
Technical Communication



On the treatment of pewter plates from the wreck of *La Belle*, 1686

Worth Carlin and Donald H. Keith

Ships of Discovery, Corpus Christi Museum of Science and History, 1900 N. Chaparral St. Corpus Christi, TX 78401, USA

Introduction

In July 1995 a remote-sensing survey undertaken by the Texas Historical Commission under the direction of J. Barto Arnold III, discovered a shipwreck in Matagorda Bay on the Texas coast (Fig. 1). A bronze cannon on the site raised the possibility that it might be the wreck of *La Belle*, a 'barque longue' (sloop of war) known to have been lost in the vicinity in 1686, during the failed attempt of noted French explorer, Robert Cavalier Sieur de La Salle, to found a colony on the coast of Texas. The site of the wreck (site designation 41MG86) was marked for future recovery and the several hundred artefacts raised from the murky waters of the Bay were brought to the Corpus Christi Museum of Science and History for cleaning, analysis, and conservation in the hope that they might securely identify the ship. Over the past year the artefacts have been conserved by the staff of Ships of Discovery, a non-profit archaeological research group based at the Museum. The artefacts include: a bronze cannon, hundreds of hawk-bells and lead shot, ceramics, a brass rapier hilt, unfinished grindstone, whetstones, copper alloy dividers, and 30 severely corroded pewter plates. This report contains chemical assays of the pewter, identifies some of its corrosion products, and details the conservation

practices used, including electrochemical stripping and polishing combined with pneumatic, soft-abrasive, final polishing.

The badly corroded pewter plates presented the largest challenge to conservation. What treatment regimen would rid the plates of corrosion which could become the sites of future on going deterioration, while at the same time preserving the numerous inscribed and impressed markings which could help identify the ship? Conservation literature contains little detailed information about treating pewter recovered from the sea, because pewter containing significant quantities of lead, or pewter from anaerobic environments is stable and requires little treatment. On the other hand, pewter with low levels of lead in aerobic conditions dissolves completely or leaves only a mushy residue of tin oxide (North & MacLeod, 1987: 90). This report presents the results and details of a conservation treatment programme for heavily corroded low-lead content pewter.

Composition of pewter

Pewter is an alloy containing tin with lesser quantities of other elements. Modern pewter contains tin together with lesser amounts of copper, bismuth and antimony. However, the pewter of antiquity contained lead in varying amounts. Early Roman pewter could contain in excess of

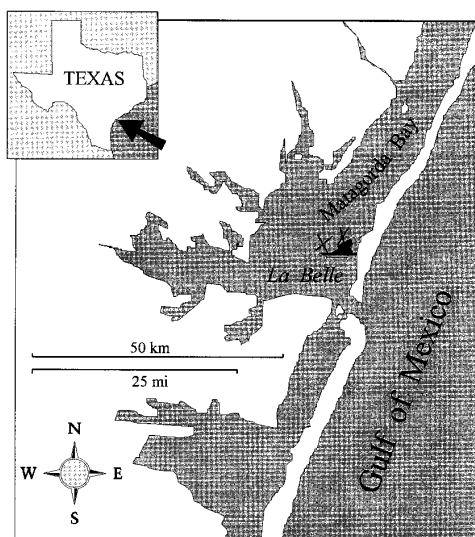


Figure 1. The *Belle* site lies in 4 m of water a few hundred metres north of Matagorda Peninsula. (Drawing: D. H. Keith)

30% lead (Cronyn, 1990: 210). Over the centuries the proportion of lead in pewter decreased and its composition became a regulatory standard imposed by guilds and governments. As early as AD 1394, the composition of pewter in Limoges was regulated by the *Règlement de la Pinterie* (Massé, 1971: 133). Not surprisingly, the amount of tin (the pewter alloy's most expensive component) determined its quality. Poor grades of pewter contained significant proportions of cheaper, more dense, lead. Increasing the amount of lead in the alloy substantially reduced manufacturing costs.

