A Non-Destructive Toolkit for Silver Plate Identification

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Abstract
How can we effectively differentiate fused plating from electroplating in decorative arts? When silver plating is intact or restored, differentiating is not always clear. This is a crucial question in silver conservation, as the plating method will likely determine the treatment of the surface. Using a combination of visual aids and non-destructive analysis, a selection of objects were studied to inform effective and suitable treatment for delicate electroplated surfaces and other forms of silver plate. The thickness of silver plate was calculated using the ratio of copper K_α and copper K_β peak heights in energy dispersive x-ray fluorescence (ED-XRF) spectra of the presentation surface; results compared favorably to 3D microscopic measurements and differences were clear between plating techniques. It was therefore found that ED-XRF used in combination with expert visual analysis can be a powerful tool in determining possible manufacture methods and ascertaining treatment steps.

Keywords
silver plate, decorative arts, visual analysis, non-destructive analysis, metal cleaning, electroplate, fused plate

Introduction

The Conservation of Silver and Copper Alloy Objects project is part of a multiphase initiative to treat objects in Winterthur Museum's collections prioritized by greatest conservation need. In October 2016, the Institute of Museum and Library Services (IMLS) awarded funding to support a two-year project to remove aged or failed lacquer coatings, then polish and recoat approximately 500 silver objects, continue analytical research related to silver surface corrosion (Pouliot et al. 2013), and commence new research on corrosion and coating issues. As the project progressed, inaccurately identified plating techniques were discovered in the museum catalogue: this accounted for approximately 5% of objects. Fused plate (also called Sheffield or silver plate) was mistaken for items with electroplated or brush-plated surfaces. Restoration techniques, fabrication methods such as electroforming, and misleading marks further complicated visual identifications. These objects presented their own unique treatment problems.

Tarnish is easily removed from a silver surface with a mild abrasive, such as calcium carbonate. This polishing technique permanently removes the most superficial layer of the precious metal. Unlike sterling or coin silver, silver-plated objects have a thin display surface of silver and a more substantial substrate of a base metal. Electroplated objects are particularly prone to mistreatment, as the precious metal display surface is microns thick and can be removed during a polishing campaign.

Identification to date has focused on destructive and non-destructive methodologies (Carl and Young 2016) not always accessible to those in smaller institutions or private practice. This paper aims to show how visual aids and portable energy dispersive x-ray fluorescence (ED-XRF) equipment can be used to identify plating methods and thus inform treatment.

A brief summary of silver-plating methods

Silver-plated objects included in this study illustrate typical plating methods used since the late 1700s. Early European application of silver plating employed steps of mechanically burnishing layers of extremely thin leaves of pure silver onto a completed base metal object.[1] By the 1700s, "French plating" described silver leaf applied onto copper alloy (brass) objects, and "close plating" described silver applied (often with tin) to iron/steel items.[2]

Innovations in rolled sheet metal production contributed the new method of fusing, via heat and pressure, a surface layer of silver onto copper. In the 1740s such "fused plate" became a patented industrial manufacturing technique to chemically fuse a silver layer to a prepared copper core, sometimes on both sides. The method was also used infrequently for silver on copper alloy. To create completed objects, the fused metal could be rolled, hammered, stamped, and joined mechanically or with silver solder.

In Sheffield and other parts of England and the United States, some manufacturers applied narrow sterling silver edges to cover joins, reinforce edges, and inhibit loss to the surface from wear and polishing during the first generation of use. Inset sections of sterling or more thickly-plated fused plate were used for hand-engraved ornaments. The fused plate body of this Argand lamp (Figure 1) bears owner's initials engraved on a silver inset that is much more obvious now due to two centuries of polishing.

Figure 1. Argand lamp, attributed to Matthew Boulton, probably Birmingham, UK, fused plate, brass, glass, tinned sheet iron; Winterthur Museum, Bequest of Henry Francis du Pont, 1965.1374

Beginning in the 1840s, faster and much more efficient methods using Faraday's principles of electrolysis were employed to deposit a nearly pure silver layer on fully-formed base metal objects and components. This fish server (Figure 2) now exhibits plating loss, particularly on the handle. The thickness of electroplating could vary by the duration of time for application and by manufacturer's intent.[3] In 1878, one company's standard to measure the silver thickness was maintained by weighing the finished white metal object (often an alloy of tin, copper, and antimony or German/nickel silver) prior to and again after plating.[4] During the same era, electroplating was used to silver-plate electroformed objects (see Case Study 4). As this brief summary indicates, verifying an object's construction and plating techniques is essential for pre-treatment queries.

