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Non-Invasive Study of Pigment Palette Used by Olga Boznańska Investigated with Analytical Imaging, XRF, and FTIR Spectroscopy

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Abstract: The scientific examination and comparative investigation of pigments are fundamental for further understanding and analysis of historic and artistic works, and particularly useful for conservators. In fine art authentication, investigations are strongly focused on the identification of the painting materials used by the author. This study is focused on the use of non-invasive analytical techniques to increase the knowledge of the painting technique of Olga Boznańska. The aim of this study was to assess the technology, painting technique, and materials used by Olga Boznańska. The pallets, tubes with the paints, and several oil paintings were studied. For each painting, a series of images were recorded using various ranges of electromagnetic radiation, including near-infrared, visible light, ultraviolet, and X-rays. In order to characterize the pigments present in the paint layer, measurements of the elemental composition by X-ray fluorescence spectroscopy (XRF) were carried out. The ground layers and paints were measured with infrared spectroscopy (FTIR). This allowed us to identify the artist's painting technique and determine how she executed her painting, how she applied the paints, and what pigments she used.

Keywords: μXRF; FTIR; artist palette; Olga Boznańska; pigments

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1. Introduction

The initiation of research into Olga Boznańska's legacy to learn more about the way she painted and the materials she used was closely linked to a monographic exhibition of the artist's works held in 2014 at the National Museum in Krakow. Very rarely do we have a situation where an artist's painting materials and paint tubes, painting palettes, and the paintings themselves are left as a legacy. As all of these objects are held in the collection of the National Museum in Krakow, it was decided to carry out a full study using only non-invasive techniques.

Olga Boznańska (1865–1940), is considered one of the greatest European female artists. She showed her paintings at prestigious exhibitions, salons, and renowned art galleries [1]. She worked in Munich and Paris. Her works have been presented at many exhibitions in Europe and the United States. She was honored with numerous awards, including a gold medal at the Munich International Exhibition (1905), the French Legion of Honour (1912), and the Grand Prix at the Expo Exhibition in Paris (1937).

Olga Boznańska is considered to be the most outstanding Polish painter of the late 19th century, working in the Realism and Impressionism movements. Boznańska's art was greatly influenced by the refined paintings of James McNeill Whistler and the free style of painting by Edouard Manet, artists combining realism with impressionism. The artist's paintings are characterized by a lightness in her handling of colors. During her Munich period, she defined the range of her palette, narrowing it down to dark colors dominated by browns, greens, grays, and black, with white and pink serving as counterpoints.

She is known as an excellent portraitist, but also a painter of still lifes, interior studies, and landscapes. The artist's painting legacy includes many masterpieces of portrait art. The original portrait formula was developed by Boznańska, in which the artist focused on the model's face, rendering the state of his or her psyche, the mood of the moment, and character traits. The painter's best-known works include *Girl with Chrysanthemums* and *Flower Girls*.

In recent years, scientific research into works of art has become increasingly widespread, allowing the materials and techniques used by artists to be characterized. The knowledge gained from research is extremely important for the proper conduct of conservation and restoration work. It also provides valuable information for finding the peculiarities of a particular artist, enabling the identification of their works and the identification of forgeries.

Due to the unique nature of works of art, it is essential to carry out analyses using non-destructive techniques whenever possible. The characterization of the materials and painting techniques using non-destructive analysis based on X-ray analytical methods, including X-ray fluorescence (XRF) spectrometry, is now widely used in the study of art objects. Several reviews can be found in the literature that summarize the most important applications of XRF to artwork studies, conservation, and restoration, proving the suitability of this technique for non-destructive analysis [1–6]. XRF analysis based on element analysis allows for obtaining a quick and accurate detection and identification of inorganic materials, especially pigments. XRF has long been an established technique for the study of painting materials owing to its non-invasiveness and speed of analysis. XRF has been applied for the analysis of different types of artworks such as paintings [7–10], wall paintings [11,12], drawings [13], and medieval manuscripts [14].

For this reason, the XRF technique was chosen as the main method for determining the composition of the paints used by Olga Boznańska. In addition, a series of images using various ranges of electromagnetic radiation, including near-infrared, visible light, ultraviolet, and X-rays, were taken of the studied paintings, and analyses of the ground layers and pigments were carried out using infrared spectroscopy (FTIR). In this way, it was possible to trace the artist's entire creative process, from the paints she used in tubes, the pigments mixed on palettes, to her final masterpieces.

