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# New Strategies for the Conservation of Paintings on Metal

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## Abstract

The conservation and restoration of painted metal objects presents a challenge due to their composite nature. Both the metal support and the paint layers can undergo independent and linked alterations, making it necessary to fully understand the processes of degradation before attempting to implement a treatment. This paper presents the first part of the CoPaiM project, detailing the selection of a corpus from the collections of the Musée des Arts et Métiers in Paris, France. A condition report on 23 painted metal objects was prepared including a description of the materials, their visible alterations and a first diagnosis of whether the degradation originated from deterioration of the paint or corrosion of the metal support. Samples of paint and corrosion products were collected from six objects in order to characterize the system by micro-analysis. A multi-technique analytical methodology was used to study the morphology, the

elemental composition and distribution and the variety of phases present in the samples, thus allowing a complete characterization of the metal, the corrosion products and the components present in the paint layers. Aesthetic alteration of the paint was observed in cases where the degradation of the metal support had led to subsequent migration of the corrosion products into the paint layers, leaving a brown-orange stain. The paint layers were determined to have oxidized over time, which could affect their stability in the composite system. The next steps of this project are to summarize the analytical data into hypotheses for the degradation mechanisms of the paint-metal system.

## Keywords

paint, metal, alteration, restoration, Raman, X-ray fluorescence spectroscopy (XRF), X-ray absorption near-edge structure (XANES)

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## Introduction

The present paper details the CoPaiM project (*Conservation of Painted Metals*), which deals with the degradation and conservation issues related to painted metal objects from cultural heritage collections. Such composite items are widely present in museum collections, including artworks, technical and industrial objects (such as painted signs, scientific instruments, models, tools), and means of transport.

Progressive degradation of painted metal objects is a common issue and its processes and associated kinetics depend on several factors: storage condi-

tions (controlled or uncontrolled environment with fluctuations of temperature and relative humidity), pollution particles, presence of other harmful materials and previous use or restoration treatments, among other factors. As a result, metal corrosion products can form and leave stains on the paint layer affecting the aesthetics of the object. More importantly, their continued development can produce an outward pressure, pushing up the paint layer and creating cracks, blistering and flaking until the paint layer is severely degraded or completely separated from the metal (Schröter 2009, Sutter 2014).

When storage conditions cannot be controlled or are not suitable for all the materials present (in large and heterogeneous collections for example), curators and conservators have looked for surface treatments to slow down or prevent the processes of degradation. However, conservation of painted metals is not an easy task as the treatment must ideally conserve and protect the surface of the object including its paint layers and corrosion products that may contain historical information such as inscriptions or engravings. The preservation of painted metal heritage therefore requires the development of conservation strategies while also taking into account the constraints of conservation ethics. Moreover, non-toxic, reversible (and if not, re-treatable) and durable treatments with no harmful volatile organic compounds are nowadays required.

The first phase of the CoPaiM project deals with the characterization of samples acquired from painted metal objects with visible surface alteration in the Musée des Arts et Métiers collection. This first step is essential to understanding the processes of degradation and interactions taking place in the paint-metal system, and provides necessary information for a complete assessment of the conservation state prior to the application of a protective surface treatment. The second phase of the project, which is not presented in this paper, concerns the creation of painted metal plates imitating the degraded surface state observed on the historic objects. A similar methodology was proposed in previous studies (Degrigny 2010, Rapp et al. 2010). These plates will be used as a laboratory test media for the application and assessment of different protective surface treatments. The information gained from this study will then be used to make an informed decision on the application of surface treatments to real objects.

## Materials: Studied collection and corpus selection

### Studied collection from the Musée des Arts et Métiers

The painted metallic objects from the large scientific and technical collections of the Musée des Arts et Métiers (Paris, France) constitute an ideal corpus for the development and assessment of protection protocols on painted metals. The museum's indoor storage building contains a diverse collection of items that vary in size (from a few centimeters to a few meters), utility (industrial, agricul-

tural), conservation state, period and materials (wood, leather, plastic, rubber, etc.). The present study focused on objects with metal supports.

