Investigating five totalizing counters manufactured by the Alphonse Darras company of the CNAM collections in Paris

Investigação de cinco contadores totalizadores fabricados pela empresa Alphonse Darras das coleções do CNAM em Paris

JULIE SCHRÖTER [1*]
CYRILLE FOASSO [2*]
LUDOVIC BELLOT-GURLET [3]
LAURA BRAMBILLA [1]

1. Haute Ecole Arc Conservation Restauration, HES-SO University of Applied Sciences and Arts Western Switzerland, Espace de l'Europe 11, 2000 Neuchâtel, Switzerland

2. Curator, Musée des Arts et Métiers (CNAM), 60 rue Réaumur, 75003 Paris, France

3. Sorbonne Université, CNRS, De la Molécule aux Nano-objets: Réactivité, Interactions et Spectroscopies (MONARIS), UMR 8233, 4 place Jussieu, 75005, Paris, France

**julie.schroter@he-arc.ch (JS) ; cyrille.foasso@lecnam.net (CF)*

Abstract

The paper reports the study of five totalizing counters preserved in the collections of the CNAM (museum of the *Conservatoire National des Arts et Métiers*) in Paris. These artefacts are part of a *corpus* of over forty counters attributed to the Darras company founded by the engineer Alphonse Darras (1860-1936). In the framework of the LacCA project at *Haute Ecole Arc*, Neuchâtel (Switzerland), dedicated to the characterization of lacquered copper-alloys, the focus of the study were the different aspects of the object's coatings. Lacquers were frequently applied on technical objects with the double aim of protecting them from corrosion and to provide a specific esthetical appearance. Five totalizing counters showing various shapes and surface colors were chosen from the lot and examined with a non-invasive multi analytical approach. The comparative study – investigating lacquering processes and materials – contributes to the historical study of these artefacts.

KEYWORDS
Transparent lacquers
Copper alloys
19th-20th century
Non-invasive methods
UV fluorescence
FTIR

Resumo

Este artigo descreve o estudo de cinco contadores totalizadores conservados nas coleções do CNAM (museu do *Conservatoire National des Arts et Métiers*) em Paris. Estes artefactos fazem parte de um *corpus* de mais de 40 contadores atribuídos à empresa Darras, fundada pelo engenheiro Alphonse Darras (1860-1936). O estudo desenvolvido no âmbito do projecto LacCA da *Haute Ecole Arc*, Neuchâtel (Suíça) sobre caracterização de ligas de cobre lacadas, incidiu sobre as diferentes características dos revestimentos dos objetos. As lacas eram frequentemente aplicadas em objetos técnicos com o duplo intuito de proteção contra a corrosão e decoração. Cinco contadores totalizadores com diferentes formas e cores, foram selecionados e examinados através de diferentes técnicas analíticas não invasivas. O estudo comparativo – investigando os processos e os materiais de lacagem – contribui para o estudo histórico destes artefactos.

PALAVRAS-CHAVE
Lacas transparentes
Ligas de cobre
Séculos XIX-XX
Métodos não invasivos
Fluorescência UV
FTIR

Introduction

The CNAM museum in Paris is part of the *Conservatoire National des Arts et Métiers* (CNAM) and one of the oldest scientific and technological museums in the world. Founded in 1794, its collections of scientific instruments and technical objects were expanded throughout the nineteenth century, especially thanks to donations from industrialists or with items from industrial, national or universal exhibitions. The present case study was carried out in the context of a project dedicated to objects made of lacquered copper alloys (LacCA) at *Haute Ecole Arc* (Neuchâtel). This coating technology can be found frequently in both decorative arts and technical heritage collections. In the latter case, the main purpose of these coatings is to provide protection against corrosion, guaranteeing both reliability of the object's function and providing a specific esthetical appearance [1]. These finishes are an integral part of the manufacturing process of the objects. If well preserved, they are evidence of the history of the materials and processes used, as well as of the know-how of the people involved in the specific production of these technical objects. Their characteristics can also potentially provide indications about age and provenance of the artefacts when studied systematically [1-2].

It is known from literature that copper alloys on technical objects were usually coated with shellac-based lacquers during the nineteenth century. These coatings, prepared by dissolving the resin in alcohol, were applied with a brush whereas small pieces could also be dip-coated [3]. Cylindrical parts were often lacquered with the help of a lathe [4-5]. The same type of lacquer recipes were still referenced in the practical guides of the twentieth century [6], even though the first synthetic polymers based on cellulose nitrate were developed in parallel for metal coatings [7]. Shellac-based recipes were also later used for the relacquering of ancient objects both by private collectors and museum conservators [1, 8-11]. However, it must be pointed out that shellac-based recipes for both copper-based decorative objects and technical instruments were often more complex. Additional binding media or plasticizers could be used to improve the coating properties as well as organic dyes to enhance the surface appearance of the metal [12-14]. Moreover, shellac – a natural animal-produced resin and wax mixture – comes in different grades and shades (seedlac, buttonlac, shellac in flakes…) and different processing and bleaching methods of shellac were developed and improved during the nineteenth century in France [15-17]. Nevertheless, only few studies dedicated to ancient lacquers on technical objects have been reported in the literature to date [13] and morphological aspects of the lacquers as well as coating thickness are rarely mentioned. A small selection of a huge but still unexplored *corpus* of counters from the Darras Company was investigated. The transparent coatings and metal substrates of five totalizing counters were characterized using non-invasive and portable techniques on site in the conservation center of the museum.

Studied pieces and their historical context

The five counters that are studied in this paper were donated to the museum in 1987, twenty-five years after the closure of the company that had manufactured them. They were probably part of a small heritage collection of the company itself. Founded by Eugène Deschiens (1826-1889) in 1866 at 123 boulevard Saint-Michel in Paris, the workshops (*Ateliers Eug. Deschiens*) were bought in 1894 by Alphonse Darras (1860-1936), a construction engineer, who developed and directed the business until his death. From 1936, his widow and his children continued the business under the name *Etablissements Alph. Darras*.

