron clamp. The ten spokes on each wheel (Curle says 'eleven') are thought to be made from willow. The hubs, one quite badly damaged, are thought to be elm and lathe turned. The spokes are fitted to the felloe and hub with a square tenon. Curle reported that a ten spoked wheel of a very similar type with a single piece of ash bent to form the felloe, was discovered at La Tène, in Switzerland, in 1882. Another wheel, of oak, much thicker and coarser and without an iron tyre was discovered at Newstead, and is also exhibited in the National Museum. Conservation work was also carried out on this wheel recently. When the Roman room of the National Museum closed in the early part of 1979 for extensive renovations the opportunity came for the conservation laboratory to treat the wheels, after which they will be displayed together in a new case specially constructed, which will sit in the middle of the room.

The condition of the wheels over the years had deteriorated quite considerably so they were very fragile. The wood had originally been wet when excavated, but had been allowed to dry out without treatment, thus causing it to warp and distort. This was aggravated further by the climatic condition of the gallery which had been too hot for much of the time consequently causing low relative humidity, the wheel remaining in these conditions for many years. One felloe had completely separated from the iron tyre, which had split, although the second tyre and felloe are still intact. The tyres and wood had only been lightly cleaned when first excavated and were still quite muddy. This had led to problems with mould growth, which was feeding on the wood and was quite active. Mould, if left for any length of time will cause damage to wood; in fact there was some evidence of this on one felloe in particular. It was discovered during preliminary investigation that the iron was in surprisingly good condition, with, in places, sound, uncorroded metal immediately below the corroded surface, yet in other areas the corrosion was quite severe.

At first, treatment began in the Museum gallery itself, but because of the chemicals used this proved impracticable and later the wheels were brought down to the laboratory. Two boards of the correct size for each wheel, 3 1/4" square were cut and a special dexion frame and platform was constructed. The most pressing problem was the condition of the wood, so this was the first job tackled in the conservation of the whole object. The felloes were first cleaned with a stiff brush to remove most of the loose dirt. A solution of warm water and a non-ionic detergent (Lissapol N) was used, very sparingly, to remove the
dirt. This was then rinsed thoroughly followed by washing with a solution of Tego B, a fungicide, to treat the mould. The wood was not allowed to get too wet and was wiped dry as quickly as possible and then slowly allowed to dry out further to prevent any further warping after the use of the water.

![Image of iron tyre and wooden felloe]

**Fig. 1.** The iron tyre and wooden felloe on a board at the lab. The iron is in the process of being cleaned.

When the broken wood was dry it was consolidated with increasing concentrations of cellulose amyl acetate. Next the broken pieces were glued together with H.M.G., a cellulose nitrate adhesive. Araldite had to be used in one or two areas for extra strength, although it is better if possible to use a reversible adhesive, which acetone will dissolve. On the felloe No. 1 which was in several pieces, very warped and also detached from the iron tyre, only one or two pieces could be joined together. The degree of warping was so great that the felloe would not fit together without undue strain being put on other areas of the wood, with consequent danger of cracking and splitting. After reassembly a wood filler, Plasmolegmo, consisting of Kaolin and clay in a water vehicle, with cellulose glues and fungicide, was used to fill the gaps. The filler is reversible, and can be removed easily. The filler when dry was painted with acrylic paints, to nearly match the colour of the original wood. Finally the wood was waxed lightly with beeswax and Toluene.

The spokes were treated in a similar way, cleaned, strengthened, and waxed. Three of the spokes which were broken, were joined together. It was necessary to use wooden dowels in addition to H.M.G. adhesive for each joint.

The hubs were treated in a different way to begin with because they had both been treated previously with shellac, which had yellowed with age. Industrial methylated spirits was used to remove the shellac off both the wood and the iron rim of the hub, which was also covered with it. The iron encrustations on the wood and as much of the iron corrosion from the rim as was possible to remove, were picked off using a pin vice and other small hand tools. Lusol, a rust solvent and lubricant, was used to help to separate the corrosion from the iron. Next the hubs were consolidated with cellulose amyl acetate as the felloes had been, loose pieces first being fixed down with H.M.G. adhesive. The rim needed
a stronger adhesive so in this case Araldite was used.

Araldite was used to glue the worst of the structural cracks in the hub wood, too, as the hub was to stand upright without any additional support. The gaps were again filled with Plasmolegmo, which when dried was painted with acrylics.

![Fig. 2 Preliminary reconstruction of wheel 2.](image)

![Fig. 3 The position of a completed original spoke, joining in the middle and at hub and felloe tenons.](image)
Fig. 4. The spokes are at this point about to be dowelled.

One of the iron nave bands was broken, had sprung apart, and was in fact tied together and held with string. It was necessary to exert pressure to pull the surfaces together by tightening the string, and then Araldite was applied as the adhesive, mainly to the inner surface, of the joint. The repair was disguised by applying Rosenberg cement over the outer surface and gap-filling the area. Rosenberg cement is an easily reversible material, used in the gap-filling of iron objects, mainly for cosmetic reasons but occasionally as an alternative to using Araldite.

The iron tyres were treated next. The corrosion and dirt was picked off, and the more stubborn corrosion impregnated with Lusol to soften and separate the corrosion layer from the sound metal. Then by using a hammer and small chisel the large lumps of corrosion were tapped off leaving a good original surface, even some bright shiny metal! This treatment was only carried out after first carefully ascertaining that the iron under the corrosion was fairly strong and sound, and therefore able to withstand this rather harsh treatment. Then the whole tyre was rubbed down with Lusol and fine grade wire wool. The Lusol was removed with toluene and finally the iron was coated with micro-crystalline wax, to which a little powdered pigment was added, this being done after the metal had been thoroughly dried with acetone. Normally iron would be boiled to remove chlorides but in this case it was not possible.

Next the wheels with hubs and spokes were placed on the dexion frame and the position of the spokes determined.
Fig. 5 Wheel 2 nearing completion with replica spokes and perspex mounts.

There were about thirty pieces of spoke, some had proved to fit together making about four original complete spokes, but many were in pieces which could not be joined together. However in these cases it was found that some correct joins with either the hub tenon or the felloe tenons could be made. Thus gradually places were found for the majority of spokes. Some had just to be placed in the middle as they did not fit to either tenon. There were still some gaps with no spokes at all, and completely new spokes were made from the hard wood Ramin for each. These new spokes were then stained to nearly match the colour of the original wood. Next little perspex supports were made to lift and hold each spoke, or part of a spoke, in its correct position in relation to the tenons in the hub and felloe. The whole job is now virtually completed and the wheels will soon be on exhibition.

When the renovated Roman gallery opens in March 1980, the wheels will first be exhibited in a small metal frame constructed by the staff at Ingliston, while the special new case is being made. This frame is to be placed in the large case on the far wall of the room. The final display will be in the centre of the room so that visitors can walk all the way round viewing it from every angle.

The ideal environmental conditions for the wheels would be a constant relative humidity (50%) and fairly constant temperature (20°C), to prevent any further deterioration in the condition of the object, which still remains in a very fragile state.
Fig. 6. The Dexion frame constructed for reassembling the wheels.
The Perth Barrel Locks

Lesley Nock

In recent years the Perth High Street Excavations have provided the National Museum Laboratories with a large number of interesting finds, most of which are from the mediaeval period. These range from leather, basketry and wooden bowls to iron tools and fine jewellery. One series of objects of particular interest were barrel locks. These posed an interesting conservation problem, as they were found to be composite objects, those made of more than one type of material.