### Diagnostic report and database elaboration

The first step of the study was to diagnose (i.e., produce a condition report on) the state of conservation of 23 objects stored in the museum's reserves and selected for the painted metals alteration study with help from the curators and conservators (from the Musée des Arts et Métiers and Institut National du Patrimoine) involved in the CoPaiM project. The origin of the degradation was investigated to determine whether the alteration was linked to paint layer deterioration, such as lack of cohesion or binder instability, or if the corrosion of the metal was responsible for the degradation of the coating.

Following this diagnosis, a database for managing the condition survey of the 23 objects was designed with input from the curators and conservators. The objective was to list the materials and coatings identified on the object, to describe the current alterations (mechanical and physico-chemical), to illustrate with photographs and to identify their state of degradation. The database is divided into four parts: identification of the object, nature of the different components (including metal, morphology and type of coating), alteration of the components (metal and coating) and diagnosis. A standard datasheet can be seen in Table 1.

### Establishment of a corpus with representative altered surfaces

A first overview of the collection showed that the types of degradation and their origins were diverse and could affect the metallic structure, paint layer and upper varnish layer, or a combination of the coating and the metal. The database allowed for the selection of six objects (Figure 1) described below with representative degraded painted metal system surfaces.

- a. The "Quadruplette" (inv. 21811-0001) is a unique object crafted by its inventor, Boyan Siméonoff, to accommodate the whole family on road trips: a four-seater bicycle supplemented by a small auxiliary motor. Designed just after World War II, it was given to the museum in 1965. It is a well-used object with an undocumented history of interventions. It is constructed mainly of iron, with some parts in copper and a white metal, with various forms of generalized

Table 1. Datasheet established for the diagnosis of the conservation state of metal painted objects

<b>Identification</b>	<ul style="list-style-type: none"> <li>• Denomination</li> <li>• Localization</li> <li>• Function</li> <li>• Type of storage</li> <li>• Size</li> </ul>
<b>Materials</b>	<ul style="list-style-type: none"> <li>• Metal:               <ul style="list-style-type: none"> <li>– nature of the principal metal</li> <li>– other metals: iron, copper, white metals or aluminum</li> </ul> </li> <li>• Coating:               <ul style="list-style-type: none"> <li>– morphology of coating, mono or multi-layer, over or juxtaposed layer...</li> <li>– type of coating: transparent or non-transparent, hot or cold paint, varnish, ...</li> </ul> </li> <li>• Other materials: organic, petroleum-based components</li> </ul>
<b>Alterations</b>	<ul style="list-style-type: none"> <li>• Mechanical and chemical degradations of the metal: uniform or localized corrosion</li> <li>• Alteration of other materials</li> <li>• Mechanical and chemical alteration of the coating:               <ul style="list-style-type: none"> <li>– optical and physical changes of the coating such as fissures, deformation, ...</li> </ul> </li> <li>• Presence of dust</li> </ul>
<b>Diagnosis</b>	<ul style="list-style-type: none"> <li>• Evolution</li> <li>• Causes of the degradation:               <ul style="list-style-type: none"> <li>– alteration due to the metal part or the coating</li> <li>– alteration due to the combination of the coating and metal</li> <li>– alteration due to the use of the object</li> </ul> </li> </ul>

and localized corrosion. The observed alterations are mainly related to coatings with adhesion problems.

- b. The reversible Brabant plow (inv. 17001) is an agricultural device dating from the last quarter of the 19th century that was inventoried by the museum in the 1930s, making it difficult to trace its history in the museum exhibition display. This iron object is covered in various areas with decorative multicolored paint. Part of the iron structure is corroded but alterations to the painted zones are mainly due to wear.
- c. The weighing scale (inv. 5005) is a scientific instrument used as a 50 kg checkweigher. It is linked to the important metrological work performed by the Conservatoire

National des Arts et Métiers (CNAM, Paris). It stood among the collection of weights and measures sent by the CNAM to The Great Exhibition of 1851 in London. Originally covered with several layers of paint, this iron object is completely corroded and only shows a few painted areas with small flakes of paint.

