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A case study for scientific research prior to conservation of marine metal artefacts

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ABSTRACT

A rare find of a high-status 17th century oval box, retrieved from a shipwreck, provided a unique opportunity to research the construction and finishing layers of an object that is untouched for 350 years. This case study was used to demonstrate the extent of data that can be gained from analytical techniques prior to conservation. The amalgam-gilt brass object was studied by optical and electron microscopy, X-radiography, micro-computed X-ray tomography, neutron tomography, X-ray fluorescence, X-ray diffraction, Rutherford backscattering spectrometry, proton-induced X-ray emission and gas chromatography. The results have led to a characterisation of the manufacturing methods used on the box and to a better understanding of the practicality of modern analytical methods and techniques in (maritime) archaeological research.

1. Introduction

During the summer of 2014, a remarkable group of maritime archaeological finds was discovered near the coast of the Dutch island of Texel. Since the moment of discovery, it has become evident that the group of finds belonged to a mid-17th century ship, most likely Dutch but still of unknown origin and destination (Vos et al., 2019). The shipwreck got assigned the working name Burgzand-Noord 17 (BZN17) after its findspot on the Burgzand-Noord sandbank (see Fig. SOI 1.1 for the geographical location). The contents of the shipwreck included objects of both organic and inorganic materials. One of the finds, a 17th century silk gown, has gained much international attention, both in the geographical location). The contents of the shipwreck included objects of both organic and inorganic materials. One of the finds, a 17th century silk gown, has gained much international attention, both in the geographical context. Especially the pristine condition of the objects, untouched for the last 350 years, offers a unique opportunity to investigate manufacturing processes of what seems to be a very rich collection.

Many metal objects were found on the shipwreck, most of which consist of precious or gilt metals, including a variety of luxury objects. Parallels for such objects survive in museums and private collections, but it is the maritime archaeological context of the finds from BZN17 that presents a unique research opportunity. In contrast to the finds on BZN17, metal objects in museum collections have often had numerous conservation treatments in order to maintain their polished appearance. Silver, for example, is still frequently polished to remove superficial tarnish or silver sulphides from the surface. Similar practice concerns (maritime) archaeological objects, which are often cleaned immediately from obscuring corrosion layers and sediment in the conservation process, thereby possibly removing layers that may contain information regarding the production process and use. Recent studies have broadened our knowledge on historic manufacturing processes, like deliberate surface finishes on freshly gilt objects (Crabbé et al., 2013; Crabbé, 2014). Current cleaning treatments usually do not take the potential presence of residues on metal into account, thereby risking probable loss of valuable information on historic production techniques.

The case study presented in this article focuses on one of the metal finds from BZN17, a unique oval metal box (Fig. 1). As far as the authors are aware, no similar boxes are known from museum collections or archaeological sites, nor analogous objects being studied extensively with multiple analytical techniques in order to gain information. In 2017, a preliminary pilot study on this box (Kuiper, 2017) explored
possibilities to find traces of original finishing layers and its promising results led to the current research.

Limited budgets, restricted resources, or insufficient time often withhold archaeological conservators from investigating objects as extensively as would be ideal. The use of analytical equipment is essential in extracting relevant art historical, metallurgical and archaeological information. The case study presented in this paper demonstrates the extent of scientific data that can be gained using a wide range of analytical techniques. The assessment of data provided by these analyses, when considering matters like functionality of techniques, their general access and non-invasiveness, is meant to aid the development of best practice for future research and conservation of (maritime) metal objects.

2. The metal box from shipwreck BZN17

The metal box from BZN17 (inventory number 5372–007) is oval in shape (length ~13 cm, width ~10 cm, height ~4 cm) with a small protrusion on one of the short sides, see Fig. 1. A D-shaped feature is positioned at the side of the box along the entire perimeter. The box has two faces which are decorated with intricate designs and positioned in the box by a rotation along the horizontal axis. Both faces, or plaquettes, portray a female figure in different postures. One side shows the female figure of Venus with a winged cherub on her knees holding up a mirror to look at herself (Fig. 1a). The other side depicts the Greek mythical story of Leda and the Swan (Fig. 1b). Two (nearly) identical copper-alloy plaquettes with the Venus-cherub depiction are known to the authors (Metropolitan Museum of Art (accession no. 1975.1.1357); National Gallery of Art (accession no. 1957.14.587), both circumspectly ascribed to sculptor Paul Hübner, active 1582–1614, Augsburg), yet no identical constructed object was discovered to date. The construction of the box, its opening and closing mechanisms and its internal structure are difficult to identify, as it is too corroded to open. Unfortunately, the exact find location of the box within the shipwreck and its contextual relation to the other finds is unknown.