At some point it became necessary for pewterers to identify their individual products with distinctive maker's marks. Fortunately for future archaeologists, these marks were registered with the guild. Although the necessary research has not yet been initiated, it is hoped that the three distinctly different markings discovered on the plates from *La Belle* will be found to represent one pewterer and two different owners.

Corrosion of pewter in marine environments

Environment is the controlling factor in the preservation of all artefacts recovered from the sea. Leaded pewter is relatively resistant to the corrosive action of sea water and the higher the lead content, the more resistant the pewter. Nevertheless, differences in temperature, salinity, oxygen concentration, water velocity, and marine biological activity all influence the stability of artefacts in sea water. Pewter can be resistant to corrosion in anaerobic conditions where stable sulphide coatings form on the surface of the artefact and resist further corrosion. But under aerobic conditions, unless it is protected by marine growth and encrusted or buried in the sea bottom, pewter with low lead content can corrode fairly rapidly.

Description of recovered pewter artefacts

Of the 32 pewter artefacts recovered, all but two were plates of one type or another, plus parts of a button and spoon. Although five plates and a plate fragment were recovered as single items, most of the plates were in nested stacks. The largest stack contained 22 plates ranging in diameter from $8\frac{3}{4}$ in (225 mm) to 14 in (390 mm). The smaller stack was only two plates of the same diameter, $13\frac{1}{3}$ in (34 cm). The stacks were fused together by corrosion products and marine encrustation (Fig. 2). Only the plates recovered as single items had the warts or corrosion pustules frequently described in conservation literature. Those that were part of a stack had a layer of gritty, grey corrosion products in addition to marine encrustation.

One very badly corroded plate (no. 778–014), that had become separated from the stack during the recovery effort, was selected to provide analytical information and to serve as a test piece for conservation procedures. Although it was the worst-preserved of all the plates in the stack (eight better-preserved plates in the



Figure 2. The stack of 22 nested pewter plates fused together by corrosion products and marine encrustation. (Photo: Jerry Livingston.)



Figure 3. The maker's mark. (Photo: Jerry Livingston.)

stack appeared to be identical to it), approximately one half of it was in good condition.

Twenty of the plates in the largest stack bear what appears to be a maker's mark (Fig. 3). The other two plates in the stack probably had the mark originally, but lost it to corrosion. In addition to identifying

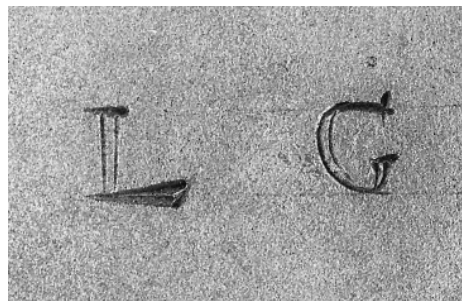


Figure 4. LG initials. Note the scribed lines above and below the letters. (Photo: Mary Caruso.)

the pewterer by his initials (I.F.), the mark may also indicate that the pewter is of fine quality (FIN). All 22 of the plates in the largest stack also bear what appears to be the owner's initials, L.G., carefully (but inexpertly) inscribed on the centre of the plate's bottom between two lightly scribed lines (Fig. 4). It is tempting to speculate that these plates belonged to Sieur Le Gros, a man of some importance whose possessions were put aboard *La Belle*

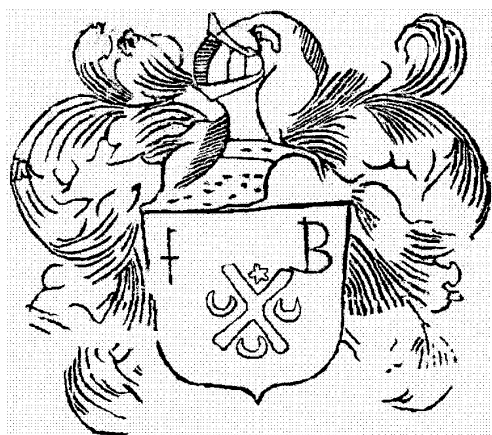


Figure 5. Tracing of the heraldic crest found on six of the plates. (Mary Caruso & D. H. Keith.)