- d. The small three-pane lantern (inv. 16726) is dated to around 1906 and belongs to the museum's railway collection. It is a display piece, never used for its intended industrial purpose. The corrosion is clearly visible on the surface of the iron alloy and the handle rivet and the black paint is showing problems with adhesion.
- e. The model of an engine boiler (inv. 36181) is of unknown provenance. It is a scale model of a large marine steam engine of British origin as shown by the name plaque. The model consists of two parts, one made of wood and the other of an iron alloy. Physical and chemical alterations are visible on the metallic part, as well as on the three types of paint layers.
- f. The set of six measuring containers (inv. 60005) is also of unknown provenance. It is dated to around 1850 by comparison with similar pieces in the collection. The set is made from an iron alloy which is uniformly corroded. The coating is the same all over the surface and consists of a brown-black paint layer over an orange paint layer. The alteration relates to the corrosion of the iron support.

### Analytical methodology

The macroscopic approach presented in the database describing the objects and their visible alterations is supplemented by microanalyses to identify the materials for the six selected objects: the nature of the metal, the phases present in the corrosion layer, the composition of the painting (pigments and binders) and the possible stratigraphy. Microsampling allowed for the application

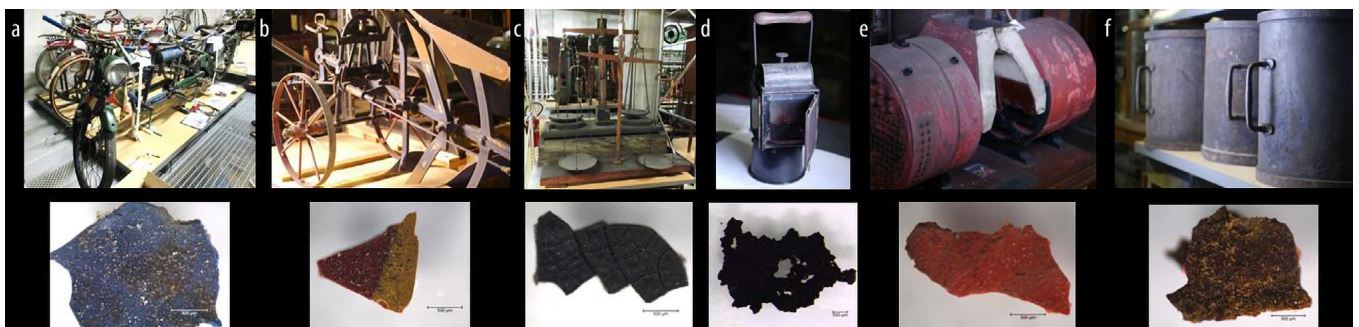


Figure 1. (a) "Quadruplette" (inv. 21811-0001); (b) reversible Brabant plow (inv. 17001); (c) weighing scale (inv. 5005); (d) three-pane lantern (inv. 16726); (e) model of engine boiler (inv. 36181); (f) set of six measuring containers (inv. 60005)



of a full analytical methodology using a multiscale and multimodal approach. The development of fast imaging techniques using synchrotron-based X-ray absorption and fluorescence spectroscopies but also vibrational spectroscopies, such as Raman, were used to achieve local characterization.

### Sample preparation

Millimeter-sized samples were collected with a scalpel from areas of interest in order to include corrosion products, altered paint layers and potential varnish or upper organic layers. Some samples were embedded in epoxy resin and cut as cross sections with a diamond wire saw. The faces were polished with SiC grit papers and with a diamond paste on a damp polishing plate, rinsed with ethanol and dried.

### Morphological observations

Samples were observed at 5 $\times$ , 10 $\times$  and 20 $\times$  magnification with an Eclipse LV100 D-Nikon Microscope using visible light in reflection and dark-field mode. A Zeiss Supra 55 VP scanning electron microscope (SEM-FEG) was used with an acceleration voltage of 5 to 20 kV to observe the topography and chemical contrast of the sample layers thanks to secondary and backscattered electron modes (SE and BSE).