Unlike other French scientific instrument or precision mechanics manufacturers of the nineteenth century (for example. Chevalier, Lerebours et Secretan, Soleil-Duboscq-Pellin, Ruhmkorff, Carpentier, Froment Ducretet, Deleuil, Richard, Brunner, Breguet, Soleil-Duboscq, or Golaz) and in spite of its longevity, the history of the Deschiens-Darras firm has not been traced and written up to now. For the historical introduction of this paper, various sources coming from archival holdings of the museum were explored, among which are trade catalogues of the manufacturer [18]. Documents from the Archives of the Commercial Court of

Paris and specific issues of the Journal of Commercial Archives of France (which published company formations, modifications, dissolutions, bankruptcy declarations as well as commercial property sales) were studied in particular [19-21].

It is known that the Paris workshops of the Alphonse Darras Company were at a later time transferred to 2 and 4 rue de Seine in Viry-Châtillon, to the location of the Stempert factory, specialized in bolt production machines. This factory had been acquired by Alphonse Darras in 1924. In 1958, Darras' widow created a new company to continue the business, and this factory remained her property until its closure in 1963.

The Alphonse Darras company, successor of *Maison E. Deschiens*, was specialized in the manufacture of telegraphic and telephone equipment as well as precision mechanics. In a context of a strong industrial expansion, the business focused on industrial control systems by means of different types of counters: totalizing counters and lap counters. These were used for measuring fluid flow, the speed (revolutions per minute) or power of the rotating machinery to which they were connected, or as odometers or tachymeters.

Due to its success, the company could invest and acquire in 1915 the *Ateliers Vve Payen*, property of the widow of Louis Payen, who, in turn, was the successor of Thomas de Colmar, a famous inventor and manufacturer, known since 1820 for his mechanical calculating machines called arithmometers.

The five counters are part of a much larger donation of 179 objects representative of the company's production, including the 49 counters given to the CNAM museum in 1987 by the Darras family. Despite all the studied objects were produced by the Darras company and are composed of a rectangular case and a frame with a transparent window displaying the counting, their size, shapes, and materials differ as it can be observed in Table 1.

This donation followed an earlier gift of nine objects in 1972 which joined other Darras objects in the museum's collection, namely a phonograph purchased by the museum in 1896 (inv. 12860), an arithmometer (inv. 20968) donated by the Damascus-Hamah Railway Company in 1962, and a Claude-type electromagnetic relay for wireless telegraphy dated 1908 (inv. 21285), donated in 1963.

Table 1. The five selected totalizing counters; images and characteristics referenced in the CNAM collection.

Code in this study	**DAR1**	**DAR2**	**DAR3**	**DAR4**	**DAR5**
Image (topframe and window)					
Image (case frontside)					
Designation	*Compteur série "ED", alternatif à 7 chiffres*	*Compteur série "ED"*	*Compteur totalisateur à commande électrique*	*Compteur série "ED", alternatif à 6 chiffres, type F*	*Compteur totalisateur série "ED"*
Inv. number	40523-0000-	40519-0000-	4082-0000-	40522-0000-	40518-0000-
Size, weight	6 × 8 × 24 cm, 2kg	5.5 × 9 × 30 cm, 3.1kg	11 × 15 × 15 cm, 2kg	6 × 8 × 25 cm, 2.1kg	5.5 × 9 × 18 cm, 1.6kg
Materials	Lacquered copper alloy, glass, (painted) iron alloy	Lacquered copper alloy, synthetic material, (painted) iron alloy	Lacquered copper alloy, glass, iron alloy, painted wood	Lacquered copper alloy, glass, (painted) iron alloy	Lacquered copper alloy, glass, (painted) iron alloy
Inscriptions	*AD*	*ATELIERS DESCHIENS.* *Système breveté s.g.d.g.,* *A. DARRAS* *Ing.r construct.r* *Paris, N° 8320* *3* is painted in black on the backside of the case	*COMPTEUR SYSTEME* *BREVETE S.G.D.G.* *N°3640* *A. Darras* *Constructeur* *Paris*	*AD*	No mark, but a circular copper label is attached

The precise dating of these counters is very difficult, since these materials were already the specialty of Eugène Deschiens and remained such until the closure of the Darras company in 1963. Four of the five counters belong to the "ED" series, made of "lacquered copper", a general designation for copper alloys like brass. Their external design did not change much between 1875 and the 1930s, as shown in the two advertising plates reported in Figure 1a-b. The third one (DAR 3), whose case is also in "lacquered copper", was already visible on some leaflets of the Deschiens company, and still in the Darras catalog in 1900, as shown in Figure 1c.

As mentioned before, some objects were probably part of a small museum of the company. In fact, they have a small iron ring with an engraved number (303, 318...) which is probably the reason why very few of them have a serial number stamp. Moreover, there are no inventories of the firm, nor the list of the types and models of its successive productions.

From the inscriptions on the objects, one could estimate that DAR2 and DAR3 date back to the same period, as they carry the inscription "breveté S.G.D.G.", (*breveté sans garantie du gouvernement* – patented but without government warranty), a mention that appeared in a law of 1848 and that disappeared with a new law in 1968. This mention was chiefly used at the end of the nineteenth century and progressively disappeared along the twentieth century. DAR 1, 4, and 5, the first two showing the mark "AD", could form a more recent second group.

Because of this dating uncertainty, material characterization, especially the study of the lacquer finish of the counters, could integrate the lack of archival information and confirm or contradict the hypothesis previously formulated.