Barrel locks were the mediaeval equivalent of door locks, not unlike our modern padlock in design. There is always a cylinder, normally with fins on the outside, into which a spring is pushed. This spring is hinged to allow it to swing clear of the barrel when the lock is released from below with a key (see Fig. 1). At first it was not obvious to us how these locks functioned until one was found with the spring still pushed home in the barrel.

Fig. 1. A typical barrel lock in the open and closed position, showing the operation of the spring.

Although the diagram above shows the basic design of a barrel lock, the Perth locks did in fact vary considerably in size and design. One of the smallest locks, 65mm long and only 15mm wide, was delicately designed with fine twisted fins and evidence of tinning. Fancy designs were also found on some of the heavier locks. One in particular, measuring 70mm by 70mm, had fancy scrolls round the barrel and a scrolled handle on the side (see Figs. 2 and 3).
Fig 2. One of the smallest of the Perth barrel locks. 6.5cm

Fig. 3. One of the largest of the Perth barrel locks showing fancy scrolling on barrel.
There were a few locks that at first did not appear to be barrel locks, and certainly showed no signs of plating or tinning. One in particular appeared to be only a large rusty lump of iron. (See Fig. 4). Fortunately there were x-rays available for most of the locks. The x-ray of this object showed clearly the fins on the barrel so characteristic of many of these locks. (See Fig. 5). Radiography is of great help to conservation in showing up the original outlines of a badly corroded object, which means that corrosion removal can be undertaken with more confidence. Perforations and patterns as well as inlays of different metals which may be totally hidden by corrosion, show up clearly on x-rays as either dark patches in the case of holes, or light areas in the case of inlays. X-rays proved to be an invaluable aid in the conservation of the Perth barrel locks. After cleaning, the lock described above proved to be fairly well preserved barrel lock with copper plating. (See Fig. 6).

Fig. 4 The original appearance of the barrel lock in Fig. 6 below.
Fig. 5. X-ray of a large corroded lump of iron revealing the barrel shape and fins of a barrel lock.

Fig. 6. Barrel lock shown in Figs. 4 & 5 after conservation.
cleaning would only damage the object or make it so fragile that it would be in danger of disintegration.

At this stage iron objects would normally be boiled in deionised water to remove soluble salts. The barrel locks however, being copper plated, it was decided not to risk damage by boiling and they were dried off thoroughly in the drying oven instead. After drying the copper was brush coated with benzotriazole in a suitable solvent. Benzotriazole is a chemical used to stabilise the copper and arrest corrosion. The finishing touch was to wax the objects with beeswax in toluene to seal out moisture and give the surface a pleasing gleam.

These barrel locks are a typical example of the conservation problems the laboratory frequently has to deal with. Composite objects always need extra care and thought. Often, as is the case here, treatment of the surface plating or coating on metal objects has to take priority over the underlying material, as this is what gives the object its character and special interest. The result of this treatment should be a stabilised object which still shows its original character.
Current Work on Large Objects

Alex Quinn

Being fortunate enough to have such a well equipped laboratory, a great variety of conservation treatments and techniques can be readily applied to artifacts small enough to be easily handled and contained.

However, treatment of large objects is often taken for granted as being just as easy to execute but in reality, regardless of how simple the treatment method used, is invariably fraught with problems of a more practical nature.

Current large artifacts for conservation include a beautiful bronze bell, cast in 1723, standing 62cm high, 76cm wide and weighing almost 450kg, and five iron wheel rims, measuring 108cm in diameter from the Roman site of Inchtuthil. All objects were under attack from corrosion, which is essentially an electrochemical phenomena occurring in the presence of water, oxygen and dissolved salts. In the case of material excavated from soils or marine sites, the salts are largely chlorides. After recovery, these salts and all moisture must be removed completely to prevent further corrosion. If this is not done successfully, the object will begin to corrode again after a relatively short period of time.

Close examination revealed that corrosion was fortunately restricted to superficial areas and that all objects were structurally sound and strong. It was decided, therefore, to use the basic treatment method of immersing the objects in baths of boiling deionised water. Most of the harmful salts, notably chloride, are soluble in water and heating the water accelerates their release from the artifact into the water, the salt content of which is constantly measured using a conductivity bridge or chloride meter or a combination of both. After a period of boiling, the wash water is drained off and replenished with fresh deionised water and reboiled. This is repeated until no further salts can be detected in the wash water or until a tolerably low level of salts is reached.

Using this process followed by fastidious drying and lacquering we can hope to effectively halt corrosion and render the object 'stable'.

In the case of the iron wheel rims from Inchtuthil, we did not possess a tank large enough to accommodate them nor sufficient heating equipment to boil the water. A specially constructed stainless steel tank had therefore to be purchased at a cost of £472 and can be seen in Fig. 1 supported above two heavy duty hot-plates which cost £335 each. It is obvious from this that conservation of large objects, quite apart from manpower and electricity costs, even using the cheapest and most readily available chemical, can prove to be an expensive venture possibly outwith the realms of contemplation of small and not so well endowed conservation laboratories.

The treatment of all five wheel rims have now been completed. Initially, all were individually washed with toluene and gently wire brushed to remove all traces of Gum Dammar (previously applied lacquer) and grease and were dealt with in two batches, three wheel rims being boiled together in Lot (1), the remainder in Lot (2). Each bath contained 250 litres of deionised water and each lot was boiled for 24 hours in two changes of deionised water, samples of which were taken after each boiling and their chloride content checked using a chloride meter (since most salts harmful to iron are chlorides).
The results obtained were:

<table>
<thead>
<tr>
<th>Lot (1)</th>
<th>1st Boiling</th>
<th>2nd Boiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot (1)</td>
<td>9mg Cl/L</td>
<td>1.5mg Cl/L</td>
</tr>
<tr>
<td>Lot (2)</td>
<td>10mg Cl/L</td>
<td>&lt; 1mg Cl/L</td>
</tr>
</tbody>
</table>

Fig. 1 The first of the Roman Wheel rims being positioned in the stainless steel tank, prior to boiling in deionised water.

Having removed virtually all chlorides from the iron wheel rims by boiling, it was then necessary to dry them thoroughly. This we did by heating the rims using three infra-red heaters in rotation for the duration of an entire day to ensure all possible moisture was driven off. While still hot, the artifacts were then lacquered using a 10% polyvinyl acetate solution in acetone to which pigment and matting agent were added.

The bronze bell will receive the same treatment accorded the iron wheel rims although fortunately it will not be necessary to buy a purpose built tank. An existing stainless steel tank, used to store acetone, has simply been borrowed for the duration of the treatment, the same aforementioned hotplates providing the heating power. It was necessary to build a support platform for the bell to facilitate raising and lowering and to avoid air being trapped inside the bell during immersion.
Fig. 2 The Bronze Bell, cast by Robert Maxwell in Edinburgh in 1723.
Fig. 3 The Bell being hoisted, on its supporting platform, into the tank. 400 litres of deionised water were required to completely engulf the object.

