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Necessity and Use of a Multilayer Test Object Based on an Anonymous 19th Century Copy of a Painting by Ivan Konstantinovich Aivazovsky (1817–1900)

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Abstract: The emergence of new research methods in the field of heritage science always raises a large number of questions related to their applicability, reproducibility of results on similar objects, complementarity with other methods, and development of new research methods. To solve such problems, it is necessary to have a test object with the required structure. A multilayer test object based on a fragment of a copy of a 19th century painting by I.K. Aivazovsky was created and described. Analytical studies of the colourful layers were carried out on a Fourier-transform infrared (FT-IR) spectrometer with an attenuated total reflectance (ATR) attachment in single-reflection mode with a diamond crystal. As part of the use of one research method, differences between painting layers of the 19th and 20th centuries were revealed. Results are presented in the IR graphs. The aim of the work was to identify the characteristics of the pictorial layers inherent in the copy of the painting by I.K. Aivazovsky. This will improve the methodology of technological expertise of the I.K. Aivazovsky's artworks.

Keywords: test object; oil painting copy; I.K. Aivazovsky; FT-IR spectroscopy

1. Introduction

As objects of museum collections and cultural heritage objects, 19th century paintings require professional storage and have a special specificity of study. The multilayer structure for most objects, coupled with restoration interventions, defects and losses, significantly complicates the process of conservation and research work in restoration centres [1]. The classic solution to such a complex problem is the organisation of well-coordinated work of specialists from various fields of scientific knowledge—art historians, physicists, chemists, restorers, etc. In essence, this is the narrow meaning of the concept of heritage science [2]. Being at the intersection of sciences, questions of the applicability of modern research methods, their complementarity, the need for sampling in specific cases, as well as the development of a methodological approach for analysing a specific painting school, as in working with a copy of Raphael from the 16th century, are particularly acute [3].

Classical research methods available and used in large museums can no longer provide the increased needs of researchers. These include radiography, X-ray diffraction, UV luminescence, IR reflectography, and IR and Raman spectroscopy, used in the classical study of Édouard Vuillard's painting *Interior, Mother and Sister of the Artist* and partially in the report of the Italian mobile laboratory [4,5]. Currently, researchers have access to a whole range of invasive and non-invasive methods for the study of paintings, such as terahertz tomography and spectroscopy, optical coherence tomography (OCT), laser-induced breakdown spectroscopy (LIBS), as well as new applications of "old" methods and various combinations of several techniques in order to find complementary pairs [6–9]. The study of Liu Kang's canvases, which aimed to give a general idea of the painting style, pictorial materials and foundations from the collection, which includes 55 artworks by the National Gallery of Singapore and the Liu family, is limited to express methods [10], while the study of Vermeer's *Girl with a Pearl Earring* includes a large number of non-invasive and portable methods [11].

To identify the composition of binders and pigments of paintings, researchers still use invasive methods that are based on taking micro-samples from the layer of interest on the object. Icon painting has historically been considered one of the most difficult objects of research, due to the huge number of unprofessional interventions in the process of existence—this explains the need for sampling [12]. Classical invasive research methods include FT-IR spectroscopy [13] and Raman spectroscopy [14], which currently are also implemented in portable non-invasive versions, but have some drawbacks [15,16]. Invasive methods violate the integrity of paintings, but provide data necessary for a successful conservation for the restoration of the object. They can also expand the understanding of the art historian and the curator of the artistic value of the object of study. One of the variants of standard operating procedures (SOP) is proposed in the work on the oil painting on canvas *St. Girolamo Nello Studio* by Nicolo Buttafoco [17].

For the development and testing of new methods for the study of museum collections and cultural heritage objects, it is customary to use test objects that simulate the internal structure, chemical composition and optical properties of real objects in the specific range of electromagnetic waves used for research. Pure pigments without any binder serve as the simplest test objects on which reflection and transmission of electromagnetic waves of various ranges are investigated. The experiment is complicated by adding a binder to the dry pigment (oil, glue, varnish, resin, wax, etc.), in order to bring its composition and properties as close as possible to the components or colour of a painting [18]. The next step is to apply a pigment with a binder on various substrates that mimic the support of works of art (canvas, wood, cardboard, metal, etc.) [19,20]. According to these principles, a complex structure of a multilayered test object is created as close as possible to real art objects: the support, background, coloured layers, and varnish layers. In addition, damage and traces of restorations can be recreated in the test object—fractures of the support and priming, cracks in the lacquer and paint layers, internal cavities containing air, water, glue, and similar defects—that are planned to be detected as a result of an examination of real works of art.