shortly before she was lost. The third mark is the most intriguing (Fig. 5). It appears only on the upper surface of the rims of six plates, four of which were found singly and two of which were nested together in the smaller stack. The mark appears to be an heraldic device composed of an escutcheon containing three crescent moons and a star separated by a cross or X, surmounted by an elaborate winged helm. The escutcheon is stamped or impressed into the plate's surface but the winged helm is engraved. The regularity of the pattern suggests it was made with the help of a template. The plates on which this mark is found are of three different diameters, and the pattern is sized accordingly to fit between each plate's rim and its central depression. As the surfaces of the plates on which this mark appears are invariably in poor condition, portions of the mark are indistinct. The Initials I or P and B are visible in the upper corners of the escutcheon of plate no. 687, and the bottom of an O can be seen on plate no. 776. None of these plates show maker's marks. Perhaps better examples will be discovered on the site in the future.

Pewter analysis

For analytical and physical testing, the test plate was divided into sections so that

sampling of the segments could be reconciled with the testing. This allowed comparable samples to be obtained to provide a control for every test piece so that before and after results were more meaningful.

Elemental analysis of a section of non-corroded metal was accomplished by energy-dispersive X-ray fluorescence spectrometry (EDXRF) set to detect elements in the atomic number range 9–92. The results of the analysis are shown in Table 1. The analysis indicates a good quality of pewter with a high tin content and low lead values. The high iron content (2.3%) is surprising. The possibility that this could be the result of poor sampling or sample contamination appears unlikely, given the results of Auger spectroscopy on a cross-section of a sample taken adjacent to the sample analysed by EDXRF¹. The sample was found to harbour randomly distributed inclusions containing substantial amounts of iron (Fig. 6). Auger scans taken across the thickness of the plate failed to indicate a differential concentration of iron through the plate's cross-section. The bulk of the metal was normal crystals containing no iron, but within the inclusions the iron content could be as high as 35% (by weight). Semi-quantitative scanning electron microscopic analysis of the metals in the corrosion product indicated approximately 83% lead and 13% tin.

Treatment

The pewter had been stored and transported in tap water from the time it was recovered from the sea until it arrived in the laboratory, where it was replaced with de-ionized water (Corpus Christi tap water can contain as much as 120 ppm chlorides). The initial objective was to separate those that were nested in the stack. As stated previously, the plates in the stack were bonded together by both corrosion products and marine encrustation. In an attempt to remove the marine

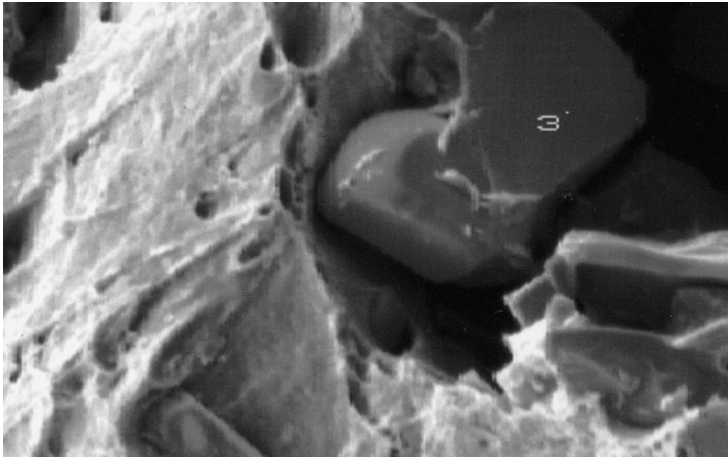


Figure 6. Auger photomicrograph of a freshly fractured pewter plate surface. Bulk of sample is largely homogenous. Note dark irregular inclusion (3, upper right) containing approximately 35% iron by weight (Lisa Magel).