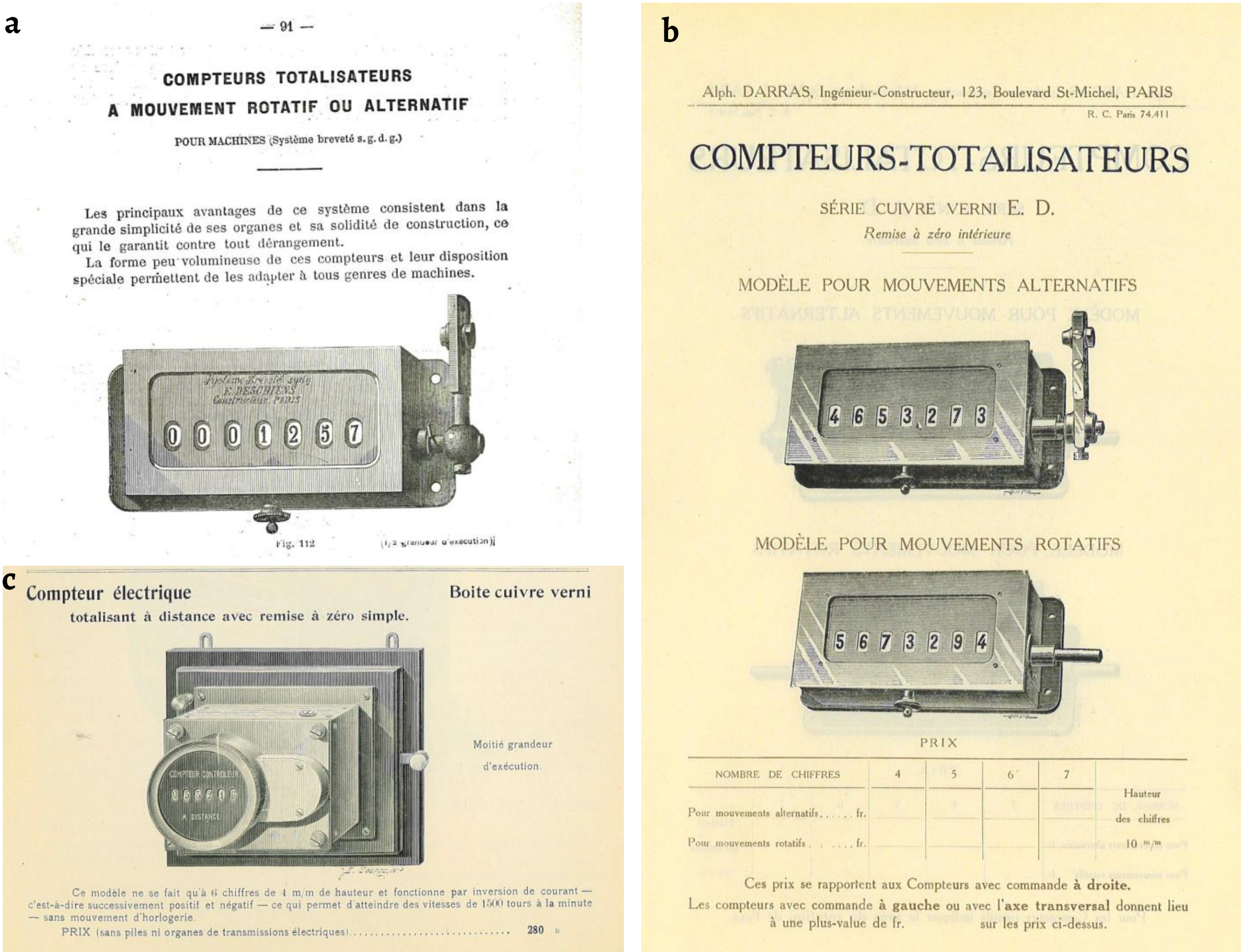


Figure 1. Excerpts from the catalogues: *a)* Deschiens *Catalogue général illustré en deux parties, 2e partie*, June 1876, p. 90; *b) Alph. Darras*, not dated, but after 1920; *c) Ateliers Deschiens-Alph Darras ingénieur constructeur*, 1900, 1st March, p. 11.

Materials and methods

Studied pieces and Analytical techniques

Observation and documentation under white light

The lacquered surfaces were documented under white light and observed under magnification. A short global condition report was produced for each object. White light images were acquired using a Canon Powershot G7X camera and an X-Rite Color Checker Passport target was used as reference. A portable Dinolite AM-413 ZT USB microscope was used for surface imaging at magnification ×50 with the *DinoCapture* 2.0 software.

Colorimetric measurements

Colorimetric measurements were carried out using a Minolta CM-2300d portable spectrophotometer with a D65 illuminant, a 10 ° observer, and specular component excluded (SCE), using CIELAB 1976 color space. An aperture of 3 mm diameter was chosen to acquire comparative data from objects of different size and shapes. On each totalizing counter, three measurements were carried out on three different points on the frame and the mean value and standard deviation calculated. The data were compared to measurements carried out under the same conditions on gilded brass samples of different gold colors: "lemon yellow gold", "orange gold", and "red gold". The reference material is made of gilded industrial UZ36 brass coupons, with mat and polished (M and P) finishing by Texier Company, Paris.

Fourier-Transfrom Infrared Spectroscopy (FTIR)

Infrared analyses were performed in specular reflectance configuration (SRefl) using an Alpha portable spectrometer (Bruker) with its R-Alpha module to obtain non-invasive, contactless measurement. The counters were placed in front of the spectrometer head at 15 mm working distance. The focusing and selection of areas was performed with an internal video camera and the analyzed area had a diameter of approximately 5 mm. 128 scans were acquired for each spectrum.

UV imaging

UV imaging was performed with an unfiltered Canon EOS 750D camera (Canon INC, Tokyo, Japan), using an 18-55 mm lens, a UV/IR cut (Baader Planetarium, Munich, Germany), and an X-Nite CC1 filter (LDP LLC, Carlstadt, NJ, USA). The counters and reference samples were placed on a black non-UV emitting cardboard background and illuminated by two UV lamps (Dominique DUTSCHER SAS, Bernolsheim, France) mounted at 45° on a custom-made stand. The main emission peak of the UV source is at 365 nm. The *UV Innovations Target* was used to calibrate the color of the pictures in *Adobe Photoshop* software. The pictures were taken in manual mode, ISO 200, and f/11 aperture; the target (low fluorescence side) was photographed with 1 s exposure time, whereas exposure was adapted for the objects and reference samples (15 s) according to a former study [22]. White balance correction was performed on the pictures in Camera Raw using the *Adobe Photoshop* Setup and Capture Workflows recommended by the calibration target manufacturer [23]. In order to assess the fluorescence color of each lacquer, the L* a* b* values of three spots on intact-looking zones of the topframe were then recorded using the color sampling tool (11 × 11 px) for each coupon in *Adobe Photoshop*.

XRF analysis

XRF analysis was performed using a Niton Thermo Scientific XL3t GOLDD+ XRF analyzer (analyze time 360 s, "mining mode" option) without specific surface preparation. This mode was chosen because we wanted to be able to identify the metal alloy, as well as chemical elements like barium, calcium, chlorine or potassium, which can be present depending on the technology used to produce the coating. In fact, fillers like barium sulfate, calcium carbonate or even chlorine may be residues coming from the lacquer manufacturing process or degradation products (like chlorides) possibly present on the artifacts. Data collection and post-processing were carried out using the *Thermo Scientific Niton Data Transfer* (*NDT*) software.