Expert and stylistic studies of Aivazovsky's painting are especially relevant. Firstly, this is due to the breadth of the artist's creative heritage: according to him, he created more than six thousand paintings. All of them are distributed among museums and private collections around the world. At the same time, it is impossible to take into account all the work, which creates a wide scope for forgers. Secondly, the artist's painting is extremely diverse and captures different genres: landscapes, portraits, and historical subjects. Without the data from technical and technological research on the structure and manner of Aivazovsky, it would be difficult for us to believe that an artist can work in such different techniques. Thirdly, the relevance of Aivazovsky's scientific expertise is also confirmed by his popularity. In a study by the staff of the Aivazovsky National Art Gallery in Feodosiya, Crimea, it was noted that the artist's works began to be forged during his lifetime. His works at Russian and foreign auctions are estimated at tens and hundreds of thousands of US dollars. The most expensive paintings known to us—*View of Constantinople with the Nusretri Mosque* and *Sunset over the Golden Horn* (1866, canvas, oil, 120 × 167)—were sold in June 1995 and October 1997 in London at Sotheby's auction, respectively, for 520 and 605 thousand US dollars. In V.D. Solovyov's reference book, the price level of I.K. Aivazovsky's painting is determined to be 10 (out of a possible 12).

This article is devoted to the spectroscopic study of a test object, created by the painting conservators of the State Russian Museum. It was based on a cut-off fragment of a copy of a 19th-century painting by I.K. Aivazovsky. The signatures of the restorers were applied to the colourful side (reverse side) with different paints and covered with an opaque layer of paint. On the side of the canvas (front side), a pencil drawing and a whitewash sketch of a man's head were applied. Such a complex structure was necessary for the development of research methodology using infrared reflectography (IRR) in the past. The second section describes the layered structure of the test object and the history of its creation. In the third section, we give a detailed analysis of the composition of pigments and binders of the front and reverse sides of the test object. To do this, micro-samples were selected and examined using FT-IR spectroscopy.

A preliminary study of the materials of the paint layers is necessary for the correct interpretation of the results of traditional (X-ray radiography, infrared reflectography, UV luminescence) and modern (THz-TDS, OCT) visualization systems and subsequent comparison.

2. History of the Test-Object Creation

A complex test object was made in the Department of Technological Research of the State Russian Museum together with the painting conservators. It simulates the structure of real objects with typical conservation and restoration tasks that museum specialists must solve. As a basis, a fragment of a large painting was used, which is an anonymous copy of a painting by Ivan Konstantinovich Aivazovsky and kept in a private collection. The copy was made by a contemporary of I.K. Aivazovsky, probably taking into account the technical features of the master. Specialists from the State Russian Museum established that the artwork is a copy of the late 19th century painting by Ivan Aivazovsky—*A Bird's-Eye View of the Prince Islands near Constantinople on the Marmara Sea*—created in 1846 and stored in a museum in Ustyuzhna (Vologda region, Russia). This copy has no artistic or material value. For this reason, as well as due to the breakthroughs of the canvas in the lower left corner, after the examination, the owner allowed to cut off a fragment measuring 21 × 22 cm to create a test object (Figure 1).

Figure 1. A Bird's-Eye View of the Prince Islands near Constantinople on the Marmara Sea. An anonymous 19th century copy of a painting by Ivan Konstantinovich Aivazovsky. Oil on canvas, 112 × 157 cm.

The condition and absence of late conservation interventions were taken into account for choosing the fragment of the painting. For the upcoming experiments, it was important to create an object where priming and paint layers would be made, with historical lead white ground having a high X-ray density.

On the empty side of the canvas, the conservators applied a red-brown primer and realised a preparatory drawing with a graphite pencil of a man's head, over which a white sketch was applied (Figure 2a) in 2000. Ten years later, on the reverse of the canvas, the painting conservators from the Russian Museum wrote their names and surnames with oil paints of different colours. When the signatures dried, they were covered with a thick layer of brown or green paint to prevent the readability of the inscriptions by the relief in oblique light (Figure 2b).

Figure 2. Image of the **front side** (**a**) of the test object with the image of a man's head and the **reverse side** (**b**) of the test object with signatures applied under brown and green covers. Red dots and numbers correspond to sampling locations for the identification of primers and paint pigments on the test object. Discussion of the results obtained for the identification of primers and paint pigments on the test object is in Section 3.