Only the inner and outer surfaces of the bell show signs of active bronze corrosion so these surfaces will periodically be brushed during treatment to aid the release of harmful salts, in this case, not only chlorides but nitrates, sulphates and possibly phosphates. Samples of the wash water will be scrutinised this time using a conductivity measuring bridge, a device employing a potentiometer which registers a null deflection when no salts are present in the sample. Several changes of deionised water will be required during boiling and treatment could be ongoing for three weeks or more to extract the salts from the superficial corrosion. Heating by infra red will continue for 2 to 3 days before painting with Incralac, a lacquer specially prepared for bronzes.
The Treatment of Lead Objects from a Marine Site

T. Skinner

The wreck of the HMS Dartmouth produced many leaden objects of various types: small weights (for plumblines?), musket shot, and various components, pipes and sheets, from the ship's scuppers. The photographs below show a scupper pipe covered in encrustation, together with a close-up of the surface detail.

Fig. 1 Scupper Pipe untreated.

Fig. 2 Scupper Pipe surface detail.
Small lead objects had previously been cleaned in the laboratory at Granton by exposure to ultrasonic vibrations. Unfortunately, these lead scupper pipes dwarfed the ultrasonic bath and an alternative method had to be found. As lead is extremely soft, manual methods of cleaning tend to injure the object, and to clean these pipes using a sandblasting tool such as the air-abrasive machine would have taken years, especially as the encrustation was extremely hard.

It was decided to treat the lead by electrolytic reduction in a dilute solution of sulphuric acid. Lead is hardly attacked by sulphuric acid in the cold, as an impervious monolayer of lead sulphate is formed. However, if the lead is protected by a supply of electrons from an external source of D.C. current, this layer of sulphate does not form and hydrogen gas is evolved at the metal surface, or cathode. The sulphuric acid, being a strong acid, dissociates in water according to the following reactions.

\[
\begin{align*}
H_2SO_4 & \rightleftharpoons HSO_4^- + H^+ \\
HSO_4^- & \rightleftharpoons SO_4^{2-} + H^+
\end{align*}
\]

The hydrogen ions, or protons, are attracted to the negatively charged cathode, where they combine with electrons provided by the electric current.

\[
2H^+ + 2e^- \rightleftharpoons H_2 \text{ (gas)}
\]

Bubbles of hydrogen gas form on the metal surface and escape. In doing so, they exert a brisk cleaning action, dislodging particles attached to the surface of the lead. At the same time, \(SO_4^{2-}\) ions are attracted to the anode (which in this case was mild steel) and there the following reaction occurs:

\[
2SO_4^{2-} + 2H_2O \rightleftharpoons 2H_2SO_4 + O_2 \text{ (gas)} + 4e
\]

As the encrustation on the lead in this instance was mainly a marine deposit of carbonate, the acid electrolysis will also help to clean the pipes by an acid attack on the carbonate.

\[
CaCO_3 + H_2SO_4 \rightleftharpoons CaSO_4 + CO_2 + H_2O
\]

This results in a softening of the encrustation, making it more easily removable by the evolving hydrogen gas. The picture below shows the apparatus used.
Fig. 3. Electrolytic reduction of scupper pipe.

The container is plastic, the anodes are mild steel plate and the wires suspending the pipe are copper. The transformer used is capable of giving a maximum of 20 amps D.C. at about 20 volts in this system. The voltage is adjusted until hydrogen gas is seen to rise vigorously from the surface of the lead; the current must be switched on before the object is immersed in the acid to prevent the formation of a layer of lead sulphate which would prevent any current passing. Occasionally the object is removed from the bath for brushing and inspection. When treatment is considered finished, i.e. when all the encrustation has been removed, the object is removed and placed in deionised water which has been boiled to remove dissolved carbon dioxide. The pH of the water is tested; if it decreases the dionised water is changed. This is continued until no trace of sulphuric acid remains. The object is then removed, air dried and coated with a 10% solution of polyvinyl acetate in acetone.

The results of this sort of treatment are illustrated by Fig. 4 below of the scupper pipe shown previously.
Fig. 4 Completed scupper pipe.

It is also interesting to note that pure lead is extremely malleable. Some of the scupper pipes were bent and distorted when found. These were easily reshaped, without damage. This can be seen in the Figs. 5 and 6 below showing the same pipe before and after reshaping.

Fig. 5 Distorted scupper pipe.
Fig. 6 Reshaped scupper pipe.
X-Ray Fluorescence Analysis

Jim Tate

The analysis of artifacts by x-ray fluorescence (X.R.F.) is in many ways the ideal tool for museum environments: results are rapidly collected, the method is virtually non-destructive and for qualitative analyses little surface preparation is necessary. The analysis refers only to the surface of the object (generally to a depth between 0.01 and 0.1mm) so some surface preparation is needed on metallic objects suffering from corrosion. If in these cases samples are removed, perhaps by drilling or filing, X.R.F. has the further advantage over chemical techniques that the samples are not destroyed and can be kept for future reference. As has already been mentioned, X.R.F. is particularly useful at the laboratories for rapid qualitative analysis of artifacts which are being treated by the Conservation Laboratory, both before and during the conservation process.

The principles of X.R.F. are very simple. Atoms, the building blocks of matter, consist of a dense positively charged core, the nucleus, surrounded by orbiting negatively charged electrons; the whole affair resembling a solar system in miniature. The electrons remain associated with their parent nucleus because of attraction between positive and negative charges. The immediate problem with such a model, which was initially proposed by Rutherford in 1911, is that the orbiting electrons ought to lose energy and tumble into a central nucleus, this rather drastic event occurring in a fraction of a second. Since we - and therefore atoms - clearly do last somewhat longer it was proposed by Bohr in 1913 that there are certain stable orbits which electrons can occupy thereby maintaining the required atomic structure. A maximum of two electrons can occupy each stable orbit: those electrons closest to the nucleus are most strongly bound, while those in the outer orbits are much more weakly bound to the parent nucleus; in fact it is these outer electrons which are used as the 'glue' binding different atoms together to form solid bodies. The separation between different electron orbits depend on the amount of positive charge on the central nucleus: this latter is the principal characteristic of different atoms, known as the atomic number.

If an electron is removed from the innermost orbits the vacancy will very rapidly be filled by an electron from one of the outer orbits (this second vacancy being fitted by an electron from further out until a 'spare' electron can be caught for the outermost orbits). The transition of an electron from an outer to an inner orbit releases energy as an x-ray, the energy of this x-ray being equal to the energy difference between the two electron orbits. Since the energies of the orbits are characteristic of the atomic species the x-ray energy will also be characteristic. Thus the type of atom can be recognised by its x-ray "finger-print".

In practice there are various ways in which the analysis can be performed. At the laboratory electrons are knocked out of their stable orbits by irradiation with x-rays from a radioactive source. The subsequent fluorescence x-rays are detected using a solid-state detector. The detector, which is a single crystal of silicon doped with lithium, gives an electrical pulse whose magnitude depends on the x-ray energy. These pulses are sorted out in a multi-channel analyser to give a spectrum of number of detected x-rays versus their energy. This spectrum has the distinct peaks which reveal the presence of each atomic species present as a major or minor constituent of the object being examined.
Fig. 1. General view of the x-ray fluorescence apparatus.