2. Materials and Methods

The elemental compositions of the pigments from tubes, on painting palettes, and in three paintings were found by non-destructive in situ analysis performed by a portable XRF ARTAX800 spectrometer (Bruker, Berlin, DE). The spectrometer consisted of a 50 kV Rh excitation tube, a Peltier-cooled silicon drift detector (with an energy resolution of 135 eV at the Mn Kα excitation line), and plural polycapillary lenses creating the X-radiation spot below 100 µm. This instrument allows for the determination of elements from aluminum (Al) to uranium (U). The operating parameters for the tube voltage and anode current during the measurements were set to 50 keV and 0.6 mA, respectively. The real-time acquisition was 45 s. The beam was focused on the analysis spot by use of a laser and a CCD camera attached to the spectrometer. Spectra 5.3 (Bruker, DE) software was used for the acquisition and evaluation of XRF spectra.

The chemical analysis of all pigments from tubes and on the painting palettes and selected colors in the paintings was carried out by infrared spectroscopy (FTIR). The infrared spectra were measured with a Shimadzu IR Affinity-1 spectrometer (Shimadzu, Kyoto, JP) using a GladiATR attenuated total reflection accessory (Pike Technologies, Fitchburg, WI, USA) equipped with a diamond crystal. A spectral range of 4000–400 cm^{-1} and a resolution of 4 cm^{-1} were acquired. A total of 250 scans were collected. IR Solution software (Shimadzu, JP) was used for FTIR analysis.

Three paintings by Olga Boznańska from the collection of the National Museum in Krakow were selected for the study. *Flower Girls* (No. inv. MNK IIb-1548) was painted on canvas in 1889, and two portraits, including *Girl with Chrysanthemums* (No. inv. MNK

IIb-1032) in 1894 and *Portrait of Jadwiga Sapieżyna neé Sanguszko* (No. inv. MNK IIb-2296) in 1910 were painted on cardboard.

Before the chemical analysis, a series of photographs of the paintings were taken in different ranges of electromagnetic radiation: ultraviolet, near-infrared, and X-radiation. The UV images were taken using a CANON 40D (Canon, Tokyo, JP) with a CANON EF 24–70, 1:2.8 lens. UV 40W, GE F40 Black Light Blue EX lamps operating in the range of 368 nm were used. The infrared images were taken at a 1000 nm wavelength with a Sony DSC–F828 camera (Sony, Tokyo, JP) equipped with Heliopan filter RG 1000. The source of light was two halogen lamps with 500 W of power.

The X-radiography was performed with a mobile digital X-ray system consisting of an Orange 1040HF (EcoRay, Seoul, KR) portable X-ray source and a flexible, wireless FPS Dix-Ray®® detector with a matrix size of 46 × 38.5 × 1.8 cm. The exposure parameters were 40 kV and 40 mAs. All the individually captured images were combined using Photoshop CS6 software.

3. Results

3.1. Tubes of Paint

Two boxes belonging to Olga Boznańska contained, among other things, a set of paints in tubes. Most of the paints came from the A. Lefranc factory (Paris). The compositions of the paints were analyzed by XRF and FTIR. The detailed analytical results are shown in Table 1. By comparing the results of the FTIR analysis with the data in the literature and combining them with the XRF data, it was possible to identify the pigments present in each tube.

The first box of painting instruments contained eight tubes of paint. There were two types of blue and yellow paint each and one white, orange, red, and brown paint each.

Based on the results of the tests carried out, two different blue paints were found. The first was a mixture of an ultramarine ($Na_8[Al_6Si_6O_{24}]S_n$) and Prussian blue ($Fe_4[Fe(CN)_6]_3$ with the addition of zinc white (ZnO). Because light elements are difficult or undetectable by XRF, the FTIR analysis allowed for the composition of the sample to be examined precisely. The strong bands observed at 1008 cm^{-1} and 1069 cm^{-1} were assigned to the Si–O–Si stretching mode and Si-O deformations in the plane of the silicate group in the blue ultramarine pigment [15]. Prussian blue was easily identified due to the presence of a band at 2086 cm^{-1}, which is caused by the vibration of C≡N in ferrocyanide ion, $Fe(CN)_6^{4-}$ [16]. The characteristic peak of zinc white was observed at 428 cm^{-1} [17]. The FT-IR spectra identified the blue paint as an ultramarine with the addition of Prussian blue and zinc white. The second paint was cobalt blue ($CoAl_2O_4$) with zinc white and a small amount of barium white ($BaSO_4$) used as a filler. The FTIR spectra showed bands at 599, 652, 805, and 1083, which can be assigned to the stretching vibrations of Al-O and Co-O in cobalt aluminate [18]. The 635, 983, 1071, and 1180 cm^{-1} bands were assigned to the SO_4^{2-} stretching vibrations of $BaSO_4$ filler [16,19].