### Elemental and structural analyses

The elemental composition of the paint and corrosion layers was identified using energy-dispersive X-ray spectroscopy (EDS) and X-ray fluorescence spectroscopy at micrometric scale ( $\mu$ XRF). EDS analyses were conducted at 20 kV at a working distance of 6.5 mm, using a Quantax EDS nano and microanalysis system (Bruker) and a silicon drift detector (SDD). Micro-XRF analyses were performed at 13 keV at the DiffAbs beamline (Synchrotron SOLEIL, France). XRF maps were collected using the continuous flyscan mode (Esteve et al. 2017) thanks to a focused incident beam of 8  $\mu$ m  $\times$  6  $\mu$ m, a four-element SDD (Vortex-ME4, Hitachi) and 50 ms dwell time. All XRF experiments were performed at room temperature and atmospheric pressure (Ar K lines from ambient air are visible in XRF spectra), implying difficulties in detecting the fluorescence signal from light chemical elements (such as Si, P). Data processing was performed using the PyMCA software (Solé et al. 2007).

### Raman spectroscopy

Two instruments were employed to identify the structure of pigments and corrosion products present in the microsamples. A Raman Senterra spectrometer (Bruker Optics) was initially used, with an infrared diode laser (785 nm), 50 $\times$  IR objective, 3 mW laser power at the sample surface and acquisition times between 2 and 10 s. The spectral resolution was about 5  $\text{cm}^{-1}$ . Follow-up analyses were performed using a LabRam HR 800 (HORIBA Jobin Yvon) with the 458 nm line of an Ar<sup>+</sup> laser and a 100 $\times$  objective. Laser power was adjusted to around 100  $\mu$ W at the surface of the sample to avoid material degradation during analysis. Spectra were collected for 3 - 30 s with 3 - 20 accumulations. Spectral resolution was about 3  $\text{cm}^{-1}$ .

### Gas chromatography coupled to mass spectrometry (GC-MS)

GC-MS was used for the separation and identification of organic components in the paint layers. A trace GC Ultra gas chromatograph (Thermo Scientific) and an ISQ single quadrupole mass spectrometer (Thermo Scientific) were used with the following specifications: non-polar fused silica capillary column (Rxi 5Sil MS, 20 m, 0.18 mm  $d_i$ , 0.18 mm  $d_f$ , Restek); carrier gas H<sub>2</sub> at 1.5 mL/min; a temperature program of 50 $^{\circ}$ C for 1 min, ramp of 20 $^{\circ}$ C/min until 320 $^{\circ}$ C and 320 $^{\circ}$ C held for 5 minutes; split injector set at 290 $^{\circ}$ C with a total flow of 50 mL/min and a split ratio of 33; automated injection; an interface temperature set at 320 $^{\circ}$ C; electronic impact ionization mode of 70 eV and ion source temperature of 250 $^{\circ}$ C. The samples required a derivatization step prior to injection, which included mixing fragments of the samples with 50  $\mu$ L of Meth-Prep II (Grace Alltech) and heating at 60 $^{\circ}$ C for 30 min prior to injection. This transmethylation is needed to cleave the oil-based and terpenoid components of the binder, and to esterify the polar groups (acids and alcohols).

### X-ray absorption spectroscopy

Following the previously described  $\mu$ XRF maps which were used to reveal, among other elements, the Pb distribution, some points of interest were selected and analyzed by collecting X-ray absorption near-edge structure (XANES) spectra at the Pb L<sub>3</sub>-edge to determine the Pb local environment. The acquisition conditions for XANES were from 12.6 to 13.3 keV, with steps of 1 eV

in the pre- and post-edge regions and 0.5 eV in the edge domain and a counting time set to 1 s.

## Results

### Metal alteration: Corrosion products

Corrosion products are present at the interface between the metal part of the object and the paint layers. To illustrate, a flake from the weighing scale was observed using SEM and revealed well-crystallized corrosion products (Figure 2).