Fig. 2. Close-up of the detector and radioactive source showing examination of one of the tortoise brooches.
The apparatus is illustrated in Figs. 1 and 2. The detector has an energy resolution of 160eV at 5.9KeV. The Canberra series 80 multichannel analyser contains various sophisticated peak identification, energy calibration and smoothing routines, has 8192 channels and can operate up to 4 independent detectors. Most commercial X.R.F. systems, whether dispersive or non-dispersive, have rather restricted sample chambers. With geometry shown in Fig. 2 museum objects of more or less any shape or size can be brought sufficiently close to the source and detector for analysis. Once the spectrum has been accumulated it can be stored on an 8" floppy disc via the Cromemco microprocessor system. The data can then be recalled at any time and a graph of the data, such as that shown in Fig. 3 plotted. A disc based microprocessor was chosen for data storage rather than the Canberra disc storage system since, for approximately the same price, far more flexibility is available. The microprocessor has 64K of storage and can run in Basic, Fortran or Assembler languages - the programs controlling the X.R.F. data handling are in Basic.

Fig. 3. X.R.F. Spectrum FO017 from Viking Brooch.

The spectra illustrated in Figs. 3 and 4 are from two 0.5cm² areas on the Viking brooch illustrated in the article by Richard Welander, excitation being by a collimated 1 Ci 147Pm bremsstrahlung source. In the first, the composition of a grey corrosion area around one of the four bronze pins shows clearly high percentages of tin and lead, suggesting that this was a tin-lead solder. The second spectrum reveals that the fragment of wire, which was hardly observable before the brooch was cleaned, is indeed silver.
Fig. 4. X.R.F. Spectrum FO020 from Viking Brooch.

At the moment X.R.F. analyses are qualitative only although it is intended to develop the interpretation to give quantitative answers as soon as possible. We are also hoping to replace the use of radioactive sources (mainly $^{147}$Prm or $^{241}$Am) with a small x-ray tube operating at up to 40kV.
A Viking Age Grave at Kneep, Valtos, Isle of Lewis

Richard Welander

In the summer of 1979 a woman's grave was found buried in sand on a coastal headland and as a chance discovery, the Procurator Fiscal was called in to make an investigation and give a legal report. Unfortunately for the archaeologists, who were later able to excavate, the site had been disturbed and no trace of the grave construction remained. However the legal report was observant of details, and with this, the excavation of the remains of the site and the collection of artifacts and skeleton, a report is being prepared by Mr Trevor Cowie of the N.M.A.S.

The burial goods clearly suggest the inhumation of a woman of rank and the style of ornament further suggest a date circa early Cl0th.

The grave goods consisted of:

2 gilded bronze tortoise brooches with clear textile remains;
2 bronze strap ends (one with buckle attachment);
1 bronze decorated ring-headed pin;
1 iron sickle (in 3 pieces);
1 iron rivet;
1 iron knife with wooden handle and traces of a scabbard;
1 bone needle case with fragments of an iron needle inside;
1 bone comb;
1 whetstone;
27 coloured glass beads;
Textile remains.

Surprisingly for a coastal site, the metalwork appears to be in good condition and a fair quantity of adherent organic remains, notably textile, has also been preserved.

On their arrival at the laboratory in late August 1979 all the artifacts were photographically recorded on black and white negatives and colour slides and individually received a laboratory number. The bone comb and needle case, as composite objects of iron and bone, required prompt attention since storage of such items is always a problem. The iron must be kept dry to prevent further corrosion and probably damage to the surrounding bone, but the bone requires a relatively humid atmosphere to prevent cracks occurring.

Towards the end of September I began work on the metalwork. Before any treatments or cleaning was done, each item of metalwork was x-rayed at the S.D.D. laboratories at Atholl Crescent on a Faxitron 43805N x-ray machine. (At that time the new x-ray room at Granton was under construction and will now shortly be in use - an invaluable addition to the laboratory's facilities.) The x-ray of one of the tortoise brooches clearly showed two fine parallel strands of metal interlaced over the decorative dome of the brooch. (Fig. 1). Under the microscope the strands were braided - each strand made of two even finer strands - they appeared to be made of silver. I decided to begin work on this
brooch and we examined the surface corrosion products using x-ray fluorescence (XRF) (see Fig. 2 and Research Laboratory Report below).

Fig. 1. X-ray of tortoise brooch showing silver braiding (on left-hand side). Scale 1:1.

<table>
<thead>
<tr>
<th>Analysis No.</th>
<th>Position</th>
<th>Principle components</th>
<th>Trace Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0017</td>
<td>Pin &amp; Centre of corrosion</td>
<td>Sn</td>
<td>Pb</td>
</tr>
<tr>
<td>F0018</td>
<td>White corrosion area</td>
<td>Pb</td>
<td>Cu</td>
</tr>
<tr>
<td>F0019</td>
<td>Metal &amp; green corrosion</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>F0020</td>
<td>Wire</td>
<td>Ag</td>
<td>Cu Zn</td>
</tr>
<tr>
<td>F0021</td>
<td>Pin (area more restricted than F0017)</td>
<td>Cu</td>
<td>Pb</td>
</tr>
<tr>
<td>F0022</td>
<td>Corrosion from different Pin</td>
<td>Sn</td>
<td>Pb</td>
</tr>
</tbody>
</table>

Comments: F0019 refers to basic metal + corrosion products (ie not to a prepared surface). The indications are a bronze with zinc, lead and tin as well as gilding. Some of the base metals may be from the corrosion products near the pins rather than from the bronze itself.

F0017 and 18 suggest a tin-lead solder at the base of the bronze pins.

F0019 shows that the surface is decorated with gold.

F0020 shows the wire is silver.

F022 indicates similar solder corrosion products as from the first pin area.

Report on XRF analysis of uncleaned tortoise brooch. (see Fig. 2) overleaf/
The XRF analysis confirmed the braided strands to be made of silver (F0020) and also that the surface of the brooch was gilded (F0019), which had been suspected as small areas of yellow metal were visible through the bronze corrosion products. The analysis also revealed an interesting piece of, as far as can be discovered, original information.

Between each of the four bosses on the brooch, there are four circular areas with a central pin extant about 0.5cm. Around the base of these areas was a white purple-grey corrosion product, markedly different from the green corrosion of the bronze, overlying the gilded surface. This material was examined and was shown to be rich in lead and with substantial traces of tin — in all likelihood a lead-tin solder. A quantitative analysis is hoped for at a later date.

The intriguing question arises as to what the solder was used for. Current opinion seems to be that the circular areas were decorated with a perishable organic material — possible amber. Does the solder fit in with this idea? A suggestion made in the earlier years of this century saw these circular areas as 'forming the settings to which were attached hemispherical projections probably formed from lead plated with silver or some other metallic substance' (Proceedings of the Society of Antiquaries of Scotland XLVIII p. 297). The evidence is very thin for either point of view!

