**French Silver**

title: Appendix

subtitle: Silver Alloy Analysis by X-ray Fluorescence Spectroscopy

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short\_title: Appendix

The alloy composition of the silver objects in this catalogue has been characterized using X-ray fluorescence spectroscopy (XRF) ([**Table 1**](#_top)). This analysis was conducted to assist with the overall technical study of the works in this catalogue, particularly to identify potential alterations and restorations. XRF is a rapid, multielemental, and completely nondestructive analytical technique and is thus well suited to the study of works of art. XRF is a surface-analysis technique that measures the composition of the silver artifacts to a depth of only several tens of microns. Therefore, the XRF results may not represent the bulk alloy if silver-enriched or -depleted layers are present on the surface of the metal. Repeated annealing and pickling of silver, as commonly occurs when raising hollow forms from sheet, is known to result in silver enrichment of several tens of microns at the surface, though repeated polishing over time can remove the enriched layer.[[1]](#endnote-1) One method for detecting surface enrichment or depletion is to evaluate the ratio of silver L and K emission lines in an XRF spectrum.[[2]](#endnote-2) This method was used to flag some measurements as potentially nonrepresentative of the bulk. Results in the table with excessively high or low silver L-to-K (L/K) ratios are marked with \* and \*\* respectively.

  Three different XRF instruments were used to analyze the objects in this catalogue, over a period of several years. The operating parameters for each instrument were as follows:

1. Bruker-Artax: This instrument uses a chromium-tube anode; the live acquisition time for each spectrum was 250 seconds; voltage was 50 KeV; amperage was 600 µA. A 315 µm–thick aluminum beam filter was used and the tube was fitted with a 1.5 mm–diameter collimator.
2. Bruker-Tracer 5i: This instrument uses a rhodium-tube anode; the real acquisition time was 60 seconds; voltage was 50 KeV; amperage was 35 µA. A 38 µm–thick aluminum beam filter was used and the tube was fitted with a 3 mm–diameter collimator.
3. Bruker Tracer III-SD: This instrument uses a rhodium-tube anode; the real acquisition time was 60 seconds; voltage was 40 KeV; amperage was 15 µA. A 300 µm–thick aluminum and a 25 µm titanium beam filter were used, and the analytical spot size was approximately 8 mm in diameter.

Substantial effort was made to calibrate each instrument rigorously so that the results are both accurate and comparable. The calibration procedure for each instrument followed the CHARMed PyMca protocol using 11 silver-alloy reference standards.[[3]](#endnote-3) Seven of these standards were manufactured by MBH Analytical (designated 133X AGQ1, 133X AGQ2, 133X AGQ3, 132X AGB 85B, 133X AGA1, 133X AGA2, and 133X AGA3), three were in-house standards from the Getty Conservation Institute (designated GCI-silver-A, GCI-silver-B, and GCI-silver-C), and one was a pure silver sample manufactured by Premion.

The uncertainties (errors) in the measurements reported here are averages. More precise estimates of uncertainty have been calculated individually for each measurement based on the “error of prediction” model.[[4]](#endnote-4) Complete data with errors are available upon request to the Department of Decorative Arts and Sculpture conservation. Detection limits associated with the final estimates were determined based on the standard formula for the critical value, or C.V., at the 95-percent confidence level.[[5]](#endnote-5)

Where gilded surfaces were analyzed with XRF, quantitative results for the base alloy could not be calculated. Spectra from gilded surfaces were evaluated to determine whether mercury was also present along with the gold, as would be expected if the gold had been applied by amalgam gilding. Where mercury peaks were clearly seen in the spectra (this was true for all analyses of gilding), an estimate was made of the amount of mercury remaining in the gold, using standardless quantification results for both gold and mercury as generated by PyMca software (see [**Table 2**](#_top)).

1. {{Mass and Masten 2012a}}. [↑](#endnote-ref-1)
2. {{Borges et al. 2017}}. [↑](#endnote-ref-2)
3. {{Heginbotham and Solé 2017}}; {{Heginbotham et al. 2019}}. [↑](#endnote-ref-3)
4. {{Heginbotham and Solé 2017}}. [↑](#endnote-ref-4)
5. {{Kadachi and Al-Eshaikh 2012}}. [↑](#endnote-ref-5)