DETECTION OF FORGERIES OF DUTCH AND FLEMISH PAINTINGS OF THE XVII–XVIII CENTURIES BY MEANS OF SPECTROSCOPIC TECHNIQUES

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Results of spectroscopic examinations of three paintings that by the formal and stylistic features can be attributed to the Dutch and Flemish schools of the XVII–XVIIIth centuries were presented. It was supposed that one of the paintings was created by David Teniers the Younger. The signature "L. de Moni" was found on the paint layer of another painting. Inorganic art pigments including those of the XIXth century were identified using laser-induced breakdown spectroscopy. Fourier-transform IR spectroscopy was used to determine the paint binders, which allowed the lower limits of the creation time of these artworks to be defined. Results of a microscopic examination of the stratigraphic structure revealed that the creation technology of these artworks differed from that of Dutch and Flemish artists of the XVII–XVIIIth centuries. Thus, all three investigated paintings were XXth century stylistic forgeries of Dutch and Flemish paintings of the XVI–XVIIIth centuries.

Keywords: laser-induced breakdown spectroscopy, identification of art materials, genre scenes, chrome yellow, falsification.

Introduction. Art works are currently not only cultural heritage objects but also subjects of financial investments. It is well known that the number of collectors increases every year, as does the number of forgeries. According to various sources, today's private collections contain 10 to 60% forgeries. It is noteworthy that forgery is not a recent problem. Many copies of the works of Durer appeared even during his lifetime, placing on them his monograms. As a result, Leopold Wilhelm of Austria acquired 68 Durer forgeries in the middle of the XVIth century, considering them originals [1, 2]. In 1671, antiquarian G. Ulenborch, in whose shop young artists were involved (according to their tastes and abilities) in the mass forgery of Italian art, sold 13 "Italian" pictures to the Elector of Brandenburg [2]. In the XVIIIth century, Dutch genre works were forged [2, 3]; in the XIXth century, they and works of Flemish artists were forged. When the demand for works of new artists appeared, the number of forgeries of French impressionists and post-impressionists increased. They were followed in turn by Matisse, Picasso, and other masters. Fabrication of works of Russian artists, especially Russian avant-garde masters, reached a broad scale at the turn of the XIXth and XXth centuries. It is well known that forgeries were not always started from scratch. The falsified signature of a popular artist was often placed on an authentic work of an unknown artist [4].

Thus, it seems obvious that neither museums nor private collectors will today take the risk of acquiring one work or another without an expert opinion of its authenticity. The task of the expert is to answer correctly the questions, "When?, Where?, Who?, and How?" the work was created. Only comparative and stylistic analysis and the personal experience of the art critic and his intuition were used for this purpose slightly more than 100 years ago. Moreover, the numerous cases of forgery in the art world indicate that such an approach turns out often to be insufficient with respect to masterfully concocted imitations. As an example of such insufficiency, one of the greatest sensations of recent time, attribution of the work "The Disciples at Emmaus," can be cited. Dr. Abraham Bredius, a recognized authority and expert on Dutch art, certified this canvas as a first-class work of Vermeer of Delft [5]. Ten years later, one of the most grandiose scandals in all of art history unraveled. A technical review found that this picture, like 14 other works of erstwhile classical Dutch art of Terborgh, Hals,

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and Vermeer that were "discovered" and sold between 1937 and 1945, were forgeries of the Dutch artist Han van Meegeren [6]. Then, scientific methods for studying works of art began to be used in the largest art museums and science centers in order to increase the quality of the examination. Today, a whole series of scientific methods that are adapted for technical investigations of works of art are known [7]. Results obtained using them have allowed trends in the use of materials and technical methods of creating works characteristic of certain epochs, national and local schools, and individual masters to be established [8]. Obviously, a work can be declared incompatible with its current attribution if the necessary technical signs attributed to one or another time, school, or master are missing.

It is noteworthy that the label "forgery" is often applied to intentional forgeries in addition to works belonging to a school or shop of a known artist or a copy or replication of works of known masters or works of an imitative nature (imitations and stylistics). The last usually refers to works created in imitation of certain items including copying and compiling elements that are interpreted according to the current esthetic and are often completed in the individual artistic manner according to the current technology. The copying and compiling principles are also characteristic of intentional forgeries. Therefore, it is not always possible to draw a clear boundary between an imitation and a forgery. Existing technical signs of an intentional forgery can be considered the presence of a signature, a modern paint layer, and, as a rule, the claim to a famous name in addition to the presence of the most characteristic features of the style and/or technical signs of the handiwork of the forged master [4].