Figure 2. Patented fish server or fish knife, marked by John and Joseph Cox, England, ca. 1848–51, nickel silver and electroplated silver; Winterthur Museum, Gift of Mr. and Mrs. C. Thomas Attix, Jr., 1999.0023

A non-destructive toolkit

Throughout the project, ED-XRF spectroscopy determined object elemental composition and helped deduce object manufacture in conjunction with visual examination methods. The following "toolkit" outlines the methodologies used for both techniques in the examination of objects to be treated.

Visual examination

Visually confirming plating methods and materials is assisted by identifying (or ruling out) techniques as well as recognizing evidence of loss of plating. Plating loss occurs from use and commensurate polishing, as well as corrosion of the exposed base metal substrate. Fused plate is easy to confirm today through observation of the copper substrate, visually thick plating, and manufacturing methods (i.e., not sand cast). Plated white metals are more challenging to identify without manufacture-specific stamped identifications or a firm's known preferences such as thin, spun Britannia metal, stamped copper, or strong, cast or drop press-formed nickel silver.[5] Adding complexity is surface restoration by electroplating or French plating, practiced from the mid-1800s until today. Thinly electroplated surfaces are sometimes difficult to distinguish from reduced original fire gilding or fused plating. As ever, seek expertise and references as well as ED-XRF spectroscopy.

Recommended steps for visual examination

- Step one
  Surface: Examine the entire surface and patina to discover character of plating method(s).
  Ask: How thick is the plating? Burnished, smooth surfaces? Brushy looking application? Detectable granular deposits or layers? Blistering? Any solid silver fills? Plating on all surfaces? Other plating (gold, tin) present? Corrosion color? Loss commensurate with function?
- Step two
  Ornament and Decoration: Ornamenting techniques using hammering, die-rolled sections, cast elements, or even drop press-formed elements can help confirm less visible materials.
  Ask: Applied by hand with solder? Integral to body construction? Chased or stamped? Pierced with fly press or by hand? Engraved on body or an inlay?
- Step three
  Construction techniques: Historically plated object components were formed by combining many construction techniques, most machine-aided. Manufacturing signs are visible on fused plate. Electroplating typically is applied to a completed object, thus overlays solder joins and hand-finishing techniques.
  Ask: Hand-raised/hammered? Rolled sheet metal? Spun or lathe skimming lines? Stamped or swaged? Seamed and soldered joins? No joins visible? Cast? Hammer marks, but superficial (not from forming)? Electroformed?
- Step four
  Weight and "feel": Fused plate is hand-raised and/or stamped and joined, thus thin-walled and vulnerable to dents and deformation. Spun, stamped, or hammered silver-plated white metal objects are often thicker gauge, stronger, and heavier in the same form. Electroplated Britannia metal can be an exception.
  Ask: Gauge consistent between all elements? Base or components filled or weighted (pitch, sand, plaster)? Resonance or density?

Analysis by ED-XRF spectroscopy

Analysis was performed with a handheld Bruker Tracer III-SD XRF spectrometer using a rhodium tube (40 kV high voltage, 9.6 µA anode current, 25 µm Ti/305 µm Al) for 60 seconds live time irradiation. The spot size is oblong in shape, approximately 1 cm × 0.5 cm. Spectra were interpreted using ARTAX software.

Additional information can be gleaned from spectra to semi-quantify plate thickness. Due to the phenomenon of attenuation from different emission lines in the ED-XRF, the thickness of a silver "coating" atop the substrate metal was calculated using the ratio of copper K_α (8.04 keV) and K_β (8.90 keV) peak heights ($Cu(K_\alpha/K_\beta)$) in terms of counts per second, using the following equation:

$$Cu(K_\alpha/K_\beta) = Cu(K_\alpha/K_\beta)_0 \exp -560d_{Ag}$$

where $Cu(K_\alpha/K_\beta)_0$ was measured experimentally from pure copper (6.986), d_{Ag} is the thickness of the silver "coating" (in cm) and "560" refers to the difference in theoretical attenuation coefficients of silver at the energies of the copper K_α (8.04 keV) and K_β (8.90 keV) emission lines (Cesareo et al. 2009). Errors in the results derive from alloying elements in the base metal or plate.