Thickness measurements

The thickness of the samples was measured with a *Phynix Surfix* Pro S gauge and FN 1.5 eddy-current probe (PHYNIX GmbH & Co. KG, Neuss, Germany) with a measurement range of 0-1.5 mm and an accuracy, with foil calibration, of ± 1.0 µm + 1 % of value. Measurements were performed both on the frame and on the case of the counters to compare the average values. Ten measurements were performed on each selected, intact-looking, lacquered spot. Thickness measurements were also carried out on lacquered reference coupons three times on each zone.

Reference material for UV imaging and FTIR

UV imaging and FTIR data of the counters were compared with the data acquired on reference material. Two lacquers based on the same recipe for precision instruments were produced with orange shellac in flakes [24]. The exact procedure for the preparation of shellac lacquers has been described before [22]. The coatings were applied to CuZn37 satin finished coupons (60 mm × 60 mm × 3 mm) by manual dip-coating. One of the two prepared shellac solutions was dewaxed before lacquering by filtering the orange shellac solution on 602H filter paper and by settling. Before application of the lacquer, the brass was degreased with ethanol. The metal was then heated around 30 °C before lacquer application. Temperature was selected according to the results of former experiments and the coated samples dried at ambient temperature [3]. Coatings of different thicknesses were produced with both the dewaxed and non-dewaxed solution. The non-dewaxed shellac solution had to be diluted with ethanol to obtain thinner layers. Additionally, two mirror polished brass coupons with a layer of bleached and dewaxed shellac, produced by industrial dipcoating, were used as references [22].

Results and discussion

Visual observations and documentation under white light

Different colors were detected at a first observation on the five counters. On the one hand, DAR2, DAR3 and DAR5 have frame and case of a similar color that can be defined as "brass-like". On the other hand, DAR1 shows frame and case of different colors, the latter manifesting a more reddish hue. Its case exhibits the same reddish color as DAR4 frame and case. The question remains whether the frame of DAR1 was replaced at a later period because its frame color differs from the case for an unknown reason. Moreover, a similar "AD" mark is present on DAR1 and DAR4, whereas DAR 5 does not present any mark at all (Table 1).

All frames and cases exhibit a satin finish, probably created by parallel machining and brushing of the metal. The cylindrical parts of the counters, like the small, knurled wheels, were manufactured using a lathe as shown by the visible circular traces on the metal. Parallel brush strokes in the lacquer are visible in raking light on the cylindric frame of DAR3. This element might have been coated with the help of a lathe.

Microscopic observations

The microscopic observation of the counters shows abraded and locally corroded lacquered surfaces. This suggests that the counters have not been relacquered during a long period before entering the museum's collections (Figure 2a-b). Brush strokes coming from lacquer application become visible with ageing and corrosion, indicating that the coating was applied manually in the longitudinal direction of each metal part. Dark corroded lines are less visible on DAR2 and DAR3. This might be due to the presence of thicker layers providing more efficient protection from corrosion. The coating on DAR3 exhibits small transparent excesses of lacquer (Figure 2c).

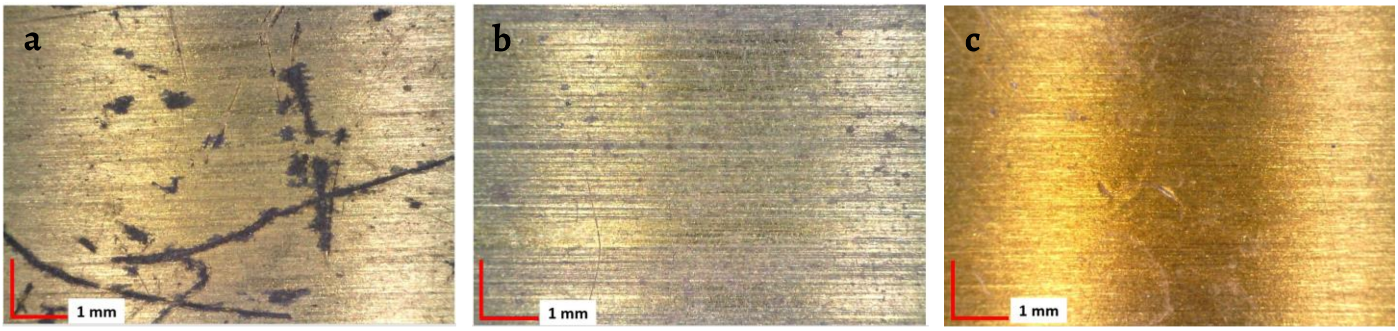


Figure 2. Detailed views of the lacquered surfaces (magnification 50×): *a)* DAR2, frame, corroded scratches and pits; *b)* DAR5, case, backside, abraded lacquer; *c)* DAR3, thick lacquer layer on the frame.

Colorimetric measurements

Colorimetric measurements performed on the counter's frames confirm the differences in surface appearance of the lacquered copper-alloy finishes detected during the visual observation and documentation under white light of the counters (Figure 3). DAR4 shows a more reddish color than the copper-alloy parts of the other objects, with a much higher red value on the a* axis. The four other counters can be, on the other hand, divided into two color groups: DAR1/DAR5, whose frame color is similar to the yellow gold reference, and DAR2/DAR3, closer to the orange gold reference. All three clusters tend systematically to a bluer hue on the b* axis and a greener hue on the a* axis compared to the reference gold color samples.