With all the pre-treatment investigations completed, I began work cleaning small areas of the surface, under the microscope, with swabs of dilute ammonia solution. The ammonia softens and dissolves the bronze corrosion products, leaving the bright gold surface. It also has the great advantage of being volatile so that on drying no trace of the reagent is left to cause damage beneath the gold surface, attacking the bronze core. Cleaning is still continuing, the textile remains have been removed from the boss (see Figs. 3 and 4) and their fibre identified as linen at the laboratory.
Fig. 3 Profile of uncleaned tortoise brooch showing textile remains, silver wire (on left) and solder areas. Scale 1:1.

Fig. 4 Plan view of uncleaned tortoise brooch. Scale 1:1.
Fig. 5. Profile of tortoise brooch during cleaning - the textile has been removed. Scale 1:1.

Fig. 6. Plan view of tortoise brooch during cleaning. Scale 1:1.
This work has only just begun and clearly there is much more to be done. The ironwork will be cleaned on the air-abrasive machine, and the ring-headed pin and strap ends, under the microscope with hand tools. The glass beads will require little treatment, other than cleaning, but it is hoped some trace of the supporting thread may remain in the central hole of some of the beads. When the treatments and analyses of this collection of artifacts are completed, I shall be writing the results up as a dissertation for the Durham University Diploma in Archaeological Conservation. I am completing my third and final year of training here at the N.M.A.S. laboratory, before receiving my Diploma this coming Autumn. The training link with Durham will hopefully continue in future years. Certainly the facilities this laboratory has to offer provides any trainee with valuable experience of a wide range of conservation and analytical techniques — an opportunity not to be missed!

Note: The contents of this grave have been claimed by the Crown as Treasure Trove.
The Treatment of Composite Objects

Lynn Whitfield

The subject of composite objects is a very diverse topic, and because of this no-one has written a concise handbook for their conservation, giving examples of all permutations of materials which may be found in artifacts and how to deal with each case separately: In our own museum the objects arise from archaeological land and marine sites, and the museums collection.

So it can be seen that when a conservator is presented with a composite object he has neither a standard to go by, nor any account of successes or failures encountered by other conservators.

First let us look at some common problems, and ways of making life easier. Often when archaeological objects come into the laboratory they are dirty, and many of the metal objects are covered with encrustations of rust, stones, bone, wood, shell and oxidation products; all this makes it very difficult to determine the actual components of the object from the outset. If a composite object is suspected, it is not so simple to just clean away to the original surface, as in many cases you do not know where that surface is! So the first necessary task is to obtain first class x-ray photographs from as many angles as possible. This will help determine the shape of the object, will reveal decoration if present, indicate its condition and should also reveal if the object is inlaid or plated, which is most important. From the x-rays one can work with a little foresight, in the initial stages of cleaning, which means faster, more precise results.

The methods available to the conservator for the effective cleaning of composite objects are mostly mechanical, although sometimes localised chemical treatment is necessary to expose particularly difficult pieces of detail. Mechanical methods can vary from scrapers, picks, an air-abrasive unit using the appropriate pressure and powder, dental burrs, vitro-tool, cavitron etc.

No composite object is dealt with more regularly than a composite object where one of the components is iron. Iron corrodes into many corrosion products and generally migrates over and around other materials in close contact with it. Very often a decision has to be made on how much to remove so that one arrives at what is believed to be the original surface and how much to leave for structural purposes.

When two dissimilar metals are in contact one will corrode in preference to the other, and in normal circumstances the more noble metal will be protected at the expense of the other. It is not surprising therefore to find that tinning, gilding, silvering and copper plate can survive well, even when totally surrounded by massive iron corrosion. Removal of iron to expose these other metals is the main problem and of course the difficulties in the subsequent stabilisation of more than one material. The work is always slow and very precise.

One interesting object we have had at the museum laboratories to demonstrate this topic has been a Targe, which is made up of six different materials (see Fig. 1). It consists of a wooden frame covered on the front with tooled leather (probably cow-hide) studded with brass studs and a central boss. The back is covered with vellum on which were three faded written labels (Fig. 2). There were also a number of iron nails and tacks over the back. All parts of the Targe needed treatment, and conservation had to be planned ahead, so as to take into account any detrimental effect any one chemical or process might
have on any of the materials.

It was decided that the labels should be preserved, and as one of the labels seemed to be of some antiquity, an attempt was made to decipher the writing by ultra-violet and infra-red photography. This was very kindly carried out by the forensic department of the Lothian and Borders Police, but unfortunately proved to be unsuccessful.

The Targe had in the past suffered extensive woodworm attack and to treat any that was still active and guard against further outbreaks the entire object was sealed in an atmosphere of para-dichlorobenzene over several weeks.

The studs were next treated. They required a swift and effective chemical reagent and ammonia solution was chosen because of its volatile properties and the minimised risk to the leather if spills occurred. In practice this reagent was very effective and caused no harm to the leather around the studs. In addition a 15% solution of ammonium thiosulphate was used with 1% Lissapol N to remove re-deposited copper from several studs and give them a bright clean finish. The boss and studs were finally polished with Duraglit and coated with microcrystalline wax.

There was also evidence of corrosion products underneath the studs reacting with the leather, thought to be caused by a reaction with the lead inside the studs. This corrosion was powdery in nature and could be simply brushed away.

It was decided to press the wood back into place next and this was achieved by gentle pressure and by means of a strong adhesive, Araldite, and firm clamping, the whole object having been acclimatised in a moderately high relative humidity. The back of the wooden frame was then coated with cellulose amyl acetate for consolidation.

The leather then had to be conserved and the cracks and splits caused by the warping of the double layered frame eased back into place. The leather could now be treated. The cleaning was done with 3% Lissapol N and the leather allowed to superficially dry before diluted British Museum leather dressing was applied in regular coats, drying between each application. Several areas of red rot were consolidated with Pliantex - an acrylic resin which, on drying, remains flexible. The consolidant was first applied to fill the cracks and gaps in the leather.

It was decided that copies of the missing brass studs would be made in case replacement was required at a later date. In order for them to look authentic, moulds were made of existing loose studs, and the new ones reproduced by electrotyping and electroplating in brass.

The last work to be done was on the vellum which had to be slowly softened in an increased relative humidity, and gently flattened back into position.

To draw some conclusion, it can be seen that composite objects pose many questions and need a great deal of thought, consideration and preparation.
Fig. 1. The face of the Targe: one quarter has been treated.

Fig. 2. The back of the Targe showing wooden construction.
Fig. 3. The completed Targe.
The Chemistry Laboratory

Helen Dalrymple

Although equipped to perform a wide range of chemical analyses, the chemistry lab is also used as a general back-up service for work done by Thermoluminescence, X-ray Fluorescence and Neutron Activation Analysis, in the form of sample preparation, microscopic examination, flame photometry and chemical spot tests.

Samples of pottery for Neutron Activation Analysis have to be small and easily handled, of uniform size and moderately robust. A dental drill is used to obtain a finely powdered sample which is compressed into a pellet and then fired in the furnace at 1000°C.

At present, the laboratory has two microscopes, one of which is a binocular with variable magnifications from x15 to x30, and the other is a monocular metallurgical microscope with a maximum magnification of x1000. Hopefully, by April, 1980 a Vickers' M17 Polarizing Microscope, with photographic attachment, will have been delivered, enabling us to keep a photographic record of microscopic examinations. This should be particularly useful in building up a reference library for fibre, wood etc identifications. The technique used is to mount a small fragment of the object in resin which can then be ground down, polished and if metal, etched with a suitable agent. Apart from metals, fragments of paint and fibres can be mounted, polished and examined in the same way, as can pottery sections.