Identification case studies

The following case studies demonstrate how the toolkit was developed and used during the project.

Case study 1: Fused plate spoon with original plating

Figure 3. Tablespoon, Birmingham, UK, 1808-23, silver plate on copper (fused plate); Winterthur Museum, Gift of Philip E. Toussaint, 2018.0009

A recent acquisition allowed us to examine the plating technique microscopically and to validate ED-XRF thickness calculations. An English fused plate tablespoon (Figure 3) showed some worn surfaces, exposing the base metal, and a crack in the bowl near the handle. ED-XRF of the exposed base metal showed pure copper, without alloying elements. ED-XRF of the silver presentation surface showed copper and silver with trace amounts of lead and gold, suggesting a non-electroplated object.

The crack exposed a cross section of the plating (Figure 4a). The base and plate metals are distinguished by their coloration and texture. However, the profile of the crack (Figure 4 b) showed a lip in the approximate location of the plate/base metal boundary. Further analysis of the ED-XRF data from the silver presentation surface semi-quantified the thickness of plate to 5 μm. This is similar to the plate thickness measured by 3D microscopy.

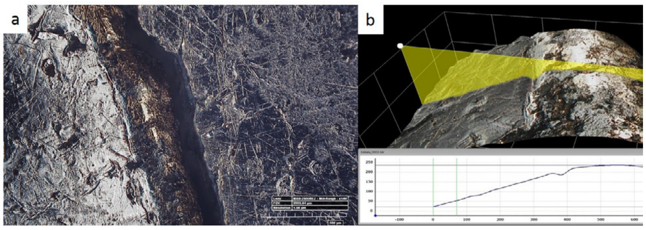

Figure 4. (a) HIROX digital microscope image (credit: Steve Buck, HIROX USA) of fused plate spoon (2018.0009) at a crack in the bowl near the handle; (b) 3D image of cross section with integrated height measurement. The red box indicates the location of the silver plate/ base metal boundary, the height of which was measured to be 8 μm

Case study 2: Argand lamp with a misidentified surface

This case study demonstrates how ED-XRF can be used to enhance visual identification and inform treatment of an object containing mixed techniques. This oil-burning lamp's metal components were previously visually identified as fused plate, but the lampshade (Figure 5) raised questions about the accuracy of this conclusion. A cleaning test revealed the silver easily abraded and therefore was too thin for fused plate.

Figure 5. Argand lamp, Sheffield or Birmingham, UK, 1785-95, silver plate on copper (fused plate) and silver-plated copper (electroplate), iron, glass; Winterthur Museum, Gift of Henry Francis du Pont, 1961.1692.001. Left to right: before treatment (BT), during treatment (DT) (shade exhibiting thin-film interference), and after treatment (AT)

ED-XRF analysis of the shade showed the presence of both silver and copper. The lamp's fuel reservoir also showed the presence of zinc, which is a common alloying element for copper used in the fused plate process (Crosskey 2011). Comparing results from the shade versus areas of suspected fused plate, the shade shows a much lower signal from silver, which implies a smaller concentration of silver and possibly a thinner plate layer.

In order to confirm this, further analysis of the data was required (Table 1). Alpha and β emission lines are absorbed differently by surrounding elements after emission, so the deeper the element or the thicker the layer on top, the more the ratios are affected. Silver L lines are less penetrating than K, so they only reveal what is happening at the uppermost surface of the object. Table 1 shows that AgL ratios for all regions of the lamp are similar, which implies that silver exists in the uppermost layer across the entire object. Silver K lines are more penetrating, so they provide information about silver beneath the plate: electroplated samples have lower ratios due to low absorption by the thin electroplate, whereas thicker plate will show higher ratios due to larger amounts of absorption from the plate. Therefore, Table 1 shows that the shade has clearly lower ratios compared to other regions of the lamp, implying a very thin, possibly electroplated layer.