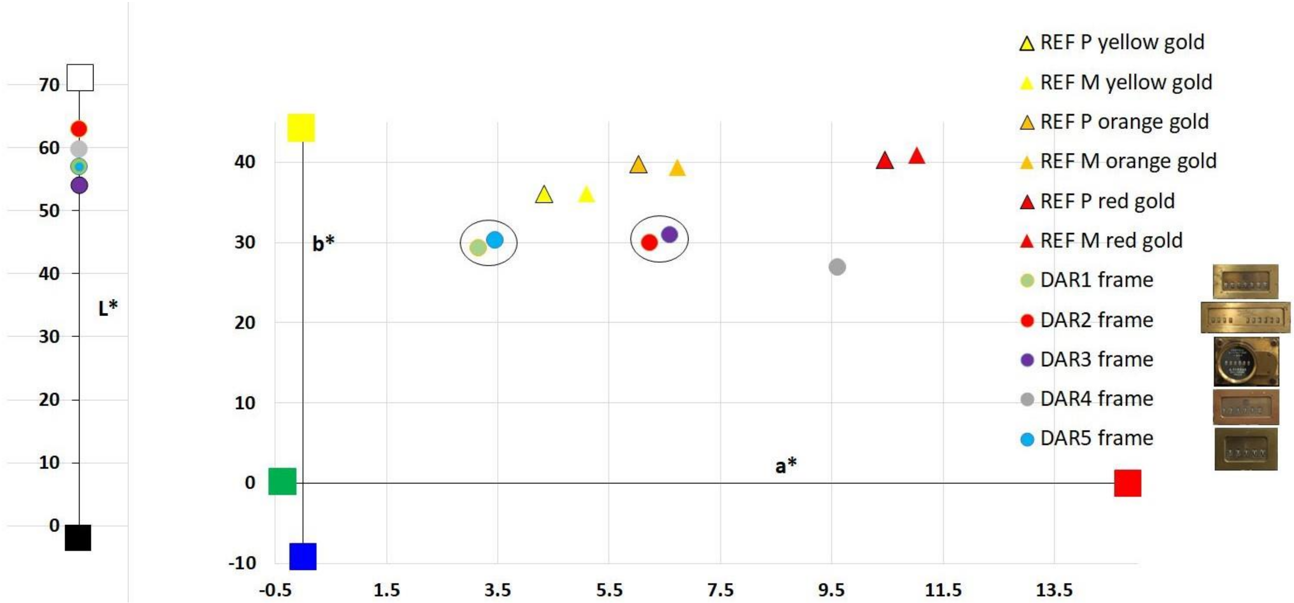


Figure 3. L* a* b* colorimetric coordinates for each object and zone on the frames.

FTIR

It was first assumed that the reddish color of DAR4, described in the previous paragraphs, could be related to a difference in lacquer composition and thickness. However, FTIR analysis did not confirm this hypothesis about the composition. In addition, no relation was found between this color and corrosion phenomena. All SRefl-IR signatures of the lacquers are similar and characteristic peaks can be attributed to the presence of shellac resin (Figure 4). Slight variations for some bands intensities ratios are visible, as, for example C-H/C=O peaks (DAR2 and DAR4 vs DAR1 and DAR5). Furthermore, FTIR analysis revealed shellac wax residues, as shown by the characteristic peak around 727 cm^{-1} in all signatures, but more visible for DAR3 (Figure 4, see arrows). Experiments showed that wax residues remain even when the resin is filtered and dewaxed by a traditional method like settling [22].

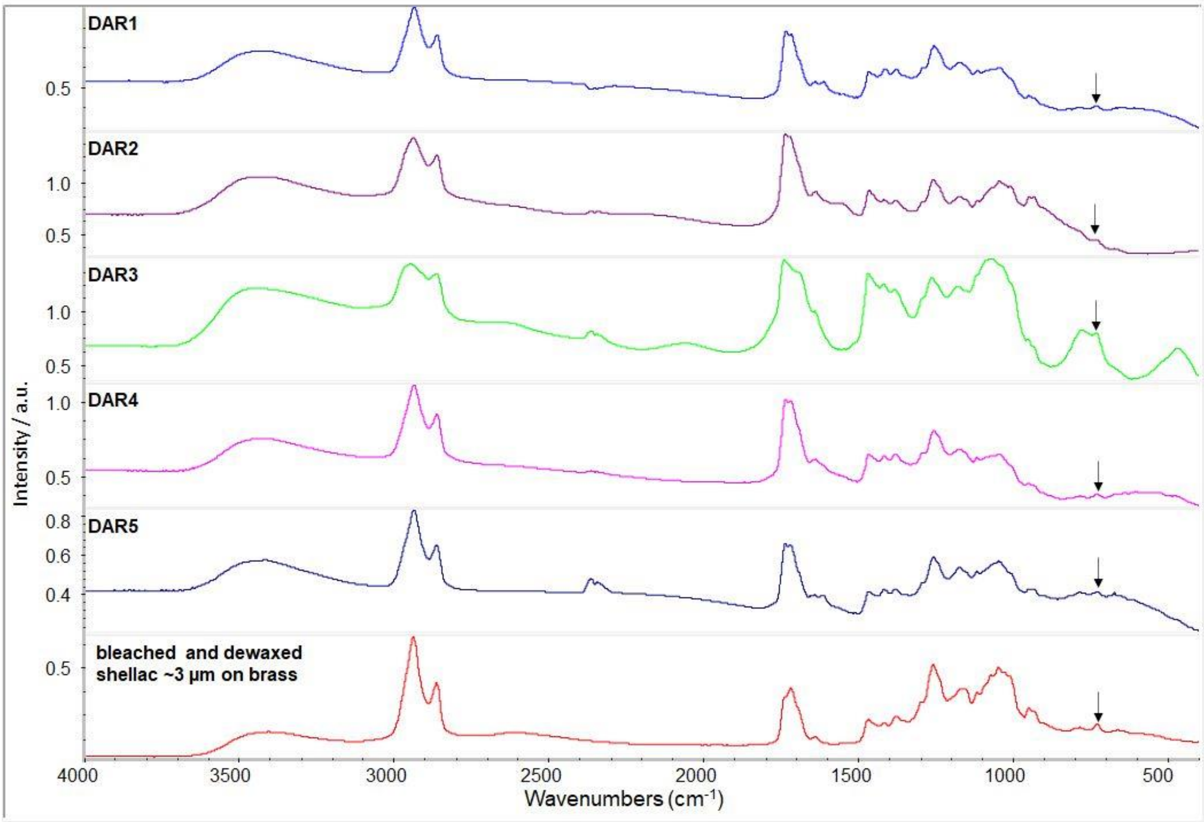


Figure 4. Representative infrared spectra for each totalizing counter compared with a reference lacquered coupon spectrum acquired under the same conditions. Residues of CO_2 are visible on the spectra of DAR3 and DAR5 around 2300 cm^{-1} due to incomplete background correction. The arrows indicate the band at 727 cm^{-1} highlighting wax traces.