Zinc yellow ($ZnCrO_4 \cdot K_2O$) was detected in the light yellow, while chromium yellow ($PbCrO_4$) was detected in the intense yellow paint. In both cases, the addition of barium white used as filler was detected. Chromium orange ($PbCrO_4 \cdot PbO$) was detected in the orange paint. The FTIR analysis of the yellow and orange paints containing Cr indicated bands in the range of 800–900 cm^{-1}. In the case of the light yellow paint, the bands were observed at 805, 878, and 942 cm^{-1} and attributed to zinc yellow [20,21]. For the yellow paint, the bands were recorded at 836 and 850 cm^{-1}. These bands are caused by the symmetric stretching mode of Cr-O of tetrahedral CrO_4^{2-} ions and were attributed to chromium yellow ($PbCrO_4$) [16]. In the analysis of the orange paint, in addition to the bands shown at 835 and 847 cm^{-1}, the signal at 825 cm^{-1} was attributed to ($PbCrO_4 \cdot PbO$) [22–25]. The other bands observed were attributed to the barite white used as a filler and to the oil binder [26].

Table 1. The compositions of the paints from boxes belonging to Olga Boznańska.

Color of Paint	Detected Elements	MID-FTIR Bands (cm^{-1})	Composition of Paint
Blue, tube 1	Zn, K, Fe (Ca, Cu, Pb)	562(sh), 698(m), 1008(s), 1069(s), 1124(m) 2086(w) 428(s), 497(s), 545(sh) 1609(m), 1623(m), 1170(m), 1240(w), 1470(m), 1720(w), 2840(w), 2926(w)	Ultramarine Prussian blue Zinc white Oil binder
Blue, tube 2	Co, Zn, Ba (Ca, Ni)	599(m), 652(s), 805(m), 1083(m), 1646(w) (w), 983(w),1070(s), 1181(m) 430(s), 500(s), 549(sh) 1730(w), 2840(w), 2926(w)	Cobalt blue Barite white Zinc white Oil binder
Yellow, tube 1	Cr, Zn, Ba, S (Fe, Pb)	805(w), 878(m), 942(m) 635(w), 981(w), 1068(sh), 1085(s), 1170(s) 1697(m), 2851(m), 2918(m)	Zinc yellow Barite white Oil binder
Yellow, tube 2	Cr, Pb, S, Ba (Fe, Zn)	836(m), 850(m) 635(w), 981(w),1068(sh), 1170(s) 1722(w), 2847(m), 2916(m)	Chrome yellow Barite white Oil binder
Red, tube 1	Fe (Cu, Zn, Pb)	476(m), 572(m) 1730(w), 2840(w), 2928(w)	Iron oxide red Oil binder
Orange	Cr, Pb (Fe)	825(m), 835(m), 847(m) 1732(w), 2840(w), 2918(w)	Chrome orange Oil binder
White, tube 1	Pb	674(m), 768(m), 834(m), 1040(m), 1379(s) 1730(w), 2850(w), 2918(w)	Lead white Oil binder
Ligth brown, tube 1	Fe (Si, K, Ca, Mn, Ti, Cu, Zn)	457(w), 662(w), 712(w), 790(sh), 801(m), 894(m), 1012 (sh), 1028(s), 1104(sh), 1124(sh), 3608(w), 3716(w) 1735(w), 2849(w), 2926(w)	Yellow ochre Oil binder
Green	K, Fe, Cr, Pb, Ca, Ba (Cu, Zn)	2089(m) 834(m), 852(m) 635(w), 983(w), 1170(s) 711(m), 872(m), 1390(s) 1730(w), 2840(w), 2926(w)	Prussian blue Chrome yellow Barite white Calcite Oil binder
White, tube 2	Zn, Pb, Ca Ba	428(s), 497(s), 545(sh) 675(m), 768(m),834(m), 1041(m), 1379(s) 711(m), 872(m), 1388(s) 635(w), 981(w), 1170(s) 1726(w), 2850(w), 2918(w)	Zinc white Lead white Calcite Barite white Oil binder
Yellow, tube 3	Cd, S (Ca, Zn, Sr, Ba, Pb)	610(m), 1105(m) 1730(w), 2846(w), 2916(w)	Cadmium yellow Oil binder
Red, tube 2 (*lacca*)	Ba, Sr, Ca (Fe, Zn, Pb)	543(m), 609(m), 640(w), 1010(m), 1039(m), 1071(m), 1235(m), 1289(m), 1360(w), 1465(m), 1585(s), 635(w), 981(w), 1170(s) 1631(m), 1740(m), 2850(m), 2920(m)	Organic red dye Barite white Oil binder
Light brown, tube 2	Fe (Si, K, Ca, Ti, Cu, Zn, Pb)	596(w), 671(w), 875(m), 1032(s), 1159(m), 1313(w) 1375(m), 1448(m), 1697(m), 2851(m), 2918(m)	Yellow ochre Oil binder
Dark brown, tube 1	Mn, Fe (Ca, Cu, Zn)	450(m), 540(m), 590(m), 630(m), 730(m), 797(m), 1080(s), 1165(s) 1720(w), 2846(w), 2918(w)	Umber Oil binder

Trace elements are in brackets.