The goal of the present work was to attribute (confirm/deny authorship) several works that could be assigned according to formally stylistic signs to the Dutch and Flemish schools of the XVII–VIIIth centuries based on results from studies of art materials using laser-induced breakdown spectroscopy and IR microscopy.

Studied Works. The work "Card Players" (Fig. 1a) was created on canvas $(32.5 \times 45.5 \text{ cm})$. The signature "D. Teniers" found on the stretcher suggested that the author of this work could be the Flemish artist David Teniers (1610–1690). Traces of the influence of Flemish masters of the first third of the XVIIth century and his contemporaries, including the known master of everyday scenes Adrian Brouwer (1605/06–1638), are distinguishable in the works of Teniers the Younger [9]. Such works as "Card Players in an Inn" (XVIIth century, private collection) (Fig. 1b), "Peasants Playing Dice" (ca. 1640, State Hermitage, St. Petersburg, RF) [9], "Figures Gambling in a Tavern" (ca. 1640, private collection), "Tavern Scene" (1658, National Gallery of Art, Washington, USA), etc. can be cited as examples. It is noteworthy that David Teniers repeated characteristically certain interior details in different works.

The work "Pumpkin Trading" (Fig. 2a) was created on wood $(38.0 \times 20.5 \text{ cm})$. The signature "L. de Moni" can easily be read in the lower left corner. This would suggest the involvement of the Dutch artist Louis de Moni (1698–1771) in the creation of this work. There is evidence indicating that Louis de Moni was a student of Jan van Kessel [10]. The principal themes of his subjects were portraits and genre scenes. It is noteworthy that the subject of the studied work "Pumpkin Trading" is extremely reminiscent of another work of de Moni, "Hunter Conversing with a Stove" (1753, private collection, Fig. 2b).

The work in which a genre scene on a village theme is portrayed (Fig. 3) was also created on wood $(37.5 \times 49.3 \text{ cm})$. No signature was found on the paint layer or the reverse. Nevertheless, this work according to formally stylistic signs can also be attributed to the Flemish or Dutch art school.

Experimental. The elemental compositions of the art materials were studied without taking samples using a portable version of a laser-induced breakdown spectrometer. The operating parameters of the double-pulsed LS-2131DM-LPS YAG:Nd³⁺-laser (Lotis TII, Belarus) were emission wavelength 1064 nm, pulse energy ~7 mJ, length of each pulse at half-height ~10–12 ns, laser emission divergence ≤ 1.5 mrad, and delay between pulses 1 µs.

The apparatus was equipped with a triple telescope that enabled the diffraction size of a point at the focusing system exit to be measured. The emission was focused on the paint layer surface by a lens with focal distance 100 mm. Plasma emission was collected at an angle of 30° to the torch axis using an achromatic quartz objective with focal distance 25 mm and was focused on the end of a quartz optical fiber of diameter 400 μ m and aperture 0.22. The second end of the optical fiber was attached to the input slit (35 μ m width) of a spectrograph.

Emission spectra were recorded in the range 270–390 nm using an MS2001i polychromator (Solar TII, Belarus) with diffraction grating 1200 lines/mm and relative aperture 1/3.6 that was equipped with a multi-channel analyzer based on a Hamamatsu S11071-1106 back-thinned type CCD area image sensor operating is line-sum mode. Use of a sensitive monochromator with a highly sensitive matrix enabled emission spectra of paint layers to be recorded reliably using low-energy laser pulses and the volume of the vaporized material to be minimized. The low energy of the laser pulses also decreased the optimum (from the viewpoint of increasing the spectral intensity) interpulse time (~1 μ s in our experiment) relative to those reported (~10 μ s) [11].



Fig. 1. "Card Players" supposedly by David Teniers the Younger (a) and "Card Players in an Inn" by David Teniers the Younger (b).



Fig. 2. "Pumpkin Trading" supposedly by Louis de Moni (a) and "Hunter Conversing with a Stove" by Louis de Moni (b).



Fig. 3. Genre scene on a village theme by an unknown artist supposedly of the Dutch or Flemish school.