Figure 2. SEM image (SE mode, 2 keV) of the corrosion products formed between the metal and the paint layers of the sample collected from the weighing scale

Otherwise, the sample (Figure 3) from the measuring containers (inv. 60005) is an interesting example with a complex multilayer system. The outer face is very dirty: a multitude of gray to brown grains covers the painting layer. The inner face (close to the metal) is brown-orange due to the presence of corrosion products. This layer is partly powdery with a shiny appearance.

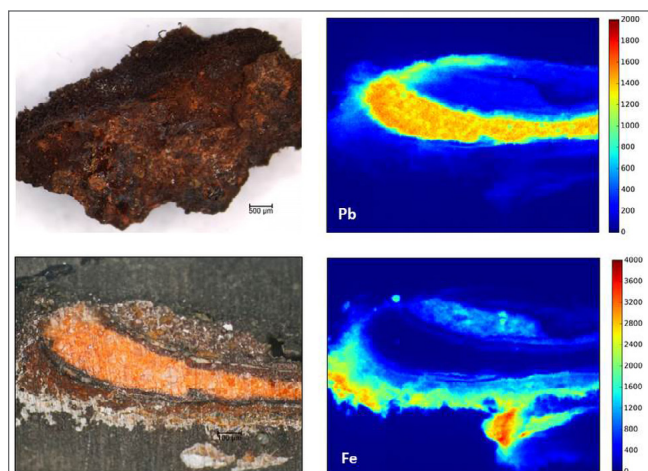


Figure 3. Paint flake sample from the measuring and cross-section series observed under optical microscope and XRF maps of major elements

The stratigraphy of the cross section is rather complex with a variable thickness (from 290 to 570  $\mu\text{m}$ ). Many porous layers of variable thickness, morphology and color (gray, orange, brown) surround a thick orange layer (55 and 200  $\mu\text{m}$ ) which contains white particles.

The XRF maps illustrate the distribution of the main elements: Fe surrounding Pb in the orange layer. The iron corrosion products were identified thanks to the analytical methodology previously described. The Raman spectra of lepidocrocite (Figure 4) but also goethite, akaganeite and maghemite were revealed and identified thanks to comparison with references (Bellot-Gurlet et al. 2009). Further analysis and data treatment are in progress.

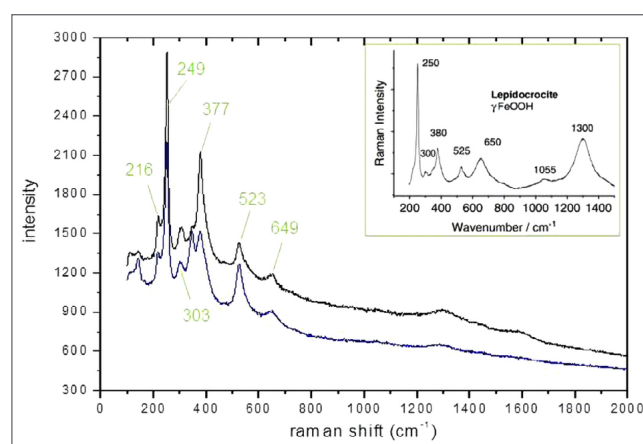


Figure 4. Raman spectra of corrosion products acquired at two points of interest on the sample from the series of measures

### Complexity of painted layers and their alteration

Identification of the pigments was performed for the entire corpus using the above described methodology through a combination of Raman, SEM-EDS, XRF and XANES. The main results are presented here to highlight the variety of pigments present in the paint layers (Table 2). This diversity and intensity of colors is visible on the cross section of the micro-samples collected on the following objects (see Figure 5, from left to right): the quadruplette, the engine boiler model and the reversible Brabant plow.