Boxes of this size could have been part of an entire toilet service, meant for use at a dressing table to ‘make one’s toilet’ (Gruber, 1982, 261). An entire luxury set would consist of multiple boxes, a mirror, candleholders, ewers and a basin (Joy, 1981). Boxes in this shape were often used to keep jewellery, cosmetics, powder or patches (Gruber, 1982, 268; Joy, 1981, 13). The boxes that were part of a toilet service were meant to stand by themselves and would usually have a distinguishable box and lid, of which only the lid would be decorated. The decorated faces in low relief would generally be repoussé work, meaning the decoration would be embossed or chased in the metal sheet using chasing punches and a hammer (Untracht, 1968, 95–117).

Still visible on the box from BZN17, despite the considerably corroded alloy and additional superficial layers, seems to be a golden surface. In past times such objects made from less noble metal were often amalgam gilded to make them appear more costly (e.g. Anheuser, 1999). In the process of amalgam gilding (also called fire gilding), a paste of mercury and gold called an amalgam would be applied to the surface of the metal object, which was made from a silver or copper alloy. The object was subsequently heated in order for the mercury to evaporate. The evaporation of the mercury resulted in a matt and often pale golden surface. Therefore, the colour and appearance of the fresh gilding was improved by implementation of a final procedure, in which colouring ingredients, like saffron or iron oxides were dissolved in a watery solution or in beeswax (see Kuiper, 2017 for an overview of historic sources and employed ingredients). Multiple historic sources describe submerging the gilt object in oil, that is subsequently burnt off, to better remove mercury (e.g. Biringuccio, 1540, 367). Theophilus (12th century, 115) calls the last step de colorando auro. It has since also been referred to as cire à dorer (FR), gilding wax (EN), Glühwachs (DE) and gloeiwas (NL).

Although historic texts give insight in the gilding practice and the application of the colouring treatment (Pappot, 2015), residues of the material itself have only once before been studied on a historic art piece (Crabbé, 2014). The box from BZN17 may retain residues of these processes, which makes it suitable as case study.

Fig. 1. Oval metal box from shipwreck BZN17. Both decorated faces are pictured, with an additional rotation of 180° for enhanced visibility: (a) Venus and Amor; (b) Leda and the swan. Images: Archeologie West-Friesland.
3. Analytical methods

As described in the previous sections, there are several art historical and metallurgical questions related to the oval box. Information gained by multiple analytical techniques can aid in answering questions about the materials used, the construction of multiple parts, the degradation products and the possible presence of remains of colouring treatments. The following two sections will describe the techniques and instruments used and how they contribute to the case study.

3.1. Visualisation techniques

To produce completely in-focus images, digital 3D microscopy (OM) was used to identify finishing techniques and characterise corrosion products on the box. The instruments used are a Hirox KH-7700 Digital Microscope, with visible light as source, and a Foster & Freeman Video Spectral Comparator (VSC) 8000, which combines multiple wavelengths (UV/visual/IR). A detached fragment of the box was embedded in epoxy resin and prepared by grinding and polishing. A Zeiss Axioplan 2 was used to study this sample after cross-section ion polishing with a JEOL IB-19530CP.

Scanning electron microscopy (SEM) was applied to the embedded cross-section, which was coated with carbon, to obtain information on the alloy, the surface finishes and manufacturing techniques. The instrument used is a Thermo Scientific NanoSEM 450.

X-radiography was used to reveal the closing mechanism, internal construction and the manufacturing techniques of the box providing two-dimensional images. The instrument used is a Balteau Baltograph X-ray system, with a rotating table, 2 mm thick copper filter and BIX- and FP-detectors. To obtain three-dimensional information, tomography was used.

Two different micrometre-resolution types of tomography were applied to provide 3D-reconstructions of the box: micro-computed X-ray tomography (micro-CT), based on mapping density differences with X-rays and neutron tomography (NT), based on interaction with neutrons. The instruments used are a custom-made scanner by TESCAN-XRE N.V. for micro-CT at Centrum Wiskunde & Informatica, the Netherlands, and the FISH-facility (Zhou et al., 2018) at Delft University of Technology, the Netherlands, is used for NT.