Fig. 1. General view of the chemistry laboratory.
Accurate weighing of samples may be carried out on the analytical balance which is accurate to 0.1mg. We also have a top pan balance with an accuracy of 5mg which can be adapted for specific gravity measurements.

The flame photometer may be used to determine potassium, calcium and sodium contents of solutions, usually of pottery or clay samples. The samples are dissolved in a suitable acid, filtered and diluted down. The photometer itself draws in the solution, atomizes it and sprays it into a flame. A specific colour of light is given off, which, by way of a suitable filter and photocell, causes a deflection on the galvanometer. The instrument is calibrated via standard solutions reading in parts per million.

Colorimetric analysis of chemical solutions in the visible spectrum are carried out using the E.E.L. Spectra.

It is hoped that in the near future analysis using chromatographic methods will be undertaken so that organic analysis can be expanded, particularly for the study and identification of dyestuffs in archaeological fabrics.
The Treatment of Archaeological Iron by the Alkaline Sulphite Method

Theo Skinner

In the presence of air and water, iron corrodes by an electrochemical process, with separate anodes and cathodes at which different reactions occur. These reactions may be summarised:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(anode)} \]

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{(OH)}^- \quad \text{(cathode)} \]

and the overall reaction

\[ 2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{(OH)}^- \]

In the presence of air and other oxidising agents the ferrous ions are further oxidised to various insoluble ferric salts, such as Fe$_3$O$_4$, Fe$_2$O$_3$ and FeO(OH).

Chloride (and other) anions may act as accelerators of corrosion of iron. The hydrolysis of iron chlorides produces an acid solution, causing local breakdown of the protective oxide films which normally act to slow the diffusion of reactants and products of the cathodic and anodic reactions, to and from the surface of the metal. This removal of diffusion control of the reactions greatly accelerates the cathodic and anodic reactions, producing an increase in the rate of corrosion.

The major factors, therefore, in the corrosion of iron are the presence of moisture and of chloride ions. Treatments intended to stabilise archaeological iron generally involve removing chloride and other anions, and thereafter in protecting the iron from moisture. It should be noted that iron chlorides are deliquescent, ie will tend to absorb moisture from the atmosphere, thus forming a solution in which further electrochemical corrosion may occur. Archaeological iron either from marine or ground sites is generally full of chlorides, the main species being the insoluble ferric oxychloride, FeOCl, and ferric chloride, FeCl$_3$. These may form up to 13% by weight of the corroded layer of cast iron from a marine site.

The alkaline-sulphite method for the treatment of iron depends on the fact that FeOCl is rapidly broken down in alkaline solution into chloride ions and FeO(OH). By prolonged washing in hot solutions of NaOH, chlorides may be extracted.

However, the rate of extraction of chloride in hot alkali alone is very small, being dependent largely on the rate of diffusion of ions through the layer of corrosion products. The alkaline-sulphite method aims to increase this rate of diffusion by chemical reduction of the corrosion layer. This reduction is brought about by the strong reducing agent sodium sulphite. This produces the following reactions in the corrosion layer.

\[ 3\text{FeO(OH)} + e^- \rightarrow \text{Fe}_3\text{O}_4 + 2\text{(OH)}^- + \text{H}_2\text{O} \]

\[ \text{FeOCl} + 2\text{FeO(OH)} + e^- \rightarrow \text{Fe}_3\text{O}_4 + \text{Cl}^- + \text{H}_2\text{O} \]

\[ \text{SO}_3^{2-} + 2\text{(OH)}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^- \]

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The reduction of FeO(OH) and FeOCl to magnetite, Fe₃O₄, results in a decrease in size, the product Fe₃O₄ (S.G. = 5.2g/cc) has greater density than FeO(OH) (S.G. = 4.2g/cc). This results in a greater rate of diffusion through the corrosion layer, with substantial decrease in the treatment time needed to remove the chloride ions from the object.

In the presence of oxygen, warm solutions of sodium sulphite will be quickly oxidised to sodium sulphate, and no reduction of any iron present will take place. In the alkaline-sulphite method, then, exclusion of air from the container is an essential feature. In practice, it appears to be sufficient to merely limit the amount of oxygen available by completely filling any container with solution and then sealing the container.

**Fig. 1.** Apparatus used in the alkaline sulphite treatment of iron.

Above is a photograph of the type of apparatus used at Granton: plastic containers, with airtight lids, are used to hold the artifacts plus the alkaline-sulphite solution. The objects are identified by attached Teflon labels. The plastic containers are kept warm by placing these in water baths with small immersion heaters, keeping the temperature at about 60°C. From time to time, samples of the solution are removed for chloride analysis. When no further increase in chloride levels occurs, the solution is changed. This procedure continues until the chloride level in the solution is stable and acceptably low. The objects are then removed, washed in deionised water, and then placed in Ba(OH)₂ to deposit any sulphite or sulphate ions as insoluble barium salts and then boiled several times in deionised water to remove the remaining chlorides. The iron is then placed in successive baths of acetone to remove any water, then dried either in a desiccator or an oven before being coated with microcrystalline wax, which affords some protection against moisture.

The factors which determine the treatment times necessary for successful treatment.
have been investigated by North and Pearson, the originators of the Alkaline-Sulphite method. The following ones were considered.

a. The value of the diffusion coefficient of the corrosion layer
b. The initial and final concentration of chloride.
c. The pH of the solution
d. The temperature
e. Frequency of changes of the solution.

The conservator has control over most of these, at least to some extent. The diffusion coefficient may be increased by reduction, either in alkaline-sulphite, electrolysis in alkali, or by heating in a hydrogen furnace. This will produce a significant reduction in the necessary treatment time. Secondly, by warming the solution, both reversible and irreversible changes in the rate of chloride extraction may occur. The reversible changes may be due to general kinetic effects, whilst the irreversible increase may be due to changes in structure in the corrosion layer.

The pH of the solution must be kept high, as the rate of decomposition of FeOCl is strongly pH dependent, pH values between 12 and 13 being best. Strangely enough, the frequency with which the solutions are changed has little effect on the total time of treatment, weekly changes being the most required. As the chloride level is monitored, the conservator knows when to change the solution, i.e., when the chloride level in solution ceases to rise. As solutions for larger objects are expensive, this is obviously the best approach. Some typical chloride graphs are shown below.

![Graph showing changes in chloride levels in some alkaline sulphite solutions containing archaeological iron.]

Fig. 2. Changes in chloride levels in some alkaline sulphite solutions containing archaeological iron.
Finally, the acceptable level of chloride at the end of treatment is largely a matter of choice. If the objects can be kept essentially free from water, higher levels of chloride may be acceptable. At Granton, we aim to remove chlorides until the concentration of chloride ions in the wash water, on boiling in deionised water, is less than 10ppm.

North and Pearson have shown that the Alkaline-Sulphite Method is a very efficient means of removing chloride from marine cast iron. However, even they reported variation in its success as a means of stabilising marine iron. Corrosion of iron produces variable structures in the corrosion layer, and these may account for some of the variable results reported. Perhaps the real answer to stabilising iron lies in the control of storage conditions such as humidity and temperature, and the nature of protective finishes.