Table 1. Elements in pewter sample detected using EDXRF spectrometry

Elements detected	Concentration (by % wt)
Sn	93.8
Fe	02.3
Cu	01.8
As	01.1
Pb	00.70
Bi	00.24
Zn	00.06

encrustation, the plates were electrolytically reduced in a dilute alkaline solution (3% soda ash plus 1.5% EDTA (ethylene diamine tetraacetic acid)). Reduction was carried out over 16 h at a cathode current density of 12 amp/ft² (0.0129 amp/cm²) using a mild steel mesh anode. This procedure was moderately successful, allowing the grouping of large plates to be separated from the smaller diameter plates. This procedure only effected removal of the marine encrustation; the plates themselves remained tightly bonded together. The plates were

then placed in 2.5% sulphuric acid solution containing 7.5 gm/l of a 30% solution of the surfactant Macol OP-30[®] (an ethoxylated nonyl phenol manufactured by PPG Industries) at concentrations of 1 oz/gallon (7.5 gm/l). The plates were removed periodically from the storage solution and scrubbed with a stiff nylon brush. Although a considerable quantity of corrosion products was removed from the plates, they were still tightly stuck together.

The topmost and bottommost plates in the stack, and all the plates that were recovered singly, were encrusted with marine shells. The predominately calcareous shells themselves were dissolved with dilute sulphuric acid but the cement-like exudate secreted by shellfish in order to anchor themselves to the substrate was much more resistant to normal chemical and mechanical cleaning techniques. It was determined that the material could be dissolved rapidly with a 5% solution of ammonium acetate. Subsequent experiments demonstrated that if an encrusted artefact were immersed in an ammonium acetate solution, the exudate would soften

or dissolve and the calcareous shell would drop off, thereby eliminating the necessity to dissolve the shells themselves.

Following immersion in a dilute acid-surfactant bath for several days, the plates were ready for final treatment and separation. After considerable experimentation it was discovered that repeated applications of a 30% solution of the Macol OP-30[®] sprayed into the gaps between the edges of the plates allowed the plates to be gently prised apart with a fingernail or soft wooden wedge. The spaces between the freshly separated plates contained a grainy mixture of metal oxides and sea salts (predominately calcite) which could be removed by scrubbing with surfactant and a stiff nylon brush. An unevenly distributed residual black film or layer of variable thickness remained. This film was resistant to dilute concentrations of a variety of inorganic acids. A 6N solution of nitric acid slowly dissolved the film, but its rapid attack on the pewter precluded its use.

Plenderleith and Werner (1976: 279) mention removing a greyish-white film on pewter recovered from the sea using short-interval electrolytic reduction. A variation of this technique was applied to one of the plates from *La Belle* to determine if it could be used to remove the resistant black layer. The plate was reduced in 2.5% solution of sulphuric acid using a 1/16 in (1.6 mm) thick sheet of lead as the counter electrode. The lead sheet was shaped to match the contours of the plate to promote more even coverage and only one side of the plate was reduced at a time. Initial results were markedly unsuccessful. Even though the current density was increased by increments to 15 amp/ft² (0.016 amp/cm²), the film remained largely unaffected.

Reasoning that oxidation of the metallic tin in the substrate would undermine and loosen the black layer, an experiment was carried out to determine the efficacy of anodic stripping. The plate surface was made anodic at a current density of 6 to

8 amp/ft² (0.006–0.009 amp/cm²) in an electrolyte of 2.5% sulphuric acid for very brief intervals after which the plate was removed and inspected to determine/monitor the changes taking place (Fig. 7). Although the initial treatments were limited to 15-min intervals before inspection, electrolysis periods were extended as confidence in the technique grew, and on average all plates were anodized for 2 h. Anodization did not effect complete removal of the corrosion products but rather changed the character of the film. At this point the current was reversed so that the plate was cathodic and the current density was increased to 15 amp/ft² (0.016 amp/cm²). The effectiveness of this anodic stripping–cathodic polishing procedure can be observed in the photograph of a pewter plate in which only half of the plate was treated in this manner (Fig. 8).