TABLE 1.	Microscopy	Study of	he Stratigraphic	Structure o	f Art Works
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Picture	Insulating glue layer (brown), µm	Primer (yellowish- white), µm	Imprimatura [*] (white)	Paint layer, μm	Lacquer
	Leather glue	Chalk with added yellow ochre and lead whites	Lead whites		
"Card Players"	47	128–130	+	40-42	+
"Pumpkin Trading"	17–19	33–35	+	28–30 (undercoat) 10–12 (glaze)	+
Genre scene on a village these	20–22	40-42	-	30–32	+

^{*}Imprimatura (Ital., first paint coat), surface color tone of already prepared primer used in practice by Italian artists from the XVIth century.

The elemental compositions of the art materials were studied after luminescent analysis in UV radiation in order to avoid the possibility of studying restored touch-ups. For this, the surface of the work was irradiated by a VSB-2 high-frequency electron-free UV lamp filled with tin vapor.

IR absorption spectra of microscopic fragments of the paint layer were recorded using a Nexus IR-Fourier spectrometer (Thermo Nicolet, USA) equipped with a Continuum IR-microscope (Thermo Fisher Scientific, USA) in the spectral range 4000–650 cm⁻¹ with resolution 2 cm⁻¹. Furthermore, the stratigraphic construction of the works was studied using a binocular microscope. For this, microscopic fragments of the work that were located next to losses of the paint layer were taken and prepared as microsections containing all structural elements of the works.

Results and Discussion. Milky blue emission of aged lacquer film was observed and small touch-ups appeared as dark spots upon UV irradiation. Portions of the paint layer on which touch-ups were observed were excluded from possible ablation regions during the elemental analysis of the art pigments using laser-induced breakdown spectroscopy. Furthermore, it was found using luminescent analysis in UV radiation that the signature "L. de Moni" that was observed on one of the works was contemporary with the paint layer on which it was written.

The microscopy study of the painting stratigraphic structure (Table 1) and laser-induced breakdown spectroscopic analysis of the elemental composition of the art materials in "Card Players" supposedly by David Teniers (Fig. 4) led to the conclusion that the white scarf on the woman's head in the center consisted of lead whites $[2PbCO_3 \cdot Pb(OH)_2]$. Lines of Fe, Al, Ca, and Mg that were identified in the spectrum probably appeared in the emission spectrum of the primer (spectrum 1). The yellow shirt of the young man sitting on the stool was done with chrome yellow (PbCrO₄) possibly with added lead whites (spectrum 2). The red beret of the young man standing on the left included cinnabar (HgS) mixed with lead whites and red ochre (Fe₂O₃ + clayey minerals) (spectrum 3). The red paint used to portray the clay pot on the floor on the right consisted of a brown oxyhydroxy pigment based on Fe (ochre, umber, etc.), lead whites, and probably ivory black [Ca₃(PO₄)₂ + CaCO₃ + C] (spectrum 4). The very strong Ca lines suggested that the black hat of the young man sitting on the stool was ivory black (spectrum 5); the Fe and Al lines, that the green pigment used to draw the green skirt of the woman in the center was green earths (glauconite), the elemental composition of which was characterized by Fe³⁺, Fe²⁺, Al, Mg, K, and Si (spectrum 6). The red shirt of the woman sitting on the hearth was a mixture of cinnabar, red ochre, and lead whites (spectrum 7). The primer was based on chalk with added yellow ochre and lead whites (spectrum 8). Thus, the pallet of inorganic pigments used to create "Card Players" supposedly by David Teniers included red and yellow ochres, green earths (glauconite), brown Fe-containing oxyhydroxy pigments, cinnabar, ivory black, lead whites, and chrome yellow.



Fig. 4. Emission spectra of materials corresponding to Fig. 1a: white scarf on the woman's head (1), yellow shirt of the young man sitting on the stool (2), red beret of the young man standing on the left (3), clay pot on the floor on the right (4), black hat of the young man sitting on the stool (5), green skirt of the woman (6), red shirt of the woman sitting on the hearth (7), primer (8).