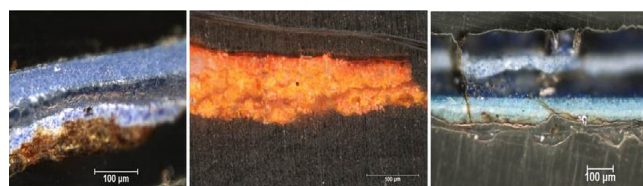


Figure 5. Cross section observed under optical microscope for (from left to right): the quadruplette, the engine boiler model and the reversible Brabant plow

Table 2. List of the main pigments identified

Object	Color	Pigment/paint layer
Quadruplette	blue and green	lazurite $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$ prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ anatase $\text{TiO}_2$ lead white $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ lithopone $\text{ZnS}$ and $\text{BaSO}_4$
Reversible Brabant plow	yellow, red and blue	minium/lead red, $\text{Pb}_3\text{O}_4$ chrome yellow $\text{PbCrO}_4$ lazurite $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$ lithopone zinc sulfide $\text{ZnS}$ barium sulfate $\text{BaSO}_4$
Weighing scale	blue	litharge/massicot $\text{PbO}$ lead white $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ lithopone $\text{ZnS}$ and $\text{BaSO}_4$ lazurite $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$ anatase $\text{TiO}_2$
Small three-pane lantern	black	
Engine boiler	red and white	lead white $2\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ minium/lead red $\text{Pb}_3\text{O}_4$ vermillion $\text{HgS}$ non-identified organic pigment
Set of six measuring containers	brown and red	minium/lead red $\text{Pb}_3\text{O}_4$ lead white $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ non-identified carbonaceous pigment

Identified pigments were confirmed to have been in use during the time periods to which the objects are dated. As an example, a large variety of elements were detected on the weighing scale micro-sample using XRF and EDS (Figure 6). The results were correlated to Raman analysis in order to identify the pigments. EDS maps revealed the main elements of Pb, Na and Ba, and indicate the presence of lead white, lazurite and  $\text{BaSO}_4$ , a compound found in lithopone.

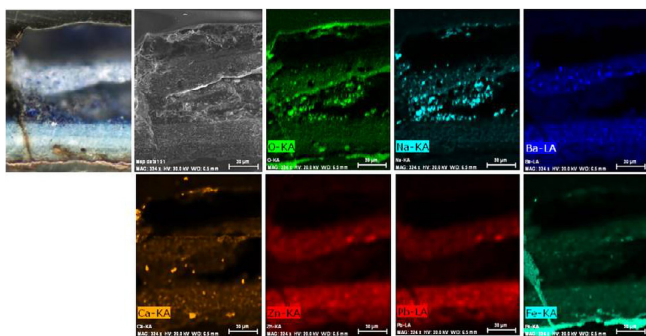


Figure 6. Cross section observed under optical microscope for the weighing scale and EDS maps of the main elements

The XANES spectra permitted the identification of different Pb compounds constituting the paint layers and determination of the Pb alteration products. To illustrate, two types of spectra were identified on the paint layer of the series of measures (Figure 7):

one corresponding to the orange pigment minium,  $\text{Pb}_3\text{O}_4$ , and the other corresponding to lead white,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . In addition, a spectrum similar to lead soaps can be found on some samples (not shown here), and can be linked to the degradation of Pb compounds in interaction with the binder of the paint layer. Such amorphous compounds were not revealed using other analytical techniques.

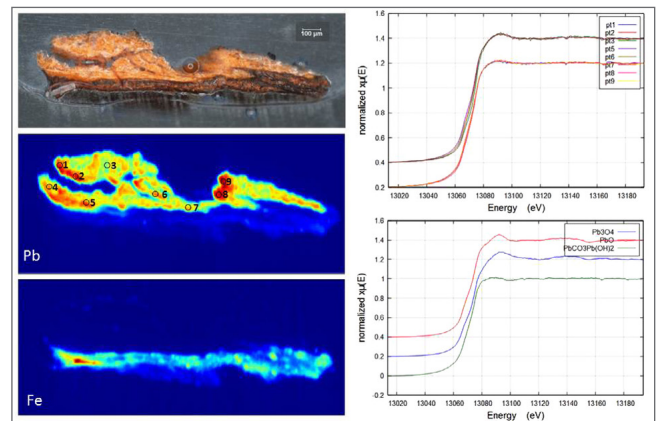


Figure 7. Cross section of a sample from the series of measures observed using an optical microscope and XRF maps showing Fe and Pb distribution. XANES spectra at Pb L edge were acquired at nine different points of interest located on the Pb XRF map and compared with references