The cathodic polishing was approximately 97% effective in removing the residual corrosion products. The remainder was removed and the plate's appearance greatly improved by mechanical polishing using a soft abrasive in conjunction with a Sears sandblast gun (no. 16817) and ceramic nozzle (no. 1095) operating at 60–80 psig (4.1 atm–5.4 atm). A variety of soft abrasive materials were tested and evaluated (Table 2). Common baking flour was found to give the best results, and was quite inexpensive².

Discussion

The differential states of preservation of the pewter plates in the stacks versus those found singly is most striking and seems to be the result of the protection afforded by marine encrustation which accumulated around the stacks. Over time, the growth of corrosion products between the nested plates appears to have forced the seawater out, thereby limiting electrolysis. Invariably, the bottom surfaces of the plates were better preserved than the top surfaces, possibly the result of galvanic cell action.

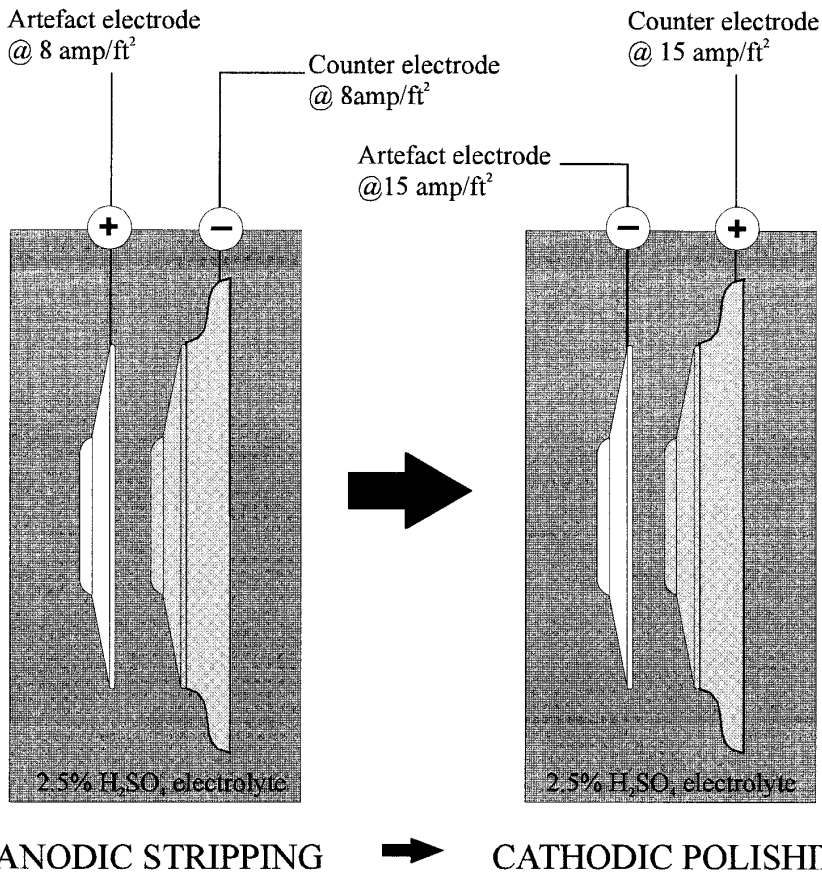


Figure 7. Schematic of stripping/polishing electrolytic cell. Stripping the artefact loosens the resistant black film, polishing reduces and brightens the cleaned surface. The plate is turned on edge to avoid trapping gasses released during electrolysis. The counter electrode is shaped to match the contours of the plate. In order to monitor the process more closely, only one side of the plate is treated at a time (D. H. Keith).