Wood was used as the base in both the work by the unknown artist and the work with the signature "L. de Moni". The direction of the wood fibers corresponded in both instances to the orientation of the works. The nature of the treatment of the board back side of both works was the same. Moreover, the compositions of the materials that were deposited on the end and reverse of the bases in order to prevent bacteriological destruction turned out to be identical according to laser-induced breakdown spectroscopy. The priming methods of the works also exhibited several common signs, i.e., the boards were glued (probably leather glue) and primed (chalk primer with added yellow ochre and lead whites). White imprimatura of lead whites covered the primer in the work supposedly by Louis de Moni. According to research of technical features of Dutch paintings [12, 13], a layer of lead whites was used as imprimatura to create works on dark primers. Imprimatura of primarily brown and gray tones was used on light or white primers. Thus, it was concluded that the bases of the studied works were prepared in approximately the same timeframe. However, the work supposedly by de Moni was created with aberrations from the Dutch art school. Serious differences were observed in the construction of the paint layer. Whereas the painting in the genre scene on a village theme was constructed using only a single paint layer and the half-shadows, mixed lights and shadows, and shades were mixed directly on the pallet, an optical mixing effect and mechanical mixing were found in the work "Pumpkin Trading".

Figure 5 shows breakdown spectra that led to the conclusion that the pallet of the work with the signature "L. de Moni" included the art pigments red and yellow ochres, brown oxyhydroxy pigment (ochre, umber), green earth, cinnabar, ivory black, Berlin blue, and lead whites. Laser-induced breakdown spectroscopy of the work without a signature (Fig. 6) identified cinnabar, green earth (glauconite), brown oxyhydroxy pigment, ivory black, chrome yellow, and lead whites.

Chrome yellow and Berlin blue were most interesting with respect to dating the studied works. Use of the other identified pigments was prominent in any art epoch. Chrome yellow, which was observed in the works supposedly by David Teniers and the one without a signature, has been used in art since 1816. This defined the lower time limit for the creation of these works to no earlier than the first quarter of the XIXth century. This automatically categorized these works as stylistic forgeries.



Fig. 5. Emission spectra of materials corresponding to Fig. 2a: white cap on the woman's head (1), red clothes of the woman (2), woman's neck (3), yellow shawl of the woman (4), sky (5), brown basket with pumpkins (6), pumpkin (7), table leg (8), primer (9).



Fig. 6. Emission spectra of materials corresponding to Fig. 3: white cloud (1), sky (2), smokestack (3), leaden cloud (4), yellowish-green leaf (5), red feather in the man's hat (6), green leaf (7), tail of the rufous horse (8), primer (9).



Fig. 7. IR absorption spectra of microscopic fragments of paint layer of the paintings "Card Players" (a), "Pumpkin Trading" (b), and genre scene on a village theme (c).

With respect to the work supposedly by Louis de Moni, the Berlin blue that was found among the pigments was discovered in 1704. This defined the lower time limit for the creation of this work to no earlier than the start of the XVIIIth century. This was fully compatible with the lifetime of the artist. However, as noted above, this work was created during the same time period as the genre scene on a village theme. Substantial aberrations from the technology for creating works of the Dutch art school were observed in its stratigraphic structure. Therefore, it was concluded that "Pumpkin Trading" was also a stylistic forgery of Louis de Moni that was created no earlier than the XIXth century.

The hypothesis that all three works were created at the same time was also confirmed by IR spectroscopy. IR absorption spectra of microscopic fragments of the paint layer of the studied works exhibited bands in the ranges 3280, 3060, 2928, 2849, 1674, and 1560 cm⁻¹ (Fig. 7). Interpretation of the recorded spectra led to the conclusion that the absorption band at 3280 cm⁻¹ was due to stretching vibrations of O–H groups involved in intermolecular H-bonds; at 3060, to secondary amide N–H bending vibrations; at 2928 and 2849, to symmetric and asymmetric stretching vibrations of C–H bonds of methyl (CH₃–) and methylene (–CH₂–) groups; at 1674, an amide I band, which is a characteristic sign of primary, secondary, and tertiary amides due to C–N and N–R carbonyl bonds; at 1550, an amide II band for N–H bending vibrations [14, 15, 16]. Thus, the paint binders in the studied works were synthetic polyamides, which shifted the lower time limit and defined the creation time of these works to no earlier than the start of the XXth century.

Conclusions. Modern highly sensitive methods of atomic and molecular analysis enabled the compositions of organic and inorganic art materials to be identified and increased the quality of technical examination of the art works.

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