Although shellac-based recipes for both copper-based decorative objects and technical instruments were often very complex, shellac and traces of shellac wax were the only materials detected by FTIR. For this reason, the question remained at this stage whether the natural color of a non-bleached resin might have influenced the visual result or if a dye may have been present. As pointed out before, the fact that a natural resin was used for the lacquering does not contribute significantly to the dating of the finish. However, the presence of different shellac grades is interesting as it points out object groups which may be related to specific production periods in the workshops. Additionally, other aspects like coating thickness were also explored in this study.

UV imaging

It has been shown in former studies that it is not possible to distinguish different shellac grades by means of non-invasive methods like FTIR [17], but that UV imaging can provide additional information [22]. The lacquered copper-based parts of the counters exhibit different hues and intensities of fluorescence (Figure 5 and Table 2). Colorimetric data for the fluorescence of these parts present a good reproducibility for all artefacts, except for DAR5 (Figure 6). This is due to the fact that the lacquer was applied in a very heterogenous way on this counter, and colorimetric data were acquired both on the thicker and thinner lacquered portions.

DAR2 and DAR3 show a uniform intense orange fluorescence. Their a* b* color coordinates tend clearly to the orange shellac references, whereas DAR4 and DAR5 tend more to blue and green on the blue-yellow and green-red axis, in the vicinity of the color coordinates of the bleached shellac reference. DAR1, on the other hand, presents even colder hues. It has been observed that bleached shellac coatings exhibit slightly colder fluorescence colors when aged artificially under UV [22].

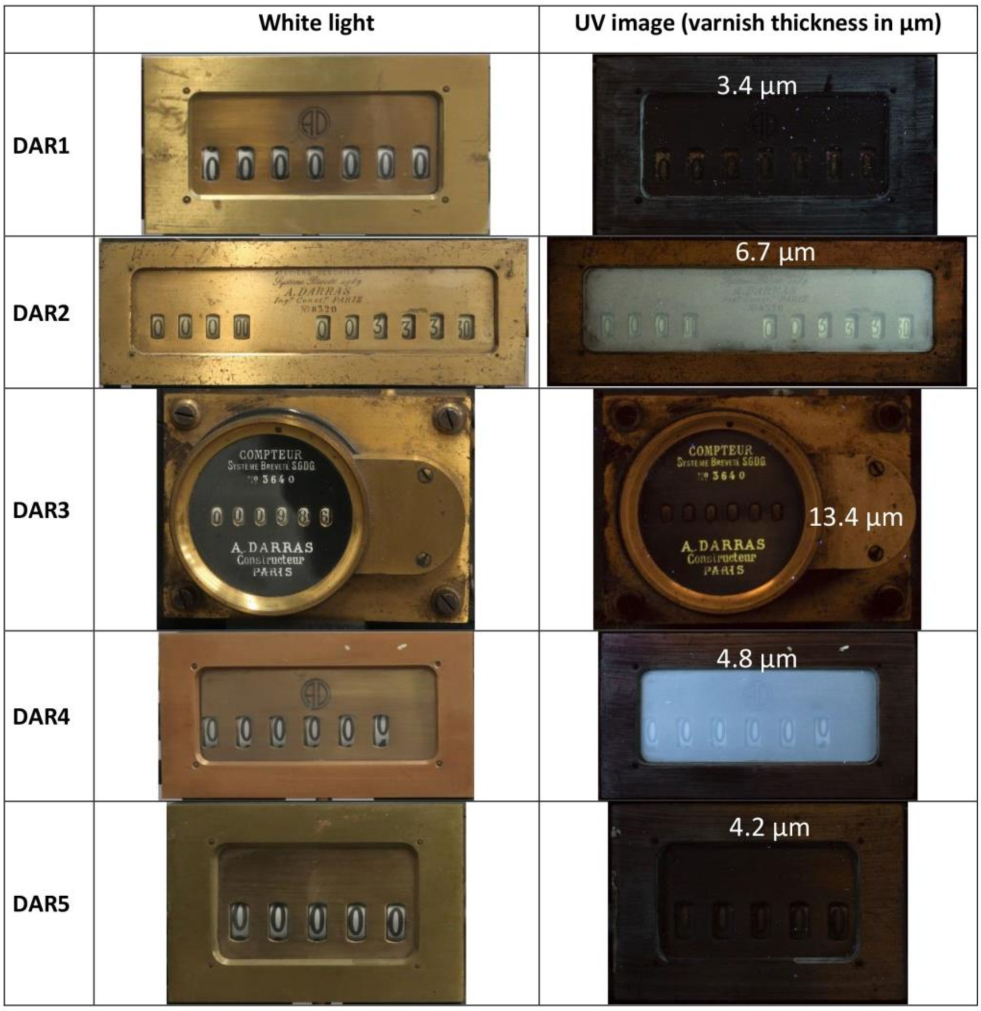


Figure 5. White light and UV fluorescence images of the frame of each totalizing counter (with average coating thickness indicated for a selected spot on the frame)