The Alkaline-Sulphite Method has been used at Granton to treat archaeological iron from ground sites eg Perth and from a marine site the wreck of H.M.S. Dartmouth. The results have been variable: some pieces survive the treatment well, while others fall apart. Some successfully treated cannon balls from the H.M.S. Dartmouth are shown below:

![Two cannonballs from H.M.S. Dartmouth after alkaline sulphite treatment.](image)

We hope to carry out investigations into the reasons for failure of the treatment; for example, does the treatment only work well for cast iron as opposed to wrought iron; are particular corrosion products associated with success or failure; or do the post-treatment conditions determine the outcome of treatment? We hope these investigations will result in a greater success rate for the treatment of archaeological iron.
 Thermoluminescence Dating
Jim Tate

"Eleventhly, I also brought it to some kind of glimmering light, by taking it into bed with me, and holding it a good while upon a warm part of my naked body". In 1663 Robert Boyle made the above statement in a Paper given to the Royal Society concerning his investigations on a large diamond belonging to one Mr Clayton. The phenomenon he reported was thermoluminescence, the emission of stored energy as light following thermal stimulation. In the past 12 or so years thermoluminescence has been developed as a dating technique which can be applied to many mineral-containing materials which have been fired or heated to a temperature in excess of about 600°C during their manufacture, and so, most obviously to pottery.

The method relies on the fact that all materials contain traces of naturally occurring radioactive elements, principally uranium (\(^{232}\text{U}\) and \(^{238}\text{U}\)), thorium (\(^{235}\text{Th}\)) and potassium (\(^{40}\text{K}\)). All of these radioactive species are very long-lived, but eventually decay giving off nuclear energy and transmuting to other radioactive elements in their decay chain until a stable element is reached. The net result is that there is a continual barrage of nuclear energy which, although very small, may be constant over times of tens of thousands of years. Thus, for example, a piece of pottery buried since its breakage some thousand years ago will, since that time, have been subjected to nuclear energy both from the surrounding soil and from the radioactive impurities within its own clay body.

The nuclear energy is apparent as three distinct forms of radiation: alpha particles which are positively charged and fairly massive, beta particles or electrons and gamma rays. The first two of these travel only short distances through solids before giving up most of their energy as heat, while gamma radiation penetrates considerable distances through even dense materials. Certain minerals, particularly quartz and feldspars, have the ability to absorb energy from the alpha, beta and gamma radiation and retain a fraction of it as stored energy. Both these minerals commonly occur mixed with the clay in pottery. The mechanism responsible is the ejection of electrons from the valence band by the radiation and their subsequent capture in traps, which may be impurities or defects in the crystal lattice. Some of these electron traps are deep and therefore effective at holding the electron for extremely long times (millions of years).

![Graph showing growth of stored energy with time](graph.png)

Fig. 1. Growth of stored energy with time.
As the time passes the amount of stored energy – that is the number of trapped electrons – will increase in, one hopes, a constant manner (until most of the available traps are filled). If the material containing the quartz or feldspar grains is heated up, as happens when a piece of pottery is fired, heat energy causes all the atoms to vibrate violently and electrons will gain sufficient energy to jump out of their traps. Most of these suddenly freed electrons will simply fall back to their natural states in the valence band, but some will fall into "luminescence centres" thereby creating a pulse of light: such pulses of light combine to give the observable thermoluminescence. Firing of the pottery thus gives a "time zero" when all the geological thermoluminescence is erased and after which electron trapping recommences. (Fig. 1).

The amount of thermoluminescence measured in the laboratory therefore depends on three things; the amount of nuclear radiation incident on the mineral grains in the pottery, the efficiency with which these grains store the energy and subsequently emit thermoluminescence, and finally the length of time since the pottery was fired. By measuring the first two of these on a sample of pottery and burial soil in the laboratory we are able to calculate its age (or, to be more exact, the time since the piece was fired).

Experimental Details

Generally a fragment of pottery about 2" x 2" x ½" is required together with samples of the soil and knowledge of burial conditions. Part of the sherd is cleaned, gently crushed and 10 to 20 identical samples prepared. The different penetrating power of alpha, beta and gamma radiation mentioned above gives rise to two forms of sample preparation. "Fine grain" samples consist of only grain sizes between 0.001 and 0.008 mm (selected by deposition in acetone); these grains experience the full alpha contribution, while "inclusions" are taken to include grains from 0.09 to 0.15 mm. By etching the outer surface of these grains with hydrofluoric acid the alpha contribution can be removed, a situation which can ease later calculations.

Fig. 2. The Thermoluminescence Equipment.
Fig. 3. Block diagram of the Thermoluminescence equipment.
To actually measure the TL the apparatus illustrated in Figs. 2 and 3 is employed. The sample, on a lcm diameter stainless-steel disc, is put on the hot plate of the oven with the light detection instrument (an EMI 9883B photomultiplier) above it. The oven is evacuated, flushed with pure nitrogen gas and the sample is then heated to 500°C, typically at a constant 10°C per second. Electrical pulses from the photomultiplier are amplified (via a Brookdeal 5032A preamplifier and 9511 photon counter), and displayed as a function of sample temperature on an X-Y recorder (Fig. 4). The signals are also fed into a Laben 100 channel analyser. The background can then be recorded by a second heating - since all TL is erased in the first heating the second heating reveals no light until about 450°C when the sample glows red hot: this incandescence is of course reproducible and can simply be subtracted from the TL "glow curve". The resulting glow curve stored in the multichannel analyser is automatically punched onto paper tape for analysis by the computer.

Fig. 4. Thermoluminescence glow curve from un-irradiated sample.

Fig. 5. Thermoluminescence glow curve from sample irradiated with beta radiation but previously unheated.
In order to calibrate the effectiveness with which the sample stores energy and shows TL a batch of samples are artificially irradiated by a known dose of beta radiation and their natural plus artificial glow curves recorded (Fig. 5). From these sets of curves a graph such as Fig. 6 may be constructed from which the amount of radiation experienced by the pottery since firing, known as the "equivalent dose", may be estimated. Unfortunately the initial part of this relation is seldom linear and an additional experiment has to be performed in order to estimate the deviation from linearity and determine the "archaeological dose". Once the annual radiation dose rate from the clay fabric of the pottery and the surrounding soil has been measured the age can be calculated as:

\[
\text{Age} = \frac{\text{Archaeological radiation dose}}{\text{Annual radiation dose rate}}.
\]

Fig. 6 Estimation of the equivalent radiation dose.

The annual dose rate can be determined in the laboratory by low level alpha counting techniques (3 EMI low background 1" photomultipliers together with Nuclear Enterprises' NIMS high voltage and scalers coupled to a digital cassette recorder). Samples of pottery and soil are sealed next to detectors which count the number of alpha radiation events which occur (typically 1 in 100 seconds). Knowing the radioactive decay chains for uranium and thorium the total radioactive dose rate can be calculated. The contribution from potassium-40 is found by measuring the total potassium content with an EEL flame photometer.

