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abstract: Surface layers on a bronze sculpture may include gilding and other metal plating, patina, and various coatings such as varnishes. The present chapter aims to guide the reader’s investigation of these layers, from thickness measurement to chemical analysis.

short\_title: Surface Layer Analysis

Surface layers on a %%bronze%% sculpture may include %%gilding%% and other %%metal plating%%, %%patina%%, and various %%coatings%% such as varnishes. The present chapter aims to guide the reader’s investigation of these layers, from thickness measurement to chemical analysis. Color measurement, which also contributes to the characterization of the surface layers, is discussed in [II.2](#II.2). Surface measurement and investigation of tool marks is dealt with in [II.4](#II.4).

Surfaces of bronze sculptures often comprise several complex layers resulting from complex series of events, from the time of the fabrication of the sculpture to the present day (see [I.7](#I.7), [I.8](#I.8)). Unfortunately, confronted by such complexity, the researcher is, here more than elsewhere in these *Guidelines*, limited with respect to sampling. Still, because of its indispensability, sampling constitutes the backbone of this chapter, which sets out the techniques, their possibilities, and their limitations. A summary synthesis/workflow of the analytical techniques discussed in this chapter is provided in **figure 305** and in **tables 10** and **5**.

## 1 Thickness of surface layers

### 1.1 Noninvasive techniques

Due to the aforementioned tendency of surface stratigraphy to be complex—composed of several thin, heterogeneous layers—measurements of thickness without sampling may yield false results, or at best partial information. Rarely can one measure the surface layer thickness directly on the sculpture, without sampling.

The thickness of simple organic coatings such as varnishes and resin can be estimated using eddy currents.[[1]](#endnote-1) In theory, eddy currents allow measurement of the thickness of any kind of surface layer, but they are very sensitive to the metal alloy underneath the coating as well as %%porosity%%, repairs, et cetera, which may lead to misleading measurements. X-ray fluorescence spectroscopy (XRF) and even handheld XRF may give quite accurate measurements of metal plating layer thicknesses, provided these layers are not too porous.[[2]](#endnote-2)

The best estimate of thickness is obtained by ion beam analysis, particularly Rutherford backscattering spectrometry (RBS), which can deal with simple metal plating layers, for instance patinas made of one or two compounds (such as cuprite on black bronzes) homogeneously distributed. These can also possibly be investigated by nuclear reaction analysis (NRA).[[3]](#endnote-3) The latter is among the more complex and less accessible techniques. It has proven useful in simple situations, but it has numerous limitations: facilities are rare (a particle accelerator with the beam exposed in air is necessary for a sculpture more than about 10 cm tall), as are experts able to interpret spectra; complex layers cannot be unraveled using such nuclear techniques; and the layers may not be thicker than 10–50 µm.

### 1.2 Invasive techniques

In most cases, sampling and subsequent metallographic preparation of cross sections is necessary. Although the preparation is the same as the one described in [II.5](#II.5) for bulk metal microstructure investigation, particular attention is required to avoid damaging the surface layer. Surface layers such as gilding or fragile patinas are easily altered during cutting, resin embedding, and polishing. Resin impregnation prior to sawing is often advantageous, and careful low-speed, low-pressure sawing is recommended. If the sample contains organic coatings, embedding resin may interfere with future organic analysis of the sample by methods such as micro Fourier transform infrared spectroscopy (FTIR). One danger during embedding is that the shrinkage of embedding resin may induce separation of surface layers from the substrate. Ion beam polishing, if it is available, is highly recommended for very fragile layers.

Once the cross section is ready, optical microscopy is generally sufficient to detect and measure the thickness of the different surface layers. Scanning electron microscopy (SEM) may be necessary for micrometric and submicrometric layers, such as those obtained by electroplating, but with high-purity gold the thickness can be overestimated due to smearing caused by mechanical polishing of the soft metal. Ionic polishing helps to avoid this problem.

## 2 Composition of surface layers: noninvasive techniques

### 2.1 Elemental versus structural analysis

A surface layer may be *fully* characterized by its elemental composition (for a definition of “elemental composition” see [I.2§1.2](#I.2§1.2)) in only one situation: when the layer is made of metal (gilding, silvering, tinning, et cetera; see [I.7](#I.7)). Oher types of surface layers, such as patina (including chemical patina) and coatings (varnishes and so on, see [I.8](#I.8)), are made of compounds/molecules that elemental analysis alone often cannot fully characterize.[[4]](#endnote-4) Structural analysis is necessary to complete the characterization and determine the molecular or crystalline forms in which the elements are arranged. For example, specific patina components such as cuprite, malachite, or cassiterite (to name but a few) cannot be identified using elemental analysis alone. Similarly, many natural earth pigments share a common elemental composition, but vary considerably in color and structure (for instance hematite, goethite, and limonite). Organic varnish components likewise cannot be identified merely by elemental analysis.