At the end of the work, the test object was not subjected to artificial drying, and importantly, it was not covered by any varnish layers on either side. The object under study is a multi-layered test object on canvas with paint layers of a human head on the front of the test object and paint layers of the 19th century with inscriptions and covering layers of the 21st century on the reverse side of the test object. Images of the front and back of the test object are shown in Figure 2a,b. Sampling locations are marked with red dots and numbers. The stratigraphy of the test object may be represented by the sketch with different layers (Figure 3).

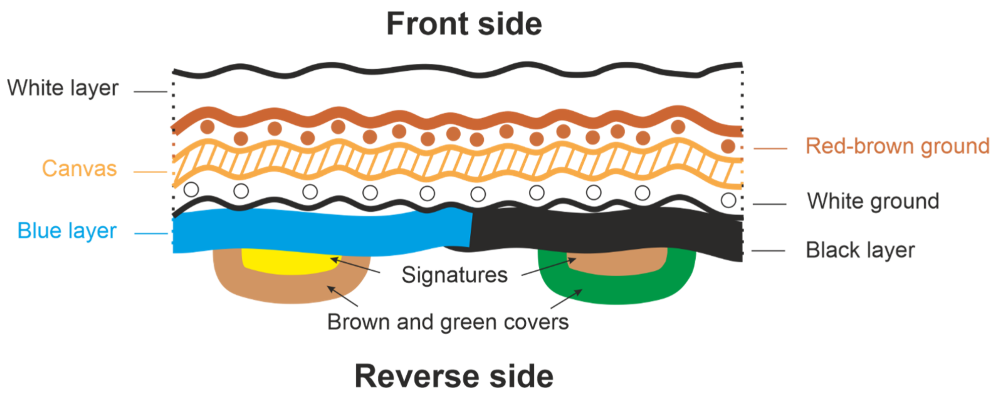

Figure 3. Test object schematic stratigraphy.

Initially, at the time of the creation of the test object, other goals were set for the researchers. It was necessary to test the capabilities of the Osiris infrared reflectography (IRR) camera when examining signatures and preparatory drawings under opaque layers of paints, and, accordingly, invisible during inspection. Therefore, some of the signatures and the drawing on the front were made using carbon-containing pigments (visible -n Figure 4) and the rest in classic colours of red (red ochre), blue (ultramarine), yellow (lemon ochre), and brown (umber) (Figure 4).

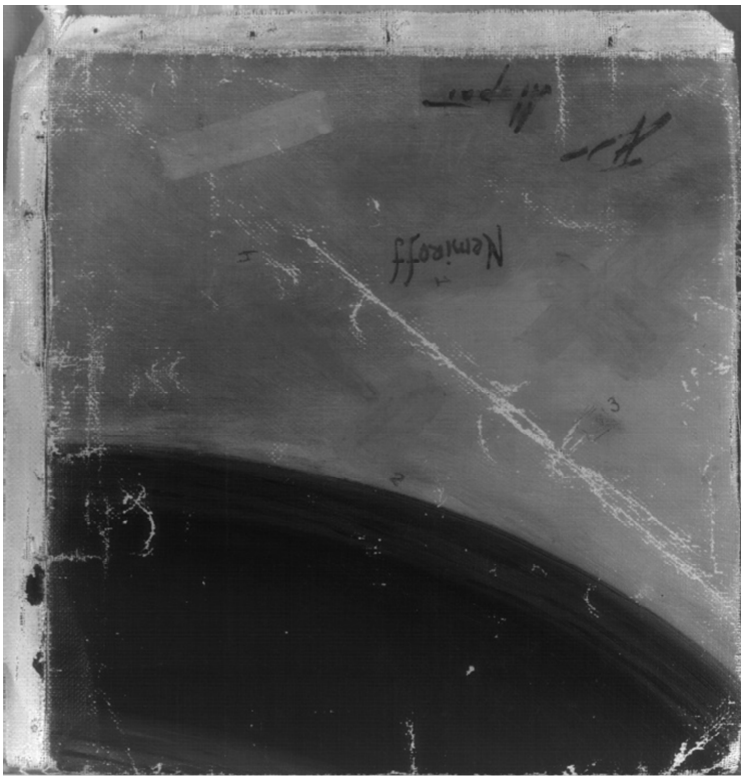

Figure 4. Test object IRR photo.