The identification of the organic content was completed using GC-MS as shown for six samples from five different objects in Table 3, illustrating evidence of aged oil (oxidation products of unsaturated fatty acids) and an organic red pigment in the precise case of the engine boiler. For example, the main peaks identified during the analysis of a red and yellow paint sample from the reversible Brabant plow correspond to methylated suberic, azelaic, palmitic and stearic acids and also to the methylated oxidation

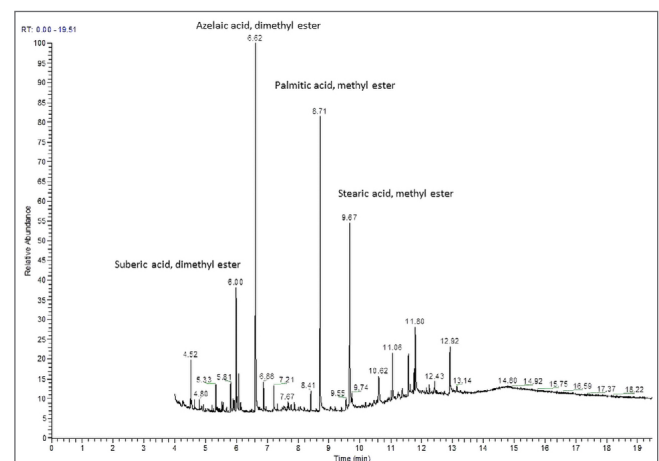


Figure 8. GC-MS measure obtained from the analysis of the sample from the reversible Brabant plow



Table 3. List of the organic compounds identified

Organic compounds	Analyzed objects				
	Quadruplette (sample P06)	Engine boiler (samples P08, P09)	Weighing scale (sample P01)	Measuring containers (sample P02)	Reversible Brabant plow (sample P01)
Heptanedioic acid, dimethyl ester (pimelic acid, dimethyl ester)	x	x		x	x
Octanedioic acid, dimethyl ester (suberic acid, dimethyl ester)	x	x	x	x	x
Nonanedioic acid, dimethyl ester (azelaic acid, dimethyl ester)	x	x	x	x	x
Decanedioic acid, dimethyl ester (sebacic acid, dimethyl ester)			x	x	x
Hexadecanoic acid, methyl ester (palmitic acid, methyl ester)	x	x	x		x
Octadecanoic acid, methyl ester (stearic acid, methyl ester)	x	x	x	x	x
11-octadecenoic acid, methyl ester, (Z)-				x	
Nonanoic acid, 9-oxo, -methyl ester	x				
Nonanoic acid, methyl ester (pelargonic acid methyl ester)		x			
Glycerol 1,3-TFMP diether, 2-methyl ether			x		x
Glycerol 1,2-methyl diether, 3-TFMP ether					x
Glycerol 1-methyl ether, 2-TFMP ether					x
Glycerol TFMP triether	x	x	x		
Dimethyl phthalate (alkyd resin fragment)					x
Naphthalene, 2-methoxy					x
Naphthalene, 1,7-dimethoxy-					x
Methyl dehydroabietate (methyl ester of Abietic Acid - resin)		x			x
Tetradehydroabietic acid, 7 methoxy, methyl ester					x
7-oxodehydroabietic acid, methyl ester					x
15-hydroxy-7-oxo-dehydroabietic acid, dimethyl derivative					x
Jalaric acid, trimethyl ester		x			
Laccijalaric dimethyl ester methyl ether - gomme lacque		x			
Cyclohexasiloxane, dodecamethyl-	x	x			
Benzenamine, N,N,3-trimethyl-		x			
Benzenamine, N,N,4-trimethyl-	x				
<b>Synthetic organic red pigment: naphthol or pyrrole</b>		<b>x</b>			

products of abietic acid (Figure 8). The presence of palmitic and stearic acids along with azelaic and suberic diacids indicates that the binder is a drying oil and the large amount of azelaic acid is a marker of oxidized drying oil (Piccirillo et al. 2005). The abietic acid degradation products reveal the presence of an oxidized (aged) resin, probably from *Pinus* species (Van den Berg et al. 2000).