### 2.2 Elemental analysis

The most common surface elemental analysis technique for bronze sculpture is XRF. Particle-induced X-ray emission spectroscopy (PIXE), is also increasingly used (see [II.5](#II.5)). Yet they all share the same drawback for surface analysis: their penetration is often much deeper than the layer thickness (typically several tens of microns, whereas many surface layers of interest may be less than one micron thick). Consequently, the analytical results are a mix of the studied surface layer and the copper alloy substrate.

Moreover, surfaces are often multilayered. Thus, as for thickness measurements, sampling is often required to overcome the complex layering of different materials. But all the problems are not solved: the analytical techniques used on cross sections require a low-size beam, smaller than the thickness of the layer thickness—their “surface resolution” needs to be appropriate—so most XRF devices do not allow for such analysis. That said, if areas of bare, unpatinated bronze are present adjacent to patina, it may be possible to identify patina elements by comparing the measured composition of both areas.[[5]](#endnote-5) Also, some attempts have recently been made using very-high-frequency eddy currents (>>1 MHz).[[6]](#endnote-6)

### 2.3 Non- and micro-invasive depth profiling

One might dream of a technique able to determine, without sampling, the elemental composition of each individual layer present on the surface of a bronze—in other words, capable of drawing a composition depth profile. Laser-induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), RBS, and NRA allow this to be achieved in theory, but each method has its drawbacks:

* Surface layers on bronzes may be too thick for these methods (more than several tens of microns).
* Light elements such as hydrogen, carbon, and oxygen are not systematically detected, although they are frequently present in the surface layers.
* Very small areas (less than 1 × 1 mm) are usually investigated because of time and damage, thus leading to potentially nonrepresentative analysis.
* In most laboratories LA-ICP-MS can only be used on extracted samples (in most favorable cases, only small statuettes not exceeding 20 cm in their highest dimension may be investigated).[[7]](#endnote-7)
* These methods are rare and costly (although handheld LIBS instruments are becoming less expensive, with prices comparable to handheld XRF instruments, about US $40,000 to $50,000).

### 2.4 Structural analysis without sampling: X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy

Although rare, some analytical techniques allow analysis of molecules directly on the bronze surface, without sampling. Techniques include X-ray diffraction (XRD), microscopes equipped with Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. Specially adapted versions of the instruments can be used directly on objects rather than on samples in the lab, but these often yield results that are not as precise or reproducible as those made with laboratory instruments. As for elemental analysis, due to the thinness and the complexity of often intermixed layers, structural analysis without sampling rarely proves fully efficient.

## 3 Composition of surface layers: invasive techniques

### 3.1 Guidance for sampling

Samples can be in powder form, prepared as a cross section, or in solution. The main advantages and drawbacks of these sample types are:

* Powder samples are much easier to acquire and prepare, but a major disadvantage is that multiple layers may be intermingled in the sample. Careful sampling under a stereomicroscope is essential.
* Cross sections allow observation and analysis of the layering, but it can be extremely difficult to remove a small, discrete sample of a chemically bonded patina. Preparation of cross sections requires special attention (see [II.6§1.2](#II.6§1.2)).
* Dissolved samples may be collected for analysis using a cotton swab or by applying and then retrieving a droplet of solvent using a micropipette. The best choice of solvent(s) may be difficult to determine, as the solubility of oil, resin, and polymer coatings will vary considerably and will be affected by aging.

Whatever the sample form, great care should be taken in identifying the most representative area for sampling.

### 3.2 Observation of cross sections

Careful observation of the cross section is highly recommended to assess the structure of the surface layers and their homogeneity. This may prove particularly useful to distinguish artificial from natural patina (see [I.8](#I.8)). The same techniques as those used to investigate the metal microstructure may be used for imaging (see [II.5](#II.5)). Improved imaging of samples using multi- or hyperspectral imaging, ultrasound tomography, and optical coherence tomography (OCT) are possible. In some situations, very-high-magnification electron microscopes, namely transmission electron microscopes, may prove necessary.[[8]](#endnote-8)

### 3.3 Elemental analysis

The same techniques as those described for metal analysis ([II.5](#II.5)) may be used, depending on the type of sample and the performances required (range of elements, sensitivity, accuracy). A variety of techniques may be used, for instance powder and solution. On cross sections, spatially resolved methods should be chosen, such as micro-XRF, SEM energy-dispersive spectroscopy (SEM-EDS), SEM with wavelength-dispersive spectroscopy (SEM-WDS), or PIXE.