3.2. Compositional analyses

X-ray fluorescence (XRF) was used to qualitatively identify the chemical elements present on the surface of the box. The instruments used are an Olympus Delta Professional X-Ray Analyzer (portable, used for local point measurements; spot size 10 mm) and a Bruker M6 JETSTREAM (macro-set-up, used for mapping entire face of the box; step size 200 μm). PyMCA software was used to process the data.

X-ray diffraction (XRD) was used to qualitatively (i.e. peak positions rather than intensities) identify crystalline components on the surface of the box, as well as in samples containing potential historical organic material. The instrument used is a Bruker D8 Discover with a Cu-Kα, source and spot size of 0.3 μm equipped with GADDS and DIFFRAC.EVA V5.2 software containing the COD-database.

Energy-dispersive X-ray spectrometry (EDS), coupled with SEM, was applied to qualitatively identify the chemical elements present in the cross-section mentioned previously and in yellow material from the box. The instrument used for the cross-section is a Silicon Drift Detector (SDD) with Pathfinder software from Thermo Scientific in a Nova NanoSEM 450 and for the yellow material a JEOL JSM-IT700HR system with integrated software.

Furthermore, the object was analysed using Rutherford backscattering spectrometry (RBS) combined with proton-induced X-ray emission (PIXE) with a 3 MeV proton beam at the NewAGLAE-facility in Paris, France (Pichon et al., 2014; Radepent et al., 2018). With RBS, it is possible to non-invasively probe the first 30 μm of the surface of the box. The aim was to evaluate the stratigraphy of the object, mainly to determine the presence of organic compounds (to facilitate location selection for GC–MS, see below) and the thickness of the gilding layer. PIXE was used complementary to locally determine the gold composition. The RBS spectra were fitted using the NDF DataFurnace simulation mode (Barradas and Jeynes, 2008). Simulations gave layer thicknesses in TFU (thin film units: 10²² atoms/cm²), that were converted to μm using an average density value of the gold layer.

Finally, pyrolysis–gas chromatography coupled to mass spectrometry (PyGC–MS) was used to characterise organic compounds in specimens from the surface of the box. The instrument used is a Thermo Scientific Focus gas chromatograph and an ISQ mass spectrometer, used in combination with a Frontier Lab pyrolyser (3030D) as sample introduction technique.
4. Results and discussion

The box has been studied in its entirety, but the results of the side with Venus and the side with Leda are comparable. Therefore, the results presented here will focus on the side with Venus.

4.1. Conservation state

Previous to or during its recovery from the seabed the object was badly damaged in especially one area (Fig. 2; bottom area in Fig. 1a).

This gave the opportunity to visually examine part of the interior of the box. On the inside of the D-shaped side, an internal sheet metal structure can be observed, which exhibits a layered or laminar structure. This morphology is markedly different from the plaquettes, where a relatively smooth surface outlines the well-visible decorations.

The following paragraph will combine results from visual examination of the corroded and fragile state of the box (with the unaided and aided eye) and X-ray diffraction for possible identification of the corrosion products.

Different types and degrees of corrosion are observed. The decorations on the gilded metal substrate of the plaquettes and gadrooning are (partly) obscured by a relatively thin corrosion layer. The corrosion varies in colour from brass-yellow to brown to black, sometimes with an iridescent purplish tarnish (Fig. 3a). XRD results show that both covellite (CuS) and chalcopyrite (CuFeS$_2$) are present on the surface (see Fig. S01 2.2), which may exhibit the same range of colours as those seen on the box (Fig. 3a), depending on their layer thickness. Both compounds are commonly found on maritime finds (Scott, 2002, 227). To a lesser extent, light green corrosion is visible on the faces of the box as well (Fig. 3b). At the moment, the nature of the compound is unknown due to the lack of reliable XRD results, but a copper-containing corrosion form is expected because of the green colour. All over the plaquettes and gadrooning, small pustules can be seen, varying in size from 100 $\mu$m to 4 mm (Fig. 3a, red arrow). Also, on several locations on both plaquettes, spots of white, powdery material can be seen and microscopic research indicates that this material invariably occurs on the inside of a damaged...
pustule (Fig. 3c). Either Zn(SO$_4$)$_2$·4H$_2$O (boyleite) or a zinc chloride compound (Zn$_2$Cl$_2$·H$_2$O$_{16}$) are possible matches according to XRD (see Fig. S01 2.3) and both are white. Their plausible presences may be an indication of a chemically unstable corrosion compound.