Results

The glow curves illustrated in Fig. 4 are for etched quartz inclusions from a sherd from the Udal excavation by Iain Crawford. They are very preliminary results, with rather low light levels and, at the moment, poor consistency.
as can be seen from the equivalent dose graph (Fig. 6). A large collection of sherds were made during the excavation with the intention of obtaining TL dates to compare with radiocarbon and stratigraphical dating. The TL dating is rather behind but is now being undertaken at the laboratory also at Cambridge University.

Using the standard high temperature technique with quartz inclusions outlined above, an absolute accuracy in the age of ±10% should be obtainable. This should not be confused with the much smaller error limits quoted on radiocarbon dates which refer only to counting statistics and do not therefore reflect overall accuracy of the ages. One of the factors which makes it difficult to get much better than ±10% at the moment is uncertainty in the radiation dose during burial due to dis-equilibrium in the radioactive decay chains. A particularly elegant solution is to use grains of the mineral zircon rather than quartz or feldspar. Zircons have a very high uranium content, consequently the natural radiation dose comes almost entirely from within each individual grain (in contrast to quartz where nearly all the radiation comes from impurities in the clay matrix). By using zircon grains it should therefore be possible to avoid the need for detailed knowledge of the burial conditions thereby greatly increasing the use of TL as a dating tool for archaeologists. Unfortunately, like most ideal solutions there is a snag, in this case simply that zircons are rather rare minerals, large pieces of pottery having to be destroyed in the hunt for one or two elusive grains!
Neutron Activation Analysis

Apart from stylistic and visual inspection, pottery fragments are often examined microscopically in order to classify them into different types according to the minerals which appear in their fabric. The hope is that the pottery clays will retain a 'fingerprint' reflecting the chemical composition of the clay which the potter used, so that pottery made in different sites can be neatly distinguished. The statistical accuracy of any such classification will generally depend on the number of minerals or chemical elements which can be detected. Chemical analysis, although giving suitable answers, is likely to be tedious to perform for a large batch of samples with perhaps ten analyses for each. With neutron activation analysis it is possible to measure the amount of several different trace elements simultaneously for each sample of pottery. Moreover the analysis technique lends itself to automatic operation and the data reduction to computer application which, in the ideal case, should make the procedure moderately straightforward.

The equipment necessary has several similarities to that for x-ray fluorescence examination, but in the case of neutron activation it is the atomic nucleus which is excited rather than the surrounding electrons. Since the nucleus is very tightly bound together considerably more penetrating power is required for this excitation and the characteristic energy emitted is consequently more energetic. Rather than immediate fluorescence while irradiating the sample with a radioactive source, the specimens are irradiated by slow neutrons in a reactor to make them mildly radioactive. What happens is that the neutrons in the reactor interact with the nuclei in the sample to form unstable isotopes. The isotopes, being unstable, then revert to some stable form, releasing characteristic radioactive energy. The most probable time taken for half the number of activated nuclei to decay (ie the half-life) depends on the particular type of nucleus: thus aluminium has a half life of 2.3 minutes while for europium it is as long as 12.7 years. Even with immediate access to the sample after irradiation it would therefore be difficult to analyse for aluminium although in contrast some days delay between irradiation and measurement is clearly unimportant for europium. Pottery samples from the laboratory are currently irradiated at the reactor at East Kilbride making it practicable only to measure those samples with a half life in excess of about a week.

In measuring the radioactivity - as gamma radiation, that is high energy x-rays - it is important to present each sample to the detector in the same geometry. To do this about 100mg of pottery are removed from the sherd or pot using a dental drill or vibrating tool, having first removed the outer surface which is likely to be tainted with burial soil etc. When removing such a small amount representative sampling is important: if there is doubt it may be necessary to make two separate drillings. The powder is then compressed into a 6mm diameter 1.5mm thick pellet in a hand operated press. Unsuccessful pellets can be held together by mixing with cellulose filler which after analysis is burnt off so that the weight of powder can be determined. The other pellets can also be fired (at 1000°C for 10 minutes) for increased strength.

The pellets are then packed into as small a volume as possible and sent to the reactor at East Kilbride for irradiation (18 hours at a flux of $3.8 \times 10^{12}$ neutrons/cm$^2$/sec), the uniformity of irradiation being checked by steel monitors distributed amongst the pellets.
Once back at Granton the pellets are unpacked in the hot laboratory and placed in individual polythene capsules to avoid the possibility of spreading any activated powder. These capsules are then loaded into the sample changer on the right in Fig. 1 (here the lead shielding has been removed). The detector is a lithium drifted germanium crystal supplied by Nuclear Enterprises in 1972. When supplied the detector had a resolution of 3.1 keV (at 1332 keV); it is now double this, possibly because the detector has at some time been allowed to warm up - like the X.R.F. detector it is usually kept at liquid nitrogen temperature (-196°C).

Fig. 1. The apparatus for measuring activated pottery pellets.

Pulses from the detector are amplified and accumulated in the Nuclear Data 1024 channel analyser on the left in Fig. 1. After a preset counting time (10,000 seconds) the data is written onto cassette tape, the specimen automatically changed and a new cycle begun.

Once all the pellets have been measured the cassette tape is replayed into the Wang computer (see below). As well as manipulating the numbers, the computer draws a graph of the spectrum from each pellet (Fig. 2 - here the dots have been joined to make the peaks clearer and the identifying symbols at the top added). The spectrum extends from 188 keV at channel 0 to 1633 keV at channel 1024. As can be seen, the low energy peaks (Th and Cr) are hardly separated due to the poor detector resolution. Having located the peaks the computer integrates over a specified number of channels and then subtracts a background estimated by summing the channels on either side. At present no attempt is being made
to perform a least squares fit to the data.

Fig. 2. Gamma spectrum of activated mediaeval pottery.

The spectrum illustrated in Fig. 2 is for a piece of mediaeval pottery, one of twenty pieces provided by David Caldwell of the National Museum, and part of the first test run. In order to compare the spectra from different samples the elemental compositions are being determined by reference to pellets of an analysed clay standard irradiated and counted at the same time as the pottery. Simply by eye, differences are apparent between the spectra, these of course also being reflected in the computer calculations. However at the moment it is difficult to separate the pellets into different clusters, that is groups of pellets having similar compositions distinct from those pellets in other groups. This is probably simply because the samples were initially chosen from pieces of pottery which looked different, that is each piece is more or less the only member of a group. Analysis of the results to form possible clusters is a moderately involved process with a large number of statistical tests having to be made. We are at the moment working to write or adapt a programme for the Wang computer to perform these manipulating on the neutron activation results.
Fig. 3. The Wang 16K BASIC computer.

Fig. 3 shows the Wang 2200B minicomputer which was bought for the laboratory in 1972. The computer is programmable in BASIC and has 16 k-bytes for the user programme and data. Programmes and data can be stored on cassettes and replayed into the memory via the unit to the right of the screen. Peripheral instruments shown to the left of the console are for reading cassettes from the neutron activation and thermoluminescence equipment, reading punched paper tape and for outputting printed data from the computer. The last of these three units is an IBM writer/plotter and is capable of working, under programme control, in two modes. In the first it acts as a normal typewriter, while in the plotting mode it can be used to draw graphs or diagrams with x or y increments as small as 0.01 inches. As has been mentioned, Fig. 3, with the exception of the identifying symbols at the top, was plotted by the computer.