### 3.4 Structural analysis

When using a powder sample, micro-chemical/solvent testing may prove very rapid and efficient, although infrequently used.[[9]](#endnote-9) For powder and possibly solution samples, some of the more common techniques for characterizing the structural composition of bronze surface layers—in this context exclusively patina—include XRD, FTIR, gas chromatography with mass spectrometry (GC/MS and pyrolysis-GC/MS), and Raman spectroscopy.

On cross sections, spatially resolved techniques are recommended. This includes XRD, FTIR, and Raman microscopies (including surface-enhanced Raman, or SERS), and reflectance FTIR. In circumstances in which a synchrotron beam is available, cross sections or thin sections maybe analyzed using micro-FTIR, time-of-flight secondary ion mass spectrometry (TOF-SIMS), false color imagery, and/or photoluminescence.

Most published studies concerning structural analysis of surface layers on bronze sculpture to date focus on %%corrosion%% products. The characterization of organic coatings is significantly less common,[[10]](#endnote-10) while the characterization of intentional chemical patina recipes is perhaps least common.[[11]](#endnote-11) However, all these methods have limitations, starting with their incapacity to detect all compounds in a comprehensive manner. The fact that a given compound is not detected does not mean that it is not present in the surface layer.[[12]](#endnote-12)

## Notes

1. See {Heginbotham, Beltran et al. 2014}. [↑](#endnote-ref-1)
2. {Cesareo et al. 2009}; {Lopes et al. 2016}; {Karydas 2007}. [↑](#endnote-ref-2)
3. {Ioannidou et al. 2000}; {Mathis et al. 2007}. [↑](#endnote-ref-3)
4. For example, the elemental analysis of a patina may measure the amount of copper (Cu), tin (Sn), and oxygen (O). But this elemental composition may correspond to several “structural” compositions. The three types of atoms Cu, Sn, and O may be present in two distinct compounds, namely cuprite (Cu20) and cassiterite (SnO2), or in other forms such as a mixed oxide (CuSnO). [↑](#endnote-ref-4)
5. Chromium was detected in the patina on a sculpture by Henri Matisse (French, 1869–1954) ({Boulton 2007}, 86). Iron was identified as a patina component on a work by Edgar Degas ((French, 1834–1917) ({Lindsay, Barbour, and Sturman 2010}). Platinum was detected on a work attributed to Louis-Simon Boizot (French, 1743–1809) ({Bewer and Scott 1995}). [↑](#endnote-ref-5)
6. The thickness of both copper sheet (1.2–1.5 mm) and patina (approx. 40 µm) on a Renaissance statue has been investigated by eddy currents. Such a device cost around US $6,000 in 2019. The technique was initially developed to measure the thickness of nonconductive coatings in the automotive industry (JM Welter, personal communication). As for ultrasonic testing, eddy currents are very sensitive to any perturbation in the surface layers. A skilled operator is necessary. [↑](#endnote-ref-6)
7. {Dussubieux, Golitko, and Gratuze 2016}. [↑](#endnote-ref-7)
8. Studies of black bronzes are exemplary ({Craddock and Giumlia-Mair 1993}; {Craddock 2009}; {Delange, Meyohas, and Aucouturier 2005}). Elemental analysis or structural analysis alone does not enable an understanding of the patination process; only a combination of both approaches, including sampling, have allowed researchers to unravel the mystery. XRD performed directly on the surface has revealed a simple patina composition, namely cuprite Cu20. Surface elemental analysis (PIXE) as well as bulk metal analysis via inductively coupled plasma atomic emission spectrometry (ICP-AES) identified a specific copper alloy, sometimes referred to as Corinthian bronze, with several percent of gold. Transmission electronic microscopy on samples (thin sections) provided the clue to the problem ({Notis 1988}; {Benzonelli, Freestone, and Martinón-Torres 2017}; {Mathis et al. 2005}): nanoparticles of gold dispersed within the cuprite layer proved to be responsible for the specific *shakudo* color. [↑](#endnote-ref-8)
9. {Odegaard, Carroll, and Zimmt 2005}. [↑](#endnote-ref-9)
10. See the studies carried out on Italian Renaissance patina using gas chromatography mass spectrometry (GC-MS) ({Stone 2010}; {Pitthard et al. 2011}; {Aucouturier, Mathis, and Robcis 2017}), and the studies of black bronze patina ({Giumlia-Mair 1995}; {Benzonelli, Freestone, and Martinón-Torres 2017}). [↑](#endnote-ref-10)
11. UV-visible photoluminescence generated by a synchrotron beam has led to a useful characterization of various cuprite compounds that might be applied to patina studies ({Thoury et al. 2016}). [↑](#endnote-ref-11)
12. {Stone 2010}; {Pitthard et al. 2011}. [↑](#endnote-ref-12)