3. Identification of Binders and Pigments on the Test Object by FTIR Spectroscopy

In order to determine the composition of primings and pigments on the test object, FT-IR spectroscopy (TENSOR 37, Bruker) was used. The spectra were recorded in an ATR (MVP-Pro™, Harrick) mode in the range 4000–380 cm^{-1} with a spectral resolution of 4 cm^{-1}. Sample preparation was carried out by crushing the sample and placing it on the surface of a diamond crystal. Single-point ATR measurements were performed by recording a total of 128 scans and averaging the resulting interferograms. All spectra were processed using extended ATR correction (1 reflection, angle of incidence 45°, average refractive index 1.5). In some cases, uninformative regions of the spectra (2400–1850 cm^{-1}) were removed and baselines corrected. For identification of substances, the obtained spectra were compared with the library data in the FT-IR spectrometer.

3.1. Front Side of the Test Object

First of all, the study of pigments, priming and binders was carried out from the front side of the test object. It consists of brown ground (Figure 5 (2)), on top of which is applied a pencil drawing of a male head, and typical academic whitewash painting (Figure 5 (1)).

The main components of the emulsion primer are iron hydroxide ($Fe_2O_3 \times nH_2O$), evidently sienna, kaolin, and quartz. It is worth noting that priming of this type was widespread in etude academic painting of the 19th century. Emulsion primers are opaque white, filler, and a mixture of two types of binders—oil and protein. The presence of the oil component is confirmed by intense absorption bands of asymmetric $\nu_{as}(-CH_2-)$ and symmetric $\nu_s(-CH_2-)$ stretching vibrations of the methylene group at 2919 cm^{-1} and 2850 cm^{-1}, stretching vibrations of the carbonyl group $\nu(C=O)$ at 1736 cm^{-1} and stretching vibrations of the ester bond $\nu(C-O)$ at 1160 cm^{-1} [21]. A strong shift of the carbonyl absorption band towards lower frequencies—1711 cm^{-1} (Figure 4 (2))—is worth noting. This is due to the processes of hydrolysis of triglycerides and the appearance of free fatty acids, which are most pronounced in the presence of iron-containing pigments [21,22].

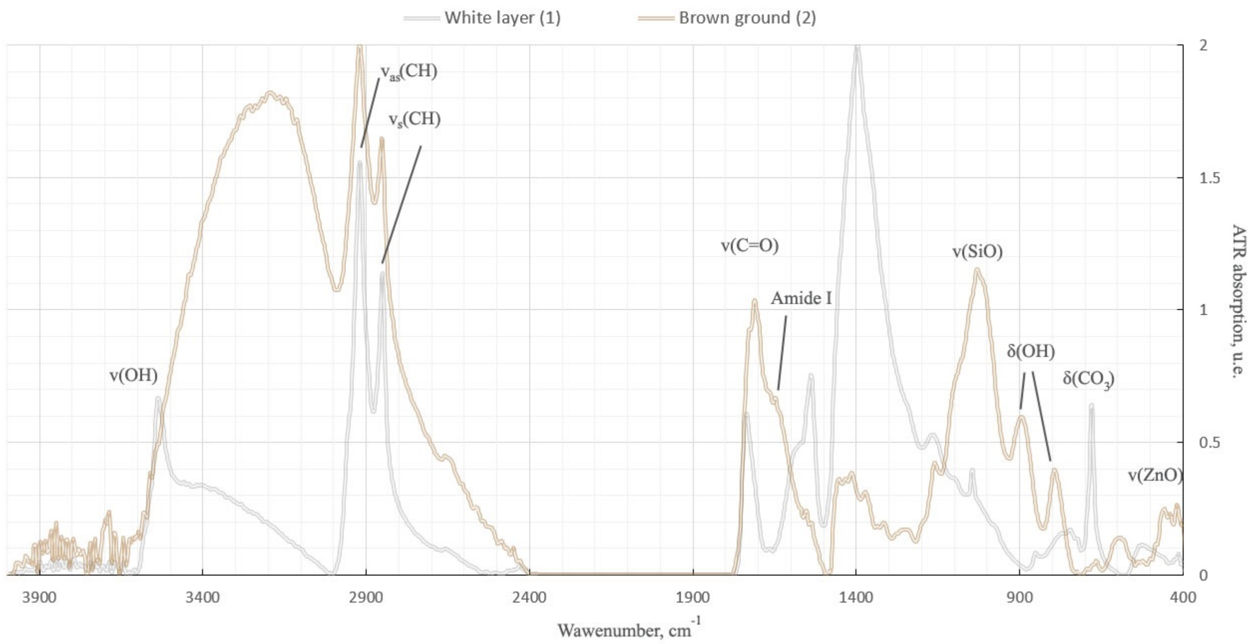

Figure 5. ATR-FTIR absorption spectra of two paint samples taken from the front side of the test object: (1) grey spectrum—white layer; (2) red-brown spectrum—red-brown ground.