There are several possibilities to account for this type of galvanic activity, the most likely cause being differential aeration (oxygen concentration at the solution metal interface). This type of corrosion was shown by Evans to occur with similar metals in a common electrolyte (Mantell, 1960: 554). Fortunately, the bottoms of the plates were cathodic with respect to the tops, which protected the makers' marks as well as the presumed owner's initials.

The use of reductive electrolysis to clean metal artefact surfaces and to remove

chlorides is a well-known and quite common conservation technique. The use of anodic stripping has not been reported to our knowledge. It is an aggressive and hazardous technique in that the artefact can be defaced or destroyed if caution and restraint are not employed. The use of mechanical or chemical techniques will result in loss of some metal in every instance when a surface is cleaned, and common guidelines have been established through usage. Responsible conservators, through experience and testing seldom damage artefacts. The same is true with anodic

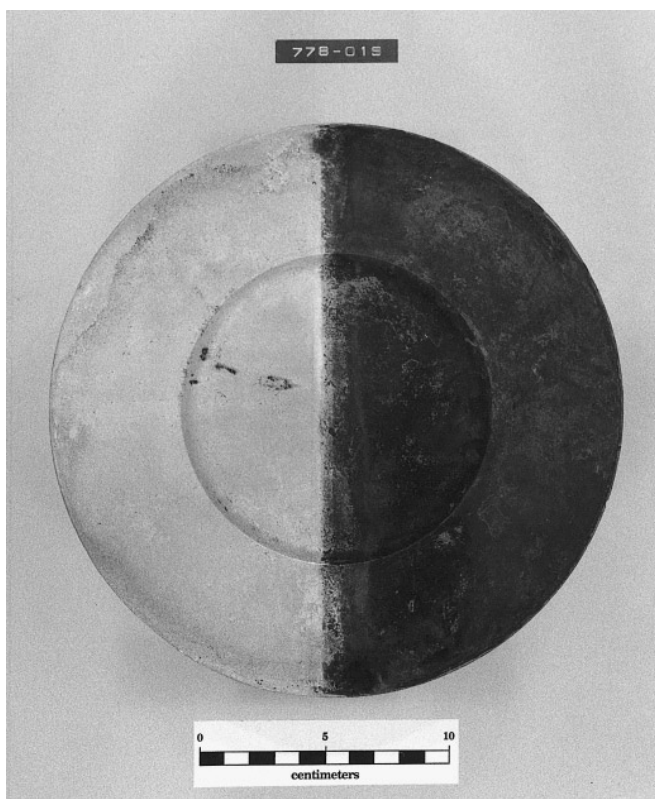


Figure 8. Plate no. 778-015. The right side exhibits the resistant black film that covered all the plates after gross cleaning. The left side has been electrolytically stripped and polished, but not flour polished. (Photo: Mary Caruso.)

Table 2. *Soft abrasives evaluated for final pewter polish*

Abrasive	Effect
Fine pumice	Too hard; overly abrasive
Corn starch	Hygroscopic; clogged pneumatic apparatus
Corn meal	Too hard; hygroscopic; clogged apparatus
Corn meal/corn starch (5:1 ratio)	Appropriate hardness; hygroscopic
Wheat flower	Appropriate hardness; minimally hygroscopic

stripping techniques, with the advantage that a worst case condition can be calculated using some simple assumptions and

the electrochemical equivalents of the elements to determine the maximum amount of metal that will be stripped from the artefact.³

For example: if one assumes for the sake of convenience that a pewter plate containing 93.8% tin, is 100% tin, and if it is made anodic in a solution that does not attack tin, then the worst case condition would be that all of the electrical current would be dedicated to dissolving the tin as $\text{Sn}^0 \rightarrow \text{Sn}^{+2}$, resulting in the loss of 2.214 g of tin metal per amp-hour of current applied. The calculations were performed as follows:

To calculate the mass of tin in a 0.01 cm thickness of a plate 22.25 cm in diameter,

multiply the area of the plate times the specified thickness times the specific gravity of tin. Therefore,

$$\begin{array}{rcccl} \text{Area of plate} & & \text{thickness} & & \\ 0.7854 \times (22.25 \text{ cm})^2 & \times & 0.01 \text{ cm} & \times & \\ \text{Specific gravity of tin} & & \text{mass of tin lost} & & \\ 5.75 \text{ gm/cm}^3 & = & 2.236 \text{ g per } 0.01 \text{ cm} & & \end{array}$$

To calculate the thickness of metallic pewter that would be lost from the surface of the same plate during 2 h of electrolytic stripping at a current flow of 2 amps, multiply the time in electrolysis by the current by the electrochemical equivalent for a change of valence from Sn^0 to Sn^{+2} . Therefore,

$$\begin{array}{rcccl} \text{electrolysis} & & \text{electrochemical} & & \\ \text{time} & \times & \text{equivalent} & \times & \\ 2 \text{ h} & \times & \text{Sn}^0 \rightarrow \text{Sn}^{+2} & \times & \\ & & 2.214 \text{ gm/amp/h} & & \\ & = & \text{mass of metal oxidised (g)} & & \\ & & 8.856 \text{ g tin} & & \end{array}$$

$$\begin{array}{l} \text{So: } [8.856 \text{ g tin}] / 2.236 \text{ g/0.01 cm} = \\ 0.0396 \text{ cm} \approx 0.4 \text{ mm thickness lost} \end{array}$$

Thus a worst case scenario for a 22.25 cm diameter pewter plate anodically stripped for 2 h at 2 amps would be the loss of 0.4 mm of plate thickness. In practice, some corrosion products are being oxidized as well, thereby decreasing the amount of metallic tin that otherwise would be dissolved. In the case of the artefacts that were anodically stripped,

metal losses of the magnitude of 0.4 mm were not experienced, but it had been predetermined that a loss of this magnitude would be acceptable if necessary. Used responsibly, anodic stripping is an effective, time-saving procedure.

Acknowledgments

The authors would like to thank the Texas Historical Commission for entrusting the *Belle* artefacts to our laboratory for documentation, research cleaning, conservation and exhibition in the Corpus Christi Museum of Science and History. Funding for this work was provided by Ships of Discovery, the Friends of the Corpus Christi Museum, and the Texas Historical Commission. Dr M. P. Sudhakaran of the Corpus Christi Water Department also provided generous services. The actual artefact recording, bathing, scrubbing, and blasting was performed by Flora Craig, Laura Tutt, John King, Mary Caruso, Juan Rodriguez, and Audrey Flores. Thanks also to Lissa King Magel for obtaining the critical Auger procedures. Messrs Charles Holifield and Michael Feeney provided the SEM and EDXRF analyses *gratis*. John de Bry of the Center for Historical Archaeology supplied research material and critical translations of French documents.

Notes

- [1] The Auger assays describe the average composition of an area 400–500 Angstroms in diameter.
- [2] The only safety precaution required in addition to ventilation was ensuring that the air gun was electrically grounded to obviate the possibility of explosion.
- [3] The electrochemical equivalent of an element is the number of grams of that substance set free by the passage of one coulomb of electricity through an electrolyte. Electrochemical equivalents are proportional to chemical equivalents.

References

- Cronyn, J. M., 1990, *The Elements of Archaeological Conservation*. London.
 Mantell, C. L., 1960, *Electrochemical Engineering*, Fourth Edition. New York.
 Massé, H. J. L. J., 1971, *Chats On Old Pewter*, Third edition. New York.
 North, N. A. & MacLeod, I. D., 1987, Corrosion of metals. In Colin Pearson (Ed.), *Conservation of Marine Archaeological Objects*, London, 68–98.

Pearson, Colin, 1987, *Conservation of Marine Archaeological Objects*. London.

Plenderleith, H. J. & Werner, A. E. A., 1976, *The Conservation of Antiquities and Works of Art*, Second edition. London.