The external sides of the box are covered with a thick, partly cracked corrosion layer that extends to the gadrooning on the faces (Fig. 2) and that exhibits two differently coloured areas: brown (covellite and chalcopyrite), and blue-black (predominantly covellite, see Fig. S01 2.4; all

Fig. 4. Elemental XRF-maps of the entire face of the box with Venus, showing the distribution of the major elements. Lighter areas correspond to higher elemental concentration.
confirmed by XRD). The blue-black areas appear blue in cross-section (Fig. 2) and inside and through the cracks, the gilding layer can be distinguished (Fig. 3d). Pustule-like features are present here as well, but it is unknown whether these originate from decorative features of the original metal or whether it is comparable to the pustules seen on the faces. The typical blue colouration seen with the unaided eye, combined with the XRD results, indicates that this compound is covellite.

Another coloured material can be seen on the box, preferably along the edge of the gadrooning: yellow (Fig. 3e). As described in section 2, colouring treatments were regularly carried out after amalgam gilding. As this yellow compound could be a remnant of a pigment intentionally added in the 17th century, the results of its chemical analysis will be described in section 4.4.

The difference in conservation state between the different components of the box can be attributed to different types of dezincification during corrosion of brass alloys (>15 wt% Zn) in water (Brock 2001, 1662). In brasses containing only the alpha-phase, uniform layer corrosion is preferred, while in two-phased brasses, plugs or pits may form. Rolled sheet metal usually has a heavily deformed single-phased microstructure, while cast metal has a two-phased dendritic microstructure. This implies that sheet metal is susceptible to form a lamellar structure, while cast components may develop pits. These pits can
become filled with higher-volume corrosion products over time. When a
gilding layer is present on the brass, this can lead to visible expansion
(pustules).

4.2. Elemental composition

Although, prior to this research, the type of metal alloy of the box
was unknown, it was likely that it concerned a gilt silver object, based on
visual examination and as most other gilded metal items among the finds
had already been analysed as such. However, point analyses by portable
XRF (see SOI 3.2 for spectra) on the surface of the faces of the object
show mainly copper (Cu), gold (Au), mercury (Hg) and zinc (Zn), with
traces of lead (Pb), nickel (Ni), antimony (Sb), silver (Ag) and tin (Sn),
which can be interpreted as originating from a copper alloy with zinc
(brass), gilded with an amalgam of mercury and gold. Iron (Fe) and
sulphur (S) are present as well in major quantities, which most likely
come from the marine environment, as are calcium (Ca) and arsenic (As)
in trace amounts. The lack of reliable calibration standards prevents a
quantitative analysis of the chemical composition. In addition, the
amount and type of contamination from the maritime archaeological
context is unknown, which makes the data more difficult to interpret.

To provide an overview of the distribution of chemical elements
along the surface of the box, macro-XRF was applied to the decorated
faces and the results of the major chemical elements found on the Venus-
side are shown in Fig. 4.

Copper is omnipresent on all parts of the face and on the side of the
box, while zinc is locally present, especially in the gadrooning. Locations
with relatively high zinc content correspond to areas with white pow-
dery corrosion as described in the previous section. Both the heavily
corroded side of the box and low-relief areas of the surface are rich only
in copper, iron and sulphur, while gold, mercury and zinc are notably
absent there (black areas in Fig. 4). This suggests that Cu, Fe and S are
part of the corrosion that is also visibly different with the naked eye
(blue-black at the side and brown-black on low-relief areas, see Fig. 2).
This is in accordance with XRD results (section 4.1). The high-relief
areas mostly consist of Au and Hg, for which nearly identical images
were produced. Even though a slight peak overlap between both ele-
ments should be taken into account, this confirms that the object was
amalgam-gilt using an amalgam of Au and Hg. The variation in
composition we have measured with both XRF instruments on different
parts of the box is best attributed to the presence of corrosion layers of
different thicknesses, obscuring the underlying gilding layer in varying
amounts, and measuring the underlying copper-based substrate in varying
amounts as well.

A fragment was found detached from the box and its origin could be
reconstructed with high certainty, see Fig. 2. An embedded cross-section
of this fragment was studied by OM and SEM-EDS. A clear gilding layer
with a thickness varying between 10 and 100 μm is found in between a
dark-coloured matrix and a blue-green layer (Fig. 5a).