The protein in this case appears on the spectrum as the main absorption bands of amide I and amide II. Amides are characterized by the presence of two intense absorption bands: amide I at a frequency of 1650 cm^{-1} (mixed stretching absorption band $\nu(C=O)$

and deformation out-of-plane vibration $\delta(N-H)$) and amide II at a frequency of 1550 cm^{-1} (mixed absorption band of the stretching vibration $\nu(C-N)$ and bending vibration $\delta(N-H)$) [23]. On the spectrum, we do not see a typical picture with separate absorption peaks of amides, because the presence of water in the crystal lattice of an iron-containing pigment absorbs in the region of 1625 cm^{-1} [21,24].

The spectrum does not contain white or typical fillers of modern factory primers, which indicates a manual primer by the author. Siena ($Fe_2O_3 \times nH_2O$), was used as a colouring agent. The main features of iron hydroxide in the IR spectrum can be attributed to the absorption bands of out-of-plane δ(OH) and planar δ(OH) bending vibrations of the hydroxyl group at 893 cm^{-1} and 788 cm^{-1} [24,25], respectively. Also, on the red-brown IR spectrum, kaolin was detected, determined by the absorption bands of the stretching vibrations of the hydroxyl group (ν(OH)) 3696/3651/3621 cm^{-1}, the stretching vibration of the bond ν(Si-O-Si) at 1033 cm^{-1}, and quartz, discovered due to the presence of the vibration of the ν(Si-O), bond, detected as a shoulder on a wide kaolin silicate band and deformation vibration above 450 cm^{-1} [26,27].

The whitewash of the male head, according to the IR spectrum, corresponds to the composition of lead–zinc white ($2(PbCO_3) \times Pb(OH)_2$; ZnO). Currently, lead white is not produced on an industrial scale due to the high toxicity of production. In the mid-infrared range, the grey IR spectrum (Figure 5 (1)) shows the main absorption bands of the lead components—the stretching vibrations of the hydroxyl group $\nu(OH)$ at 3537 cm^{-1}, asymmetric $\nu_{as}(CO_3^{-2})$ and symmetric $\nu_s\left(CO_3^{-2}\right)$ stretching vibrations of the carbonyl group at 1396 cm^{-1} and 1045 cm^{-1}, and out-of-plane $\delta\left(CO_3^{-2}\right)$ and planar $\delta\left(CO_3^{-2}\right)$ bending vibrations of the carbonyl group at 851 cm^{-1} and 679 cm^{-1} [28]. We also note in the low-frequency infrared region of the grey IR spectrum of white paint the absorption bands of zinc. They corresponded to a broad peak at 525 cm^{-1}—stretching vibrations of zinc oxide $\nu(Zn=O)$ [29]. The spectrum contains metal salts of carboxylic acids—the region of the spectrum in the range of wave numbers 1650–1500 cm^{-1}. Because in the ink layer there may be two types of white capable of forming carboxylates, it is not possible to distinguish between them. The peak at 1538 cm^{-1} is the asymmetric stretching vibration of zinc or lead stearate $\nu_{as}(COO–)$ [29,30]. Additionally, the binder, which was oil, was determined from the IR spectrum of the white paint.

3.2. Reverse Side of the Test Object

FT-IR spectra of microsamples from the reverse of the test object brought to light that the painting materials of the 19th century have the characteristic features corresponding to their period of time. The layers are arranged in the following order: lead–zinc oil primer, on which lies a blue and black ground, consisting of a mixture of lead–zinc white, sienna, Prussian blue with an oil binder. On top of the blue and black layers, the conservators applied their signatures with different colours and covered them with an opaque brown or green paint. It is difficult to determine the material with which the conservators applied the signatures due to the thinness of these layers.