The dark red paint was identified as iron red, with FTIR bands at 475 and 572 cm^{-1}, which is typical for hematite (Fe_2O_3), while yellow ochre containing goethite ($Fe_2O_3 \cdot H_2O$)

(bands at 457, 662, 790 and 894 cm^{-1}) and silicate (strong band at 1028 cm^{-1}) was recognized in the light brown paint [15]. The white paint was identified as lead white ($2PbCO_3 \cdot Pb(OH)_2$).

In the second box containing the artist's painting utensils, six tubes were found. These included green, white, yellow, red, and light and dark brown paints.

The green paint with the commercial name *Green Cinnabar* was found to be a mixture of Prussian blue with chrome yellow. The XRF spectra obtained during the analysis of this paint are shown in Figure 1. The FTIR analysis confirmed the presence of chrome yellow (bands at 834 and 852 cm^{-1}) and Prussian blue (band at 2089 cm^{-1}).

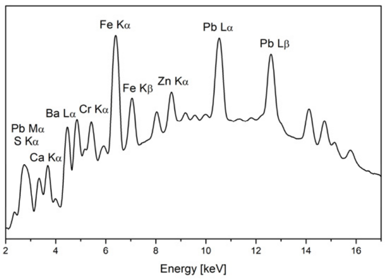


Figure 1. XRF spectra of *Green Cinnabar* paint (a mixture of Prussian blue with chrome yellow) from the tube.

The white paint was identified as a mixture of zinc white, lead white, and barium white with added calcite ($CaCO_3$). In the yellow paint, cadmium yellow (CdS) was detected based on the XRF data, and the FTIR bands observed at 610 and 1105 cm^{-1} were assigned to sulfide stretching. Upon examination of the red paint, the presence of red organic dye deposited on barium white was detected, confirming the description from the label residue (*lacca*). The FTIR analysis showed the presence of a band at 1360 cm^{-1}, attributed to the stretching vibration of the C-C group, a band at 1465 cm^{-1}, which can be assigned to combinations of vibrations of the C-C, C-OH, C-O, or C-H group, and a strong band at 1585 cm^{-1}, typical for aromatic CC stretching vibrations. The observed results indicate the use of alizarin dye [27] The FTIR spectra obtained during the measurement of this paint are shown in Figure 2.

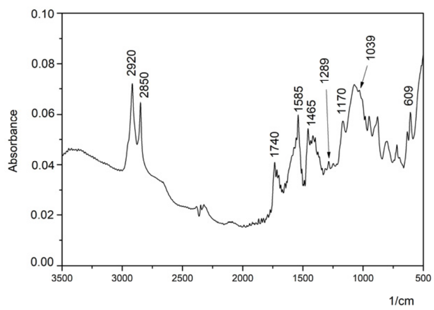
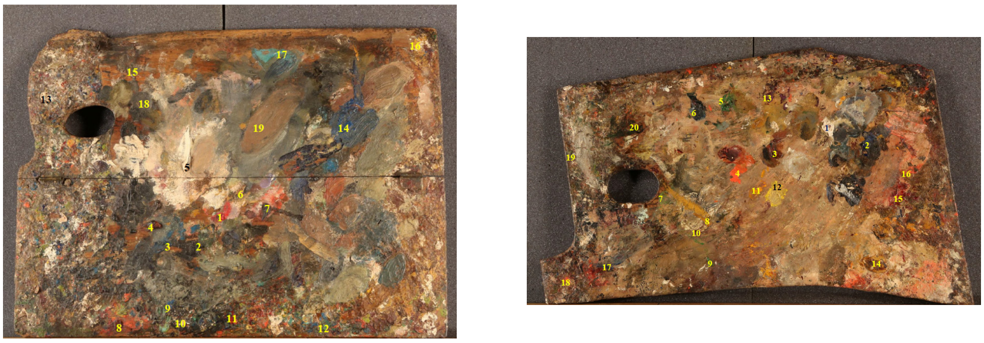


Figure 2. FTIR spectra of red organic dye (*lacca*) deposited on barium white from the tube.

In the case of the second light brown paint, the main ingredient was also yellow ochre with the addition of lead white. The dark brown paint was based on umber. The presence of hematite and manganese oxides was confirmed by bands at 450 and 540 cm^{-1} (Fe_2O_3), at 590 and 730 cm^{-1} (MnO_2), and at 630 cm^{-1} (Mn_2O_3) in the FTIR spectra [28].