SEM-EDS analyses (see SOI 4 for more details) of the gilding area
(Fig. 5b) show the layer is composed of gold-rich areas (white), con-
taining traces of mercury and silver, dispersed in a matrix of copper and
sulphur (grey). The presence of mercury and the globular morphology
is consistent with the process of amalgam gilding on copper (Anheuser,
1999, 24, 34). A relatively thick layer with undeformed gold-rich areas
(Fig. 5b) is the result of the application of a large amount of amalgam
paste that is not subsequently burnished, while a thinner, more compact
layer is a typical result after burnishing (Fig. 5c). The copper-based
matrix in which the gold-rich areas are dispersed is most likely an
infill that has formed during corrosion of the brass box during its pres-
ence in the marine environment. The microstructure and composition
(Fig. 5c) of the dark-coloured vertically oriented parts as analysed with
SEM-EDS (see SOI 4 for more details) lead to the conclusion that these
parts are corroded brass components, which belong to the interior sheet
metal structure and profiled decoration strip. The blue layer could be
identified with SEM-EDS as a layer consisting of copper, sulphur and
traces of iron, consistent with the XRD results on the exterior of the box:
chalcopyrite (CuFeS$_2$) and covellite (CuS). The presence of trace
amounts of silver in nearly all phases present in the entire cross-section
indicates that silver is present in the alloy materials in the form of traces
in the copper matrix and/or inclusions.

The thickness of the gilding layer on two locations on the Venus-
plaquette was deduced by simulations based on non-invasive RBS and
PIXE measurements on areas where the gold was well visible. The RBSSpectra were fitted considering 3 layers: a substrate of corroded brass, a
gold layer with porosity and one organic layer on top (see SOI 5 for
determine the thickness of the gilding. A roughness of around 25% of the virtual section along the longitudinal axis of the box, with the Venus-casting. Two old deformations can be seen as well (areas E1 and E2, see Fig. 6); bottom side of the Venus-plaquette, showing a smooth outline, indicative of showing the possible opening mechanism with the Venus-side on top; (b) the Fig. 7.

Reconstructions made from neutron tomography. (a) Interior of the box showing the possible opening mechanism with the Venus-side on top; (b) the bottom side of the Venus-plaquette, showing a smooth outline, indicative of casting. Two old deformations can be seen as well (areas E1 and E2, see Fig. 6); (c) virtual section along the longitudinal axis of the box, with the Venus-plaquette shown on top and the one with Leda on the bottom.

data). The heterogeneity of the surface made it difficult to precisely determine the thickness of the gilding. A roughness of around 25% of the thickness of the gold layer was necessary to properly fit the spectra. The simulations show that the gilding layer thickness in the measured areas can be assumed to be $4 \mu m \pm 1 \mu m$, which is considerably lower than the values deduced with OM and SEM (10–100 $\mu m$). This is probably due to the fact that the cross-section for OM and SEM originates from an area on the box that is less prone to wear than the high-relief areas used for the RBS-simulations.

4.3. Construction

The two decorated faces of the oval box in this research would seem to suggest that the object was not meant to stand on its own on for example a table, but instead might have been carried with a person, perhaps suspended from a chain of some sort. To further research the construction and manufacture of the object that is too corroded to open, it was analysed by X-radiography (Fig. 6).

Area A shows the internal structure of the protrusion on one of the short sides of the box. It can be identified as a knob, that could either be a suspension part or that could have been used to open and close the box. Boxes of this type have usually a tight-fitting lid (press-fit), sometimes even without a hinge. If a hinged mechanism is used, the opposite side of the box has usually a small knob that can be pressed to open the lid. A hinge could not be identified on this object, since the box is damaged on the expected location.

This damaged area has enabled the identification of a hollow structure of the D-shaped side (Fig. 2), and the X-ray images clarify that this area is hollow along the entire perimeter of the box (Fig. 6, D) and several larger and smaller cracks are seen, indicative for mechanical instability. Also, the internal sheet metal structure is present along the perimeter.