Table 1. K and L ratios and plating thickness for various sampled parts of the Argand lamp (Figure 5)

Lamp part	CuK ratios	AgL ratios	AgK ratios	Plate thickness (μm)
Shade (DT) spot 1	6.84	1.87	2.62	0.37
Shade (DT) spot 2	6.93	1.82	2.89	0.14
Shade support (DT)	5.69	1.61	6.36	3.67
Shade rim (DT)	3.87	1.76	5.91	10.6
Fuel reservoir (AT)	4.20	1.68	5.85	8.71

In order to semi-quantify the thickness of the plate, CuK ratios were used to measure the absorption of these emission lines by the silver layer. The results are shown in Table 1. The shade shows a silver thickness of much less than 1 μm, which is clearly different in from the rim, the shade support, and the fuel reservoir, which was visually identified as fused plate. In fact, the shade was found to have been brush-plated in its treatment history.

Case study 3: Sugar bowl with interior/exterior differences

Visual examination of this sterling hallmarked sugar bowl (Figure 6) revealed worn areas having a copper substrate, suggesting silver plate, and a yellow color on the interior, suggesting gilding or preferential tarnish. ED-XRF data collected from the exterior of the bowl showed a similar composition of Ag and Cu with traces of Zn and Ni, while data obtained from the interior showed Ag and Cu only. Small amounts of gold were also detected in the interior, suggesting the silver-plated interior had been gilded.

Figure 6. Sugar bowl, marked for "R.P.," London, UK, 1927, fused plate, electroplated gold; Winterthur Museum, Gift of Mr. and Mrs. James A. Drain, 1982.0272.002. Left to right: BT and AT

As discussed previously, further analysis of the ED-XRF data can provide more information about the plating and layer structure (Table 2). In general, the lower the α/β ratio, the more attenuation: either self-attenuation by a thick layer, or attenuation by a covering element. Table 2 demonstrates that AgL ratios for all exterior surfaces are similar, indicating that silver is present in the uppermost layer across the entire object. However, the AgL ratios for the interior are higher, suggesting a different surface treatment, e.g. gilding. Because silver K lines are more penetrating, they detect silver beneath the uppermost layer: gilded interiors show lower ratios due to the attenuation by the gilded layer of the silver emission K lines from the underlying silver.

Table 2. K and L ratios and plating thickness for various sampled parts of the bowl

	CuK ratios	AgL ratios	AgK ratios	AuL ratios	Plate thickness (μm)
Side	5.77	1.70	5.94		3.41
Side	5.74	1.71	5.86		3.51
Base	5.95	1.78	5.42		2.85
Handle	5.81	1.68	5.62		3.28
Interior	4.94	3.30	4.72	1.93	3.64

To semi-quantify the thickness of the plate, CuK ratios were used to measure the absorption of these emission lines by the plating or gilding (Table 2). The results from the gilded interior are not accurate because the copper is silver-plated *and* gold-plated. However, the exterior plate is of a uniform thickness, approximately 3 μm.

Case study 4: Electroformed Kettle

This hot water kettle (Figure 7) is designed to rest on a pierced base, which holds a small lamp. The copper substrate is visible in some areas, but not around the curve of the body, where abrasion typically occurs. The body and lid are very thin, with no clear signs of hammering, repousse tool work, or joins from assembled stamped components. The rigid upright handle with the appearance of a riveted swing handle confirmed the visual assessment that the vessel was not fused plate but entirely electroformed. The interior of the electroplated body contains a rectangular tab to which a diode was attached during electroforming. ED-XRF results show copper and silver only, with trace amounts of mercury and arsenic (Figure 8), and plate thickness was calculated as 4.5 μm, confirming the object's visual identification.

Figure 7. Hot water kettle, probably made in England or the United States, 1850–1900, electroformed and silver-plated copper, rattan; Winterthur Museum, Bequest of Henry Francis du Pont, 1958.1965. Left to right: BT and AT

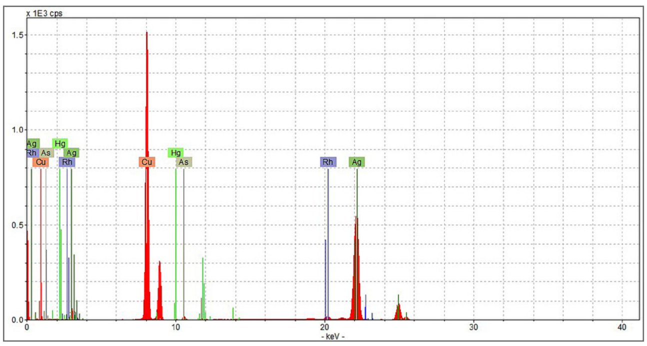

Figure 8. Spectrum of an exterior section of electroformed kettle in Case study 4; Winterthur Museum, 1958.1965