Infrared spectra of the layers described above are presented in Figure 6. White primer (Figure 6 (3)) consists of lead–zinc white mixed with an oil binder. It is worth noting that the differences in the intensities of the main peaks of lead–zinc white, as well as the wide band of water vibrations in the high-frequency region of the spectrum of the painting of the 19th century, indicate the non-simultaneous application of these layers.

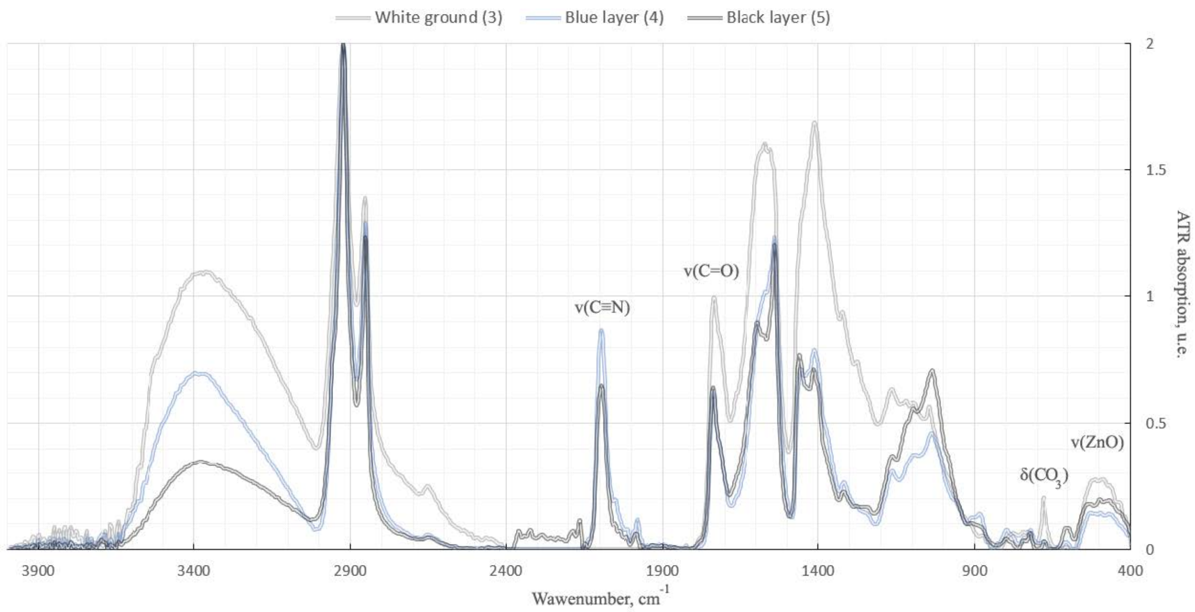

Figure 6. ATR-FTIR absorption spectra of 3 paint samples, taken from the reverse of the test object: (3) grey spectrum—white ground; (4) blue spectrum—blue layer; (5) black spectrum—black layer.

The blue background was applied with Prussian blue (Figure 6 (4)), which is iron hexacyanoferrate ($Fe_4[Fe(CN)_6]_3$ x $Me_4Fe(CN)_6$ x nH_2O). The main absorption band of Prussian blue in the spectrum can be seen at 2095 cm^{-1}, due to the presence of the stretching vibration of the cyanide group ν(-C≡N-) [31]. Note that in a large study in 2002, the main base blue pigment was cobalt aluminate [32]. The second background paint may be a black carbon-containing paint (Figure 6 (5)) due to the absence of pronounced absorption bands other than the blue layer [33].

The conservators applied signatures to the blue layer of paint and covered it with dense layers of various paints: brown (6) and green (7) (Figure 7).