Small white spots and more stretched patches are visible on the interface between plaquette and gadrooning (Fig. 6a, area B1, ~20 mm diameter) and at the base of the D-shaped side (Fig. 6b, area B2, ~15 mm diameter), which can be interpreted either as soldering residues, possibly lead or silver, as gold residue from gilding or as a relatively large amount of copper alloy. These areas are not distinguishable by neutron tomography. Since the presence of lead would have led to visible voids in reconstructions based on the used neutron tomography set-up, this material can therefore be eliminated. The observation that these areas have the same grey value as their surroundings also indicates that large amounts of gold and silver can be ruled out. But, unexpectedly, the gilding layer could not be clearly distinguished from the base metal (=non-ferrous metal, neither precious nor noble), even though its presence is confirmed by other techniques. The voxel size of the NT set-up is ~150 $\mu m^3$, while the gilding layer is estimated to have a thickness up to 100 $\mu m$ (see section 4.2), leading to apparent invisibility with NT. Therefore, the chemical composition of the patches is still inconclusive.

A fragment of another object from the shipwreck is adhered to the Leda-side of the box at location C, which can be seen with the unaided eye. The high brightness of this area in the radiographs suggests a material with a relatively high density compared to copper, which is confirmed by XRF where a high concentration of silver is measured.

Due to the limitations of X-radiography (two-dimensional imaging of a three-dimensional object), no conclusive observations on the box construction and the method of plaquette manufacture (casting or embossing) could be made. To create a three-dimensional visualisation of the box, both micro-CT and neutron tomography (NT) were applied. For this specific object, the results of NT are of higher quality than those of micro-CT, whose results will therefore not be shown in this article.

Fig. 7a shows that the possible opening mechanism is now incomplete, with the knob (see Fig. 6) located at the left of the rectangular opening. This shape suggests perhaps the use of a spring system with the steel spring now completely disappeared, probably due to corrosion.

From the reconstructions made from NT, it can be deduced that the backs of the plaquettes roughly follow the form of the decoration (Fig. 7b), and the thickness measures about 2–3 mm, consistent with manufacturing by casting. The gadrooning and other sheet metal structures are embossed, based on their shape and thickness (~1 mm). This is in agreement with the observation of different corrosion morphologies on the different box components (section 4.2).

On the lower side of the Venus-plaquette, a small hole is visible with the naked eye. This area is also visible in the reconstruction made with NT, where a small patch can be seen (Fig. 7b, area E2). Between the female figure of Venus and the mirror additional protruding material is visible in the NT reconstructions (Fig. 7b, area E1). This area was faintly visible on the X-radiographs as well. On both locations, no visible higher-density areas can be identified with NT. The smooth outline of E1 suggests that it is an area where the mould has been altered to accommodate additional metal, to serve as a cast-on reinforcement. Area E2 is probably repaired after the emergence of a casting defect, by soldering a patch underneath. Silver solder would be most plausible since lead-tin solder would melt away during the gilding process. In both cases, these areas could only be identified as repairs after using the complementary neutron tomography data.

From the data yielded by visual examination, optical and electron microscopy, X-radiography and tomography, it is possible to make an illustrative reconstruction of the box construction. The most plausible construction, based on data and comparable historical techniques, is...
shown in Fig. 8.

4.4. Organic surface finish

Both XRF and SEM-EDS analyses confirmed the gilding to be an amalgam gilding. The maritime context of the oval box possesses a high potential of finding original organic finishing layers, as explained in the introduction. Therefore, this section describes the multiple techniques that were employed to detect such components.

Since organic compounds like wax tend to be fluorescent under UV-light with different wavelengths (Measday et al., 2017), imaging with wavelengths of 365 and 600 nm was applied to one of the faces of the box. No organic coating is detected that fluoresces with these wavelengths. Only dust particles and small hairs show fluorescence.

The RBS analyses could not ascertain the presence of organic compounds.

For analysis by GC–MS, five small surface samples were scraped off low-relief areas of the dark-coloured material in the decoration as these would have endured little wear. A large amount of sulphur compounds is found on each sample, most probably originating from the corrosion layer as explained in section 4.1. Mercury is also present in the majority of samples, which indicates that those samples contain material ranging from the gilding up to the corroded surface. That implies that if organics from the production process are still present, they should be detected. Arsenic compounds, proteins and sugars are identified and are interpreted as residues from the marine environment, also because historical sources do not indicate the presence of proteins or sugars in the recipes for organic finishing layers. Due to the lack of contextual information on the marine environment, this cannot be tested. The fatty acid pattern in all samples might indicate the presence of an (oxidised) plant-based oil. Furthermore, pine resin/tar compounds were found in trace quantities in nearly all samples. This might indicate the possible presence of an (historic) oil/resin-varnish. These compounds are not interpreted as cross-contaminations, because then a higher amount would be expected and most probably in combination with a significant amount of human skin grease. In a single sample, some markers can be attributed to a trace amount of (altered) beeswax. Conclusive matches to known (degraded) oils, resins or beeswax could not be made at this time, due to the very low concentration and the absence of scientific data about the shipwreck and its contents.