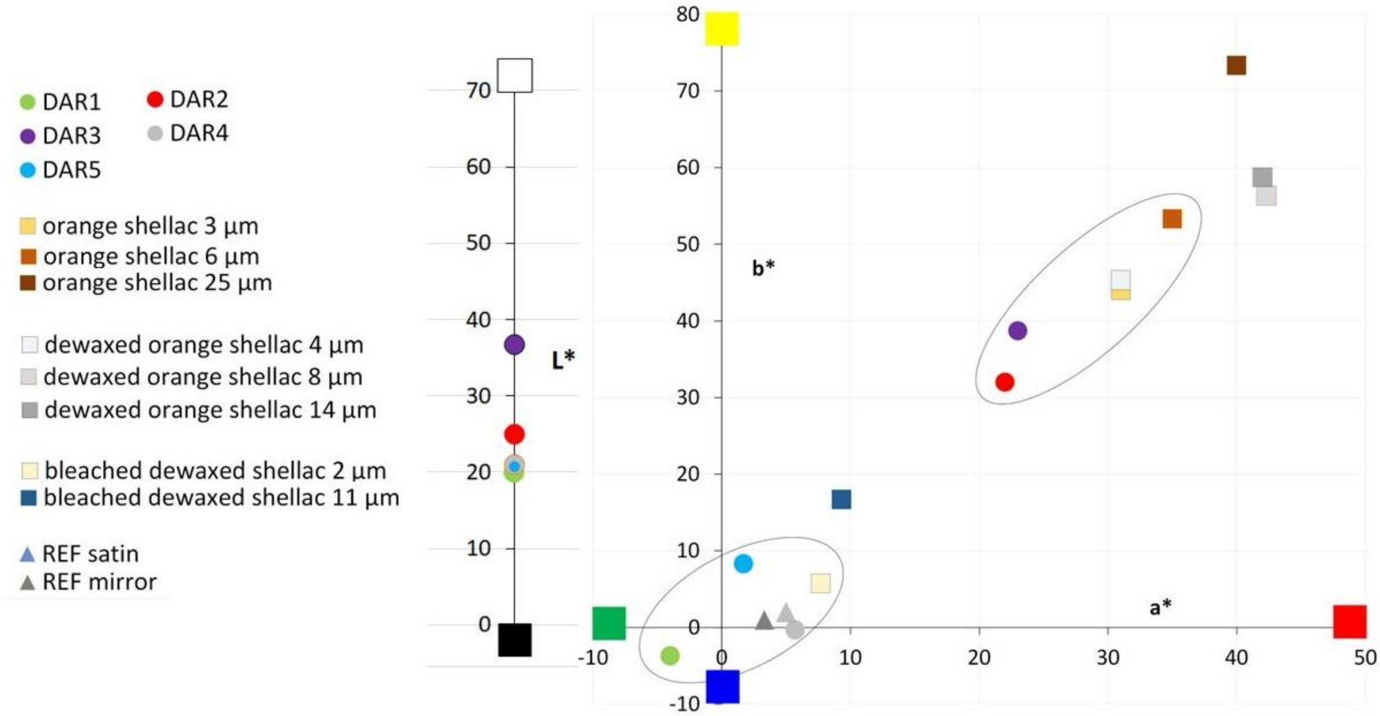
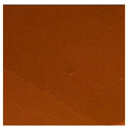
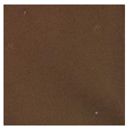


Figure 6. L* a* b* colorimetric coordinates of the lacquers' fluorescence (DAR1-DAR5, frame) compared to the reference samples of fresh shellac films.

Table 2. UV fluorescence images of diverse reference samples made of fresh shellac films with different coating thicknesses on brass.

Reference samples				
Orange dewaxed shellac			**Bleached dewaxed shellac**	
				
4.23 ± 0.06 µm	8.10 ± 0.10 µm	13.83 ± 0.15 µm	2.1 ± 0.3 µm	11.2 ± 0.6 µm
Orange shellac			**Brass (mirror)**	**Brass (satin)**
				
2.90 ± 0.36 µm	6.33 ± 0.4 µm	25.00 ± 0.89 µm	-	-

Observation and comparison under white light and UV radiation of the central windows provided additional information about the materials used for the counters (Figure 5). In the case of the transparent central window of DAR4, the icy blue color under UV radiation could be due to the presence of specific compounds in the glass like lead [25]. However, XRF or FTIR were not performed on the glass to confirm this hypothesis. DAR1, DAR3 and DAR5 counter windows are manufactured with non-fluorescent glass. Nonetheless, DAR2 central window shows a greenish-yellow fluorescence and it has slightly warped shape; for this reason it was analyzed by FTIR. The Srefl-IR signature reveals the presence of a cellulose nitrate-based material, which is consistent with the greenish-yellow fluorescence visible under long wave UV radiation [25]. Cellulose nitrate was introduced commercially in the 1860s in France and experienced an industrial decline in the 1960s [26].

XRF

XRF analysis of the metal alloy provided additional information about the surface colors (Table 3). All copper alloys are quaternary alloys, composed of copper (Cu), zinc (Zn), tin (Sn) and lead (Pb), with a high level of Zn (over 20 %). DAR4 and the case of DAR1 contains however a higher proportion of Cu, a very low concentration of Zn, and a higher amount of Sn and Pb compared to the other alloys. This explains why these surfaces look redder then on the other objects. It can be assumed that the cases of DAR1 and DAR4 are from a similar production period as they also show an identical ornamentation on the inner plate of the case, performed by circular brushing.

Table 3. Elemental composition in atomic percentage; analysis made by XRF (LOD = limit of detection).

	Object	**DAR1**		**DAR2**		**DAR3**		**DAR4**		**DAR5**	
	Spot	**Frame right side**	**Case frontside**	**Frame right side**	**Case frontside**	**Frame right side**	**Case frontside**	**Frame right side**	**Case frontside**	**Frame right side**	**Case frontside**
Elements	**Cu**	60.86	71.64	57.79	56.28	53.42	54.30	71.65	69.11	60.71	61.77
	Zn	20.51	2.17	20.25	25.97	23.95	24.49	1.54	1.02	21.60	20.53
	Sn	1.38	**6.34**	1.67	0.49	0.01	0.47	**9.00**	**7.90**	0.85	1.09
	Pb	1.66	**2.44**	1.37	0.94	0.41	1.65	**1.91**	**4.09**	1.24	1.22
	Cl	0.90	0.32	0.43	0.09	0.03	0.06	0.26	1.43	0.51	1.18
	S	0.46	0.24	1.17	0.42	0.33	0.62	0.28	0.57	0.32	0.59
	Fe	0.47	0.06	0.34	0.27	0.05	0.10	0.06	0.03	0.42	0.38
	Ni	0.15	0.16	0.07	0.06	< LOD	0.03	0.17	0.16	0.10	0.10
	Ca	0.10	0.11	0.22	0.03	0.04	0.11	0.14	0.19	0.04	0.09
	Sb	0.05	0.15	0.05	0.02	< LOD	0.01	0.15	0.19	0.03	0.04
	Ag	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.03	0.02
	Ti	0.01	0.02	0.07	0.00	< LOD	0.00	0.03	0.03	0.00	0.01
	K	< LOD	< LOD	0.09	0.03	0.18	0.17	< LOD	< LOD	0.02	0.03
	Cd	< LOD	< LOD	< LOD	0.01	0.01	0.01	< LOD	< LOD	0.01	< LOD

A direct relation can be observed between the alloy composition and the two color groups which had been highlighted for the frames (respectively DAR1-DAR5 and DAR2-DAR3). All object surfaces show a certain amount of chlorine, which is systematically higher on the frames when compared to the results obtained on the cases. This can be due to manipulation with bare hands and contamination of the surface. In the case of the DAR1, DAR4 and DAR5, its presence could also be related to the presence of bleached shellac containing chlorine residues from the bleaching process.