3.2. Painting Palettes

Wooden palettes offer a lot of valuable information about an artist's way of working. The analyzed objects are shown in Figure 3. The elemental compositions of the paints applied to Olga Boznańska's first painting palette (Figure 3a) were examined on both the obverse and reverse of the palette. When the whites were analyzed, two types of pigments were found: zinc white and lead white. Measurements of the yellow paints, in different shades, showed the use of cadmium yellow, cadmium orange, and the natural iron pigment yellow ochre. Analysis of the red paints revealed the presence of cinnabar (HgS), iron red, and a red organic pigment deposited on barium white. Analysis of the blue paints revealed the use of cerulean blue ($CoSnO_3$) and Prussian blue. For the first blue paint, XRF analysis indicated an intense signal from cobalt (CoKα 6.93; CoKβ 7.65 keV) and tin (SnLα 3.44; SnLβ 3.75 and SnKα 25.27; SnKβ 28.48 keV), while the FTIR spectra showed vibrational bands at 533, 590, and 650 cm^{-1}, which are typical of cerulean blue, a mixture of cobalt and tin oxides [15]. In the second case, the presence of Prussian blue was confirmed by a 2088 cm^{-1} band observed in the FTIR analysis. In addition to Prussian blue, ultramarine (1010 cm^{-1}) was detected in one of the paints tested. In addition, an admixture of cobalt blue was found in the paint mixture, forming a maroon color, but cobalt blue used as a separate pigment was not detected.



(**a**) (**b**)

Figure 3. Photographs in visible light of two wooden painting palettes by Olga Boznańska: (**a**) Inw. no. MNK IV-v-532/1, (**b**) Inw. no. MNK IV-v-531/4.

The greens were identified as emerald green ($Cu(C_2H_3O_2)_2{\cdot}3Cu(AsO_2)_2$) and chrome green ($Cr_2O_3$), with traces of Prussian blue. The FTIR spectra of the emerald green are shown in Figure 4. The FTIR spectra showed bands at 758, 816, 1446, and 1546 cm^{-1}, attributed to the As-O stretching vibration and carboxylic group band peaks and recognized as copper acetoarsenite [29–32].

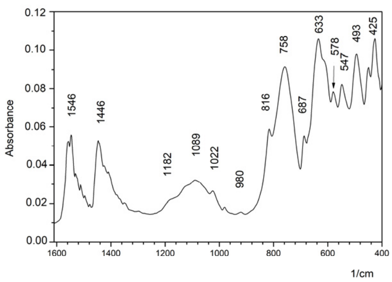


Figure 4. FTIR spectra of emerald green.

The FTIR analysis of another green paint showed bands at 492, 632, and 692 cm^{-1}, assigned to chromium oxide (Cr_2O_3) [17]. In the intense green, a mixture of chromium green with cadmium yellow was detected. In purple, a mixture of manganese violet ($NH_4MnP_2O_7$) with Prussian blue was found. The FTIR analysis showed bands at 530, 567, and 596 cm^{-1}, assigned to the vibrations of the diphosphate groups. The peaks observed at 759 and 890 cm^{-1} were attributed to the vibrations of P-O-P bridges. A strong band at 988 cm^{-1}, with shoulders at 1021 and 1076 cm^{-1}, and the bands at 1076, 1187, and 1239 cm^{-1} were assigned to the symmetric and asymmetric terminal stretching vibrations of the PO_3 groups, while the peak observed at 2086 cm^{-1} was characteristic of Prussian blue [33–35].

A very similar set of pigments was found on the second of the palettes examined (Figure 3b). The XRF and FTIR analyses of the whites revealed the presence of lead white, a mixture of lead white with barium white, and a mixture of zinc white with barium white. The characteristic peak of zinc white was observed at 430 cm^{-1} [17]. The bands observed at 635, 981, 1070, and 1180 cm^{-1} were assigned to the $SO_4{}^{2-}$ stretching vibrations of $BaSO_4$ filler [16,19]. A sharp band at 1045 cm^{-1} and a broad peak at 1396 cm^{-1}, owing to the symmetric and asymmetric stretching vibrations of the carbonate group $CO_3{}^{2-}$, were matched to lead white [36]. The measurements of the yellow paints with different shades showed the use of cadmium orange, the natural iron pigment yellow ochre, and zinc yellow in a mixture of ochre and Prussian blue. Analyses of the red paints indicated the presence of cadmium red with zinc white, cinnabar, and a mixture of cinnabar with red organic pigment deposited on barium white. The FTIR analysis confirmed the presence of alizarine. In addition, the dark reds showed the use of iron red and a mixture of iron red with cobalt blue. The XRF and FTIR analysis of the blue paints revealed the use of cerulean blue. In one of the blue areas examined, the addition of Prussian blue to cerulean blue was detected. The greens were identified as emerald green and chromium green with zinc white additive.