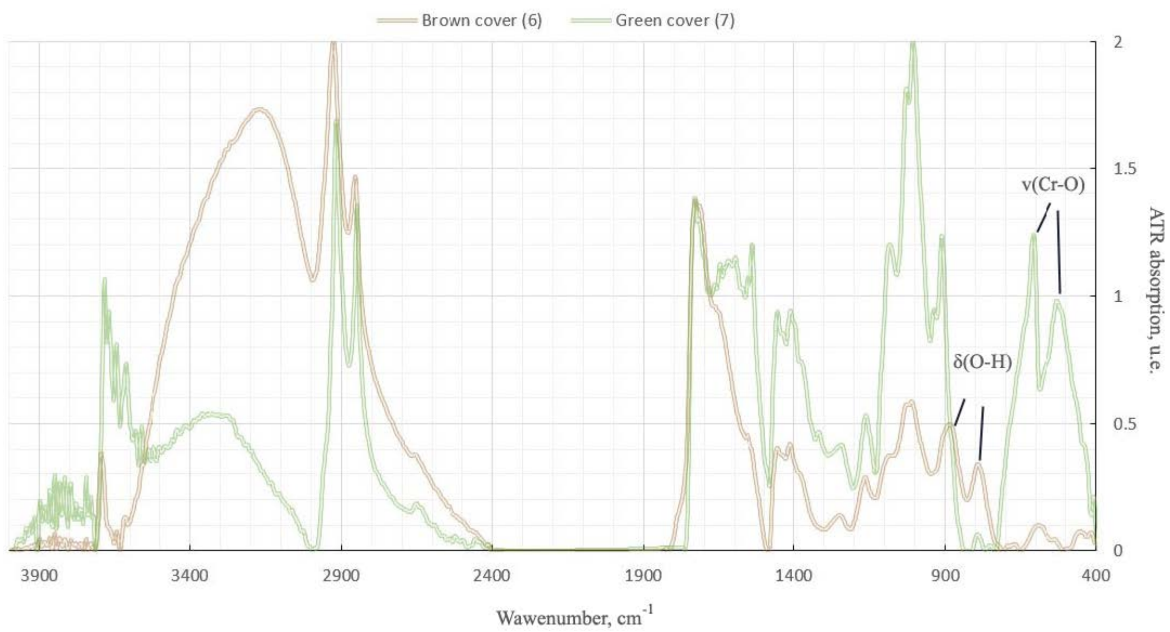

Figure 7. ATR-FTIR absorption spectra of 2 paint samples taken from the reverse of the test object: (6) brown spectrum—brown cover; (7) green spectrum—green cover.

The FTIR spectrum of the brown paint coincides with the spectrum of siena on a tempera binder from library data [34]. In turn, the FTIR spectrum of the green paint (Figure 7 (7)) coincides with the spectrum of chromium oxide mixed with zinc white. Absorption bands of chromium oxide (Cr_2O_3) appear in the long-wavelength mid-IR region—stretching vibrations of chromium oxide ν(Cr-O) at 609 cm^{-1} and 528 cm^{-1} [35,36].

4. Conclusions

Using the example of the study of a test object with a complex composition made by the superimposition of several coloured layers put at different periods of time, it was shown that the FTIR method can be successfully used for the analysis of pigments and binders for various purposes. The multilayered structure of the object and the presence of paint layers on both sides of the canvas imitates real paintings of the late 19th–early 20th century. The presence of records applied by conservators on the reverse of the test object allows us to work out modern methods and techniques in practice to differentiate the author's layers and the later interventions, as well as to identify hidden signatures.

The differences in the white from the front and reverse sides of the test object were manifested in the difference in the ratio of the absorption intensity of the main peaks of lead–zinc white on the infrared spectrum. There were also differences in the absorption of hydroxyl groups ν(OH), associated with the drying process of the oil binder and the formation of new products. This fact gives reason to believe that the time of creation of these layers is different. The main pigments and binders of the coloured layers on both sides of the test object were determined: lead–zinc white $2(PbCO_3)$ x $Pb(OH)_2$—ZnO, siena Fe_2O_3 x nH_2O, Prussian blue $Fe_4[Fe(CN)_6]_3$ x $Me_4Fe(CN)_6$ x nH_2O, and chrome green Cr_2O_3. All the discovered pigments were available to the masters of the 19th century and are characteristic of easel painting. However, when studying the reference canvases of I.K. Aivazovsky, a set of typical paints for him was determined that did not match those found on the test object. This gives an understanding of the secondary nature of the expert painting, as well as the fact that the copy of the painting by I.K. Aivazovsky is not an author's repetition.

Further work with the test object will be devoted to modern visualisation methods and evaluation of their capabilities in identifying hidden and poorly readable inscriptions. THz and optical coherence tomography (OCT) are gradually entering the complex of methods for studying works of art, expanding the possibilities of studying monumental paintings and multilayer objects. In this regard, the development of a methodology for conducting research on a test object, comparing the data obtained with classical methods (radiography, IR reflectography (IRR), UV luminescence, X-ray tomography, etc.) is a necessary stage for the restoration and preservation of works of art.

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