Treatment implications at Winterthur

The primary goal of the IMLS grant-funded project is to remove aged or failed lacquer coatings, polish, and recoat approximately 500 of the museum's most vulnerable silver objects. In general, aged coatings are removed with pressurized steam or solvent. The surface is then lightly polished with a calcium carbonate slurry. Finally, a minimum of two coats of Agateen #27 are sprayed or brush-applied.

While these steps remain the same for most types of silver plate, electroplating has been determined to be too thin to polish with calcium carbonate. For example, the Argand lampshade (Case study 2) was washed with a very dilute solution of calcium carbonate instead of being abrasively polished with a paste. Further investigation used photomicrography to explore the effects of five different polishing materials on electroplated copper coupons. Five cleaning solutions were chosen based on common silver-cleaning practices (Figure 9, Table 3) (Polidori et al. 2018).

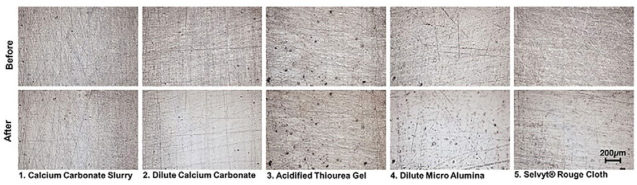

Figure 9. Photomicrographs taken before and after polishing coupons with a variety of cleaning solutions. Top to bottom: BT and AT (Polidori et al. 2018)

Since silver sulfide can act as an additional abrasive, results of the cleaning test were limited to an untarnished silver surface. As a result, tarnish was removed from the electroformed kettle (Case study 4) with dilute micro-alumina (Table 3). For this particular object, the potential for a highly reflective, burnished surface was acceptable.

Conclusion

ED-XRF can be used to quickly and non-destructively semi-quantify plate thickness. Results have shown that thin electroplate can be identified, but thicker electroplate (5 μm) can be a similar thickness to fused plate. However, the determination of manufacturing technique by non-destructive analysis is not straightforward. The main compositional difference between electroplate and fused plate is that the silver layer on fused plate is sterling standard instead of the pure

Table 3. Materials used for cleaning study and results summary from photomicrographs shown in Figure 9. Solutions 1–4 were applied using an unbleached cotton flannel (Polidori et al. 2018)

Cleaning solution	Ingredients	Result
1. Calcium carbonate slurry	Precipitated calcium carbonate in a slurry paste with 1:1 denatured alcohol: deionized water	Somewhat reduces scratches, but also adds new scratches to the surface.
2. Dilute calcium carbonate	2 g precipitated calcium carbonate in 50 mL deionized water	Significant reduction of scratches observed under magnification. Some new scratches may be present.
3. Acidified thiourea gel	2 g xanthan gum, 100 mL deionized water, 5 mL concentrated sulfuric acid, 8 g thiourea	No alteration in the scratch pattern observed. Thiourea creates a yellowed, matte surface.
4. Dilute micro-alumina	2 g 0.3 μm α-alumina in 50 mL deionized water	Reduces surface scratches by burnishing the silver. No new scratches observed.
5. Selvyt® Rouge Cloth	The manufacturer indicates that the Selvyt® Rouge Cloth is comprised of 100% cotton impregnated with a "rouge polishing compound."	Photomicrographs indicate significant scratch reduction. Note that SEM-EDS revealed that the Selvyt® Rouge Cloth contains no Fe or rouge compound.

silver on electroplate. In addition, the most prevalent substrate of fused plate is copper, with often up to 5% zinc. There are also electroplate imitations of fused plate using a copper substrate. Therefore, the presence of elements other than silver and copper in the plate and base metal, respectively, adds a margin of error to these calculations. Specifically, this error derives from the attenuation of the x-rays by the base metal. Therefore, this technique should always be used alongside informed visual inspection and expert consultation to differentiate between plating types.