In the greens with a blue hue, chromium green mixed with cerulean blue was detected. The dark brown was formed from a mixture of bone black with the natural iron pigment ochre, while bone black was detected in the pure black paint. The presence of bone black was estimated by XRF based on the high signals from phosphorus (PKα 2.01 keV) and calcium (CaKα 3.69 keV). The FTIR spectrum region of 1250–900 cm^{-1}, where $PO_4{}^{3-}$ group stretching modes are expected, showed a band at 961 cm^{-1} and confirmed the presence of bone black ($C + Ca_3(PO_4)_2$) [17].

By analyzing the painting palettes, it was possible to determine what types of paints Olga Boznańska mixed. From the painting materials she left behind, we know that she used bristle brushes made of strong bristles. Some of them were almost completely worn down to the handle. On the surface of the palettes, one can easily see traces of the search for the right color or matching shade. On some palettes, one can see that the paints are mixed extensively, varying. At other times, one can see the delicate touches of the brush gathering small portions of color transferred from the wooden board to the canvas or cardboard.

3.3. Paintings

The first painting, *Flower Girls*, presented in Figure 5, depicts three girls sitting against a window at a table, working on bouquets they are arranging from flowers lying on the tabletop. To the sides of the window, on the walls hang a portrait on the left and Japanese fans on the right. A pot with a plant stands on the floor. Through the window, a landscape with townhouses is visible, including one townhouse with a tower. This kind of treatment allows the composition to open up and develop depth, as in Japanese prints, while at the same time bringing the foreground closer to the viewer. The influence and inspiration of Japanese art, to which the artist succumbed, are well visible in this painting. Following the example of Japanese woodcuts, the painter has created here a composition full of harmony, built with clearly separated planes. In the background, there is an area of buildings, then a window, and the flower girls sitting in front of it. Despite the use of several planes, the composition is not chaotic. Boznańska builds it legibly, using harmonized color patches and a delicate and flowing drawing. She also uses a specific, fragmentary frame, in which one can also find influences of Japanese aesthetics. The artist's discreetly placed Japanese uchiwa fans on the wall also attest to her interest in Japan. The hairstyles of the flower girls are also Japanese-inspired.

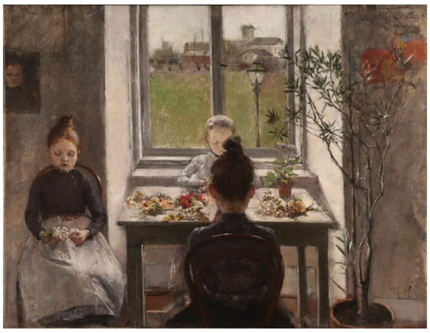


Figure 5. Photograph in visible light of the painting Flower Girls by Olga Boznańska.

The painting *Flower Girls* was painted on canvas in oil. The XRF measurement of the light ground layer visible at the edge showed the presence of lead and calcium, which indicates that the ground layer consists of lead white with calcite. Figure 6 presents the FTIR spectra obtained for the analyzed ground layer. The clear carbonyl band at 1732 cm^{-1} and the C-O stretching patterns at 1249, 1164, and 1101 cm^{-1} are diagnostic of the triglyceride ester linkages. The spectral range of 2800–3000 cm^{-1} contains bands at 2839 cm^{-1} and 2925 cm^{-1}, typical for the symmetric and antisymmetric stretching modes of the CH_2 groups. The bands observed at 678 cm^{-1} and 1022 cm^{-1} are associated with the CO_3 rocking deformation and the symmetric CO_3 stretching vibration, respectively. An additional spectral feature associated with the antisymmetric CO_3 stretching vibration was observed at 1397 cm^{-1}. The bands detected indicate the presence of lead white, calcite, and oil binder in the ground layer.

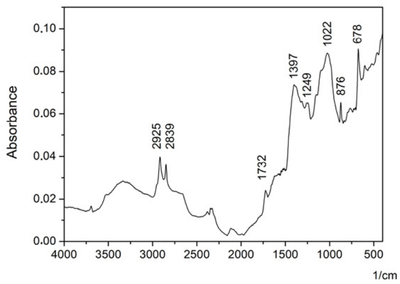


Figure 6. FTIR spectra of the ground layer of the painting *Flower Girls*.

The XRF analysis indicated that the vivid red and yellow stains depicting the colorful flowers lying on the table were painted with cinnabar, chrome yellow, and Naples yellow or with the natural iron pigment yellow ochre. The white petals were marked with lead white. The intense blue flowers were painted with cobalt blue, while the muted reds and warm colors of the pots were achieved with iron red. The greens that make up the stems and leaves of the plants, in various shades, were constructed from a mixture of yellow and blue paints—chrome yellow or strontium yellow with cobalt blue or Prussian blue, further modifying the color with a small amount of Naples yellow ($Pb_2Sb_2O_7$) or yellow ochre. The FTIR spectra showed bands at 475 and 652 cm^{-1}, attributed to Pb-O stretching and bending vibrations in Naples yellow [37,38]. The bands observed at 459, 660, 790, and 895 cm^{-1}, with a strong band at 1030 cm^{-1}, were assigned to goethite and silicate in yellow ochre. The FTIR analysis also confirmed the presence of a mixture of chrome yellow with Prussian blue. The intense light green of the grass visible outside the window was achieved with emerald green. The XRF spectra of the analyzed green paint are shown in Figure 7.