Thickness measurements

The global lacquer average thickness on frame and case for each counter is less than 5 µm. In general, the frame is coated with a thicker layer than the case, probably to protect it from a more frequent manipulation. DAR2 exhibits a slightly thicker lacquer on the frame than the other counters whereas the lacquer on DAR3 forms an exception with an average thickness around 12 µm (Figure 7). This confirms previous visual observations (Figure 2c).

As for DAR3, the case was mounted by assembling metal sheets with screws and not by soldering (Table 1). A hypothesis is that a thicker varnish – when applied before mounting of the plates – could also prevent from contact corrosion in these areas.

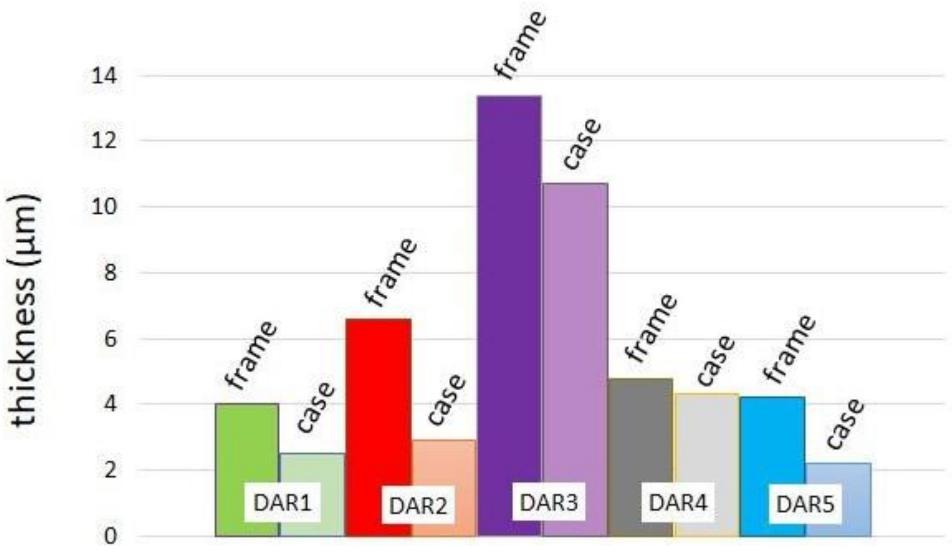


Figure 7. Average lacquer thickness on frame and case for each counter.

Conclusions

The investigation of this set of five counters from the collection of the CNAM in Paris, shows that a systematic approach to the characterization of lacquered copper alloys might be a promising additional tool for the historical study of the collection of technical and scientific objects. We conclude from visual observations that all lacquers were applied with a brush. The analytical results show that shellac coatings were systematically chosen for the copper-based parts of the studied counters, which is consistent with ancient written sources. Based on FTIR analysis and UV imaging performed on the objects, differences in the type and grade of resin can be pointed out and it can be assumed that at least two different grades of shellac were used (bleached shellac and orange shellac, both showing residues of shellac wax). It also appears that lacquer thickness is significantly higher for one counter model with a significantly different typology (DAR3), which might indicate that the lacquering technique was adapted to the manufacturing and mounting process of the metal parts and is not necessarily due to the production date of the object. Organic dyes were not identified in the lacquers by the analytical approach implemented, but XRF analysis of the alloy composition suggests that the different surface color of the cases and frames may be primary due to the alloy color and not to the color of the lacquer used.

Initially it was assumed that two counters, DAR2 and DAR3, which both present the legal mention "système brevet S.G.D.G", might date from a similar more ancient manufacturing period in comparison to the other counters. XRF analysis shows that they present a similar alloy composition despite their different typologies. Furthermore, both counters are coated with a thicker orange shellac coating. Similarities can also be pointed out for the other group of counters. DAR1 is composed of two different copper-alloys for the frame and the case: the case composition is similar to the alloy of DAR4 and the frame composition is similar to the alloy of DAR5. Furthermore, the lacquer fluorescence under UV radiation indicates a different type of shellac coating (probably bleached) and a lower average coating thickness than for the first group (DAR2 and DAR3). The observations are compatible with the hypothesis, that these three counters may indeed have been produced at a later period than DAR2 and DAR3.

Additional information is provided by systematic observation under UV radiation of the transparent windows of the counters and additional FTIR analysis on one of them. A synthetic cellulose-based material was used instead of glass for the central window of DAR2. This kind of material was used during a long time in industry before it was replaced by more stable materials. Unfortunately, its use covers a period which is almost identical to the production span of the Darras Company. One hypothesis may be that it was experimented as an alternative to the glass windows when cellulose nitrate films were increasingly developed and used in the photo industry at the end of the nineteenth century. However, in a comparative study including a larger *corpus*, this aspect could be of help for dating the counters as well as the use of different glass types.

This study was carried out entirely on site in the conservation center with only completely non-invasive characterization methods. Despite the limitations of this approach, which does not give access to the stratigraphy of the metal-organic coating system (identification of different layers, especially in the case of the thicker lacquers) or does not allow to characterize the components present in very small amounts in the lacquers, it was possible to identify the type of coating used. It was also possible to group objects according to the metal alloy composition and the specificities of the thickness of the coatings. These findings also highlight the importance of the combination of metal and coating in producing the aesthetic appearance of these objects.

Acknowledgements
The authors wish to acknowledge the Haute École Spécialisée de Suisse Occidentale for funding the LacCA project. We would like to thank Céline Paris and Aline Percot from MONARIS lab for contributing to the FTIR on site analysis campaign. We would also like to thank Aline Michel as well as the staff of the CNAM Museum, especially Rémi Catillon for giving assistance during the analysis campaign. Finally, we would like to thank Miriam Truffa Giachet for the language improvement of the final manuscript.

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RECEIVED: 2023.1.30
REVISED: 2023.2.22
ACCEPTED: 2023.5.19
ONLINE: 2023.7.9