All tested treatment methods for polishing silver plate altered the silver surface to varying degrees. The most effective cleaning method for silver-plated copper was found to be dilute micro-alumina, which burnishes the display surface while removing the least amount of precious metal. Burnishing occurs when metal transfers from high to low areas on the surface; this may be objectionable to curators or collectors given that it produces a mirror-like finish. However, since re-plating an object is generally considered unethical, cleaning methods that preserve the silver plate may be preferred despite the risks of creating a highly reflective surface.

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Notes

1 English manufacturers describe the plating as "pure," meaning the best standard achievable, but we do not have ED-XRF data today to quantify the percentage of silver (Bradbury 1912, 96; Crosskey 2011, 19).

2 Applying gold and silver onto base metals is summarized by Vitali (1997, 19–21) and by British plating experiments in Glanville (2006, 90–97) and Crosskey (2011, 14–62).

3 John Hodges, who worked for Matthew Boulton, cites a proportion of 24:1 copper to silver for candlesticks (Crosskey 2011, 24 and note 37). Approximately 12 plated finishes were available in early flatware electroplating (Glanville 2006, 98). In the United States, silversmiths sought recipes and replicated plating methods, using British terms like "heavy," "best," and "Albata," as well as "triple" and "quadruple" plate and symbols "A-1" for superior quality and "EP" for electroplated (Hogan 1972, 10).

4 Percy (1878, 490–91). The author describes switching from a galvanic battery power source to a "magneto-electric machine," thus removing mercury from the plating workshop. Site-specific "washing" or "brush plating" techniques placed a thin layer of silver or gold on an isolated location, replacing fire gilding.

5 Early electroplate was self-regulated in the United States, thus hundreds of names were created, sometimes omitting the word "plate." Typical abbreviations: "EP" for electroplate, "triple" or "quadruple plate" and EPNS for electroplated nickel silver. British marks include: EPNS and EPGS for electroplated German silver, EPCA for electroplated copper alloy, EPBM for electroplated Britannia metal.

References

Bradbury, F. 1912. *History of old Sheffield plate*. London: Macmillan.

Canadian Conservation Institute. 2017. The science of silver tarnish and its cause. *Understanding how silver objects tarnish*. www.canada.ca/en/conservation-institute/services/workshops-conferences/regional-workshops-conservation/understanding-silver-tarnish.html#a3 .

Carl, M. and M.L. Young. 2016. Complementary analytical methods for analysis of Ag-plated cultural heritage objects. *Microchemical Journal* 126 (May): 307–15.

Cesareo, R., M.A. Rizzutto, A. Brunetti, and D.V. Rao. 2009. Metal location and thickness in a multilayered sheet by measuring Kα/Kβ, Lα/Lβ and Lα/Lγ x-ray ratios. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 267(17): 2890–96.

Crosskey, G. 2011. *Old Sheffield plate: A history of the 18th century plated trade*. Sheffield, England: Treffry Publishing.

Glanville, P. 2006. Manufacturing and marketing in Europe, 1600–2000. *Feeding desire: Design and the tools of the table, 1500–2005*, eds. S. D. Coffin et al., exhib. cat.: 76–101. New York: Smithsonian Institution, Cooper-Hewitt, National Design Museum.

Hogan, E.P. 1972. *Victorian silverplated holloware*. Princeton, New Jersey: The Pyne Press.

Percy, R.T.. 1878. The American at work. Among the silverplaters. *Appletons' Journal* 5(6): 481–94.

Polidori, T., K. Rovito, and R. Grayburn. Electroplated silver during a re-lacquering campaign at Winterthur: Treatment and analytical insights. Poster presented at the *AIC's 46th Annual Meeting, Houston, 29 May–3 June 2018.*

Pouliot, B., J. Mass, C. Matsen, W. Donnelly, K. Andrews, and M. Bearden. 2013. Three decades later: A status report on the silver lacquering program at Winterthur. *Objects Specialty Group Postprints, Volume Twenty,* eds. L. Kaplan, K. Dodson, and E. Hamilton, 32–48. Washington, DC: The American Institute for Conservation of Historic & Artistic Works.

Vitali, U. 1997. A quest for the *domus aurea* in the resurgence of gilding. In *Antiquity revisited: English and French silver-gilt from the collection of Audrey Love*, eds. A. Phillips and J. Sloane, exhib. cat., 17–27. New York: Christie's.

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