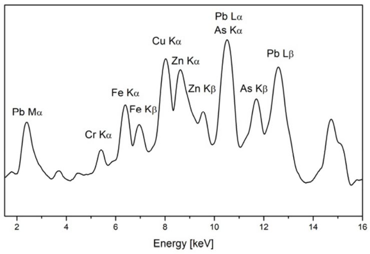


Figure 7. XRF spectra of green paint in the painting *Flower Girls*.

The grey color of the walls was painted with a mixture of zinc white and lead white with bone black, a small amount of cobalt blue, and ochre. The light-colored faces of the girls were painted with a mixture of lead white and zinc white with the addition of chrome yellow and iron pigments. The brown tones of the hair were achieved with a mixture of iron pigments—umber or ochre—and iron red with an admixture of cinnabar and yellow paints—chrome yellow and Naples yellow.

One of Olga Boznańska's finest works, *Girl with Chrysanthemums*, shown in Figure 8, was painted in Munich in 1894. It is a true display of color limited to subtle shades of silvery-grey hues, framed by delicate brushstrokes. Here, the artist created a new type of children's portrait, breaking with the previous convention of depicting small models in refined clothes and elegant and stylish interiors. The portrait depicts a serious little girl standing alone. Dressed in a simple ash-colored gown with puffed sleeves, the model weaves her hands in which she holds a bouquet of white chrysanthemums. In the image of the girl, portrayed against a neutral and whitish-grey wall, the attention is drawn to her pale face with large eyes, uncanny in their blackness, shining as if in a fever. The expression of these eyes looking straight ahead with tension, curiosity, and boldness makes the portrayed, like a hypnotist, establish a psychic contact with the viewer. The portrait exudes a mood of thoughtfulness, sadness, mystery, and understatement. Boznańska builds psychological depth primarily through the facial expression and gaze and the gesture of entwined hands grasping the chrysanthemums.

Figure 8. Photograph in visible light of the painting *Girl with chrysanthemums* by Olga Boznańska.

The painting *Girl with Chrysanthemums* was painted on cardboard using an oil technique. The wall and the dress determine the color tonality of the painting, stretched on a grey scale, from under which the brown of the cardboard sub-image shines through at the edges. The silvery and ashen tones are complemented by subtle color accents–a golden-red storm of hair, the pink of the lips, the white of the chrysanthemums, the green of the stems, and finally the dark brown, almost black of the glittering, wide-open eyes, whose glow is emphasized by delicate flecks.

Figure 9 presents the X-ray and UV analytical photographs of the painting *Girl with Chrysanthemums*. The X-ray photograph (Figure 9a) shows how in the initial stages of the works, the painter spread the wet paint in different directions quite vigorously. It was only on this that the impastos and more concrete stains were applied. Minor corrections are also visible, indicating that the painter, not entirely satisfied with the result, continued to search for a more accurate form. The paintings lack precise under-drawings, showing that the artist sketched with oil paint just before applying the actual paints.

(**a**) (**b**)

Figure 9. Analytical photographs of the painting *Girl with Chrysanthemums.* (**a**) X-ray photograph; (**b**) UV light.

The XRF analysis showed that the pale complexion of the portrait was achieved with a mixture of zinc white and lead white with the addition of a small amount of ochre and iron red. The presence of zinc white was also clearly visible when the image was illuminated with UV light. The bright, intensely fluorescent spots visible on the girl's face indicate where zinc white was used (Figure 9b). In contrast with the pale face, the girl's intense red lips were painted using cinnabar with a touch of iron red. The dark eyes were marked with iron pigment with added cobalt blue and bone black. The black pupils were also applied with bone black. The copper hair was painted with ochre. The dark grey color of the dress was obtained from a mixture of lead white, ochre, and blue paints–Prussian blue and cobalt blue—and traces of bone black. The white spots of the flowers were applied with lead white, and their intense yellow centers were marked with cadmium yellow. The XRF spectra of the yellow paint are shown in Figure 10. The green stems of the chrysanthemums were painted with cinnabar green, a mixture of Prussian blue, and chrome yellow. The greyish tint of the wall was achieved with a mixture of lead white and bone black, with the addition of a small amount of ochre. The signature visible in the lower right corner was applied in bone black. The painting was painted very thinly in places. Subtle half-tones and short, delicate brushstrokes introduced a refined dilution of the paint layers.