As mentioned in section 4.1, yellow material is visible on multiple locations on the box. In the colouring treatment after gilding, the use of iron oxide as pigment is described in historical sources. SEM-EDS analyses show that sulphur, iron and oxygen are present, as well as traces of copper and zinc, in multiple samples (see Fig. SII 4.9 and Fig. SII 4.10). With XRD, no corresponding compound matches can be found (see Fig. SII 2.5). The powder-like morphology in combination with the absence of an iron oxide phase leads to the conclusion that the yellow material is a corrosion product, adhered to the brass of the box.

5. Conclusions and future perspectives

A 17th century oval metal box from a maritime context was researched and used as case study to demonstrate the extent of scientific data that can be gained from analytical techniques when lack of time or resources are no impediment. Comments on the applicability of these techniques are given in this section in order to aid future studies. Yet, it is not the current aim to develop a standardised protocol.

Optical microscopy was used to study the object closely, to identify

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1 Personal communication with Henk van Keulen and Saskia Smulders.
The use of XRD is gaining more attention within archaeological science, combining visual examination with XRD, both non-invasive techniques. However, such standards and their incorporation into user-friendly software are being developed in the field of cultural heritage. The combined use of two other non-invasive techniques (RBS and PIXE) provided local thickness measurements of the gilding layer. However, this requires highly specialised data analysis on a facility that has very limited access.

The different corrosion products were successfully characterised by combining visual examination with XRD, both non-invasive techniques. The use of XRD is gaining more attention within archaeological science, and more knowledge about its application to cultural heritage material is gained. A set-up with a 2D-detector allows the analysis of artefacts with dimensions like the oval box and this set-up is becoming more common. Also, portable XRD-systems are under development, which facilitate the analysis of non-flat surfaces. Multiple non-invasive imaging techniques were used to unravel the construction of the box. X-ray imaging is a well-known and well-used technique and was therefore applied first, with a (less-standard) rotating set-up that allowed semi-3D-visualisation. Even though the majority of the information needed was provided, no reliable conclusions could be made upon this data alone. Therefore, more high-end neutron tomography was applied. The resulting reconstructions provided additional information on solder types, ways of manufacture and construction. It is expected that the resolution, power and sample-size of micro-CT will increase in the near future, as well as the facilities becoming more accessible, which will be a good option to visualise the interior of an object. Also, alignment protocols and software development for X-radiographic set-ups with a rotating table are currently under development, thereby enabling tomographic output from more traditional equipment.

Unfortunately, no remains of organic finishing materials that were intentionally applied after amalgam gilding were conclusively found using non-invasive microscopy with UV-light and by analysing scrapings of the surface of the box by GC–MS. Both techniques are well-accessible and relatively inexpensive, but standards and a reliable reference database for archaeological material are still under development for GC–MS. RBS/PIXE shows potential in non-invasively detecting organic compounds on the surface, but its highly specialised nature is limiting its use.

A broken-off fragment of the box, embedded in resin and prepared as cross-section, has allowed the confirmation and semi-quantification of chemical elements and box construction by optical microscopy and SEM-EDS. In order to confirm hypotheses formulated by the results of non-invasive techniques, analyses on scrapings or fragments are often more conclusive.

The applied analytical techniques build up a picture of a high-quality luxury item with a complex construction. Despite the fact that the box is made from brass, it has all the characteristics of a precious metal object. The object is virtually completely mineralised, making it initially very difficult to understand its construction. 3D-visualisation techniques were used successfully to overcome this problem and provided not only essential information on the construction but also identified repairs and supplied evidence that the decorative plaquettes were cast. Most of the techniques described in this pilot study are complementary and every technique uniquely contributes to the answers on questions about manufacture and conservation. This information could all be extracted prior to cleaning and conservation of this object and can serve as an important case study for future research on very fragile and corroded objects, aiding stakeholders in the archaeological process in making well-informed decisions about research and conservation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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References