### Interaction of metal/paint layers

The condition report was prepared to determine the origin of the observed alterations: either physical causing constraint on the paint layers; or of chemical origin due to diffusion of chemical species throughout the layers. Chemical interactions between the two layers can lead to significant visual changes. The most obvious is due to the migration and diffusion of metallic ions into the paint layers. Iron corrosion often leads to an orange-brown color change in the paint layer, especially when the colors are pale and thus easily overpowered. This phenomenon could be observed on part of the collected samples.

To illustrate, the sample from the model of an engine boiler shows white granular paint layers which are tinted due to corrosion of the iron support (orange, brown). The paint layers are mainly constituted of Pb (inside layer) and Zn (top layer) suggesting the use of white pigments such as lead white and zinc white. The orange color visible in both layers is clearly due to the presence of Fe, as revealed by the XRF map (Figure 9). Fe is not present in the original pigment. After oxidation of the underlying metal, the metallic ions (mainly Fe<sup>3+</sup>) most likely diffused from the metal into the paint layers.

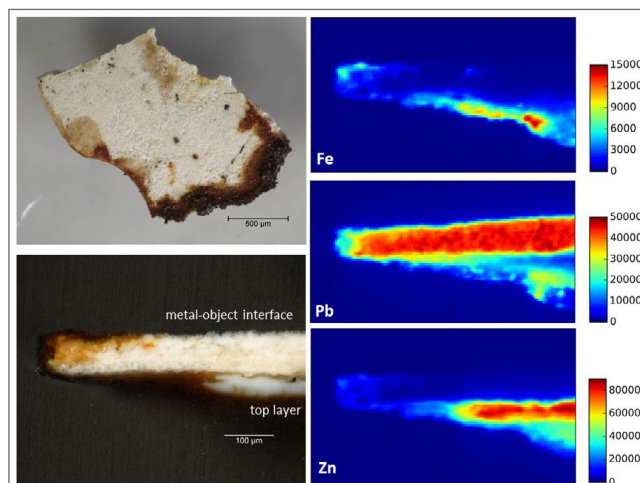


Figure 9. Paint flake sampling from the model of an engine boiler (top layer), cross section observed using optical microscope and XRF maps of major elements



## Conclusion and perspectives

This study has highlighted a rich and promising corpus both in terms of conservation-restoration and the establishment of protection protocols for painted metals. Following the first step of the CoPaiM project, some requirements for protective surface treatments will be determined.

Previous studies (Schröter 2009, Sutter 2014) note the use of coatings to protect painted metal against possible external aggressions or inhibitors to stabilize the metal and prevent damage due to corrosion (Rocca and Mirambet 2007). In fact, the complexity and plurality of alterations to historical painted metal objects requires this two-stage restoration: metal stabilization and paint protection.

The second part of the CoPaiM project will focus on laboratory tests on painted metal plates in order to assess and validate a protective surface treatment while fully respecting the ethical principles of conservation and restoration. The effectiveness of corrosion inhibitors and coatings will be evaluated by applying accelerated aging techniques and monitoring the samples in order to test the stability of the protected system.

Considering the environment in the museum and storage room, some of the painted metal plates will be exposed under light and to regulated climatic cycles corresponding to atmospheric corrosion conditions, while others will undergo a more complex environment in which the insertion of pollution particles, such as concrete dust, will simulate a specific indoor environment.

Some of the other painted metal plates will experience natural aging at selected exposure sites in the museum reserves to assess the treatments over a long period of time. The degradation of metal and paint layers exposed to an uncontrolled and polluted environment presents new challenges for the characterization of their reactivity and the establishment of efficient protective surface treatments.

The final objective of the project is to develop a formulation and a treatment protocol whose composition and application have been validated on real museum collections.

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