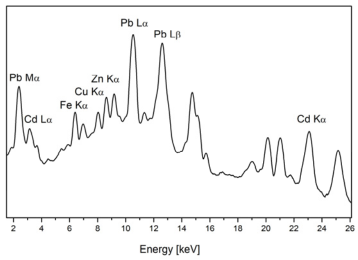


Figure 10. XRF spectra of yellow paint in the painting *Girl with Chrysanthemums*.

The next painting examined was a *Portrait of Jadwiga Sapieżyna neé Sanguszko*, with grey hair and in a black dress. The image of the examined painting taken in visible light is presented in Figure 11. The portrait depicts Jadwiga Sapieha (1830–1918), the mother of Cardinal Stefan Sapieha (1867–1951), Archbishop of Krakow. The subject sits opposite in a stylish armchair upholstered in gold cloth. Her hands with rings rest on her knees. In the background is a wall upholstered with patterned fabric in blue tones. A characteristic feature of Olga Boznańska's portraits is sadness, mystery, and lack of a smile, while the people portrayed give the impression of being reserved and secretive. This painting portrays an elderly lady, elegantly posed in an armchair, whose face Olga Boznańska recreated with reverence, especially her eyes, gazing intensely at the viewer and reflecting the character of the dignified portrayed. With similar care, the artist painted the delicate hands, no longer young, adorned with elegant jewelry. The aristocrat's dress, on the other hand, has only a schematic cut. A similar convention is maintained for the background of the composition, which Boznańska, in her typical way, left unfinished, with fragments of the canvas showing through. This painterly treatment gives the painting a lightness and enhances its painterly qualities.

Figure 11. Photograph in visible light of the painting *Portrait of Jadwiga Sapieżyna neé Sanguszko* by Olga Boznańska.

Olga Boznańska's portrait of Jadwiga Sapieha was painted on cardboard in oil. At the turn of the 20th century, unconventional painting substrates, such as plywood and cardboard, became common. This was when the widespread use of cardboard as a substrate for painting took off. The production and distribution of cardboard for painting purposes was so widespread that a division of cardboard for painting purposes was adopted in

England [32]. Among these was a special type of primed cardboard. Figure 12 presents the FTIR spectra obtained for the analyzed cardboard. In the FTIR spectra, bands characteristic of the C-O stretching vibrations of β-glycosidic bridges (1050 cm^{-1}), C-O-C skeletal vibrations of pyranose rings in cellulose (1100 cm^{-1}), C-C stretching vibrations of cellulose chains (1150 cm^{-1}), and C-H stretching vibrations in the methyl and ethyl groups of cellulose chains (1315 and 1420 cm^{-1}) were detected. Additional bands at 1530 cm^{-1} and 1637 cm^{-1} were attributed to protein glue. In addition, the intense, broad band at about 3300–3400 cm^{-1} was assigned to the proteinaceous substance [39].

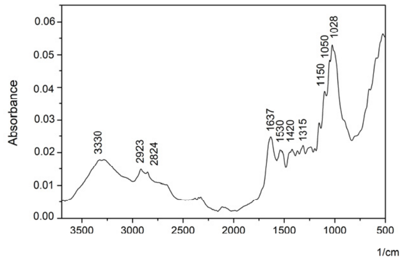


Figure 12. FTIR spectra of the cardboard support of *Portrait of Jadwiga Sapieżyna neé Sanguszko*.

The portrait's face and hands were modelled using natural iron pigment (ochre), cinnabar, lead white, and barium white. The reddened eyelids and the corners of the eyes were applied with cinnabar. The blue iris of the eye was marked with Prussian blue, with the addition of emerald green and a small amount of cerulean blue. The XRF spectra obtained during the analysis of the discussed area are shown in Figure 13. The dark shadows on the face were applied with a bleached mixture of iron red with cerulean blue. The lip line was painted with iron red with added cinnabar. The jewelry adorning the hands of the portrait subject was applied with a bleached cadmium yellow. The white collar was marked with lead white with the addition of barium white. The black mantilla and the dress of the portrait sitter were painted with bone black with the addition of Prussian blue, cerulean blue, and lead white. Bone black was also used to outline the chair on which the portrait sits. The yellow color of the backrest was achieved with cadmium yellow, iron yellow, chrome, and ochre paints. The greenish background was applied with emerald green and chromium pigments, which were additionally enriched with color spots: blue—applied with cerulean blue; red—obtained from cinnabar and iron red; and yellow—marked with iron yellow. The FTIR analysis of the various green areas indicated the presence of bands at 492, 632, and 692 cm^{-1}, attributed to chromium oxide (Cr_2O_3), and at 480, 588, and 637 cm^{-1}, assigned to viridian green ($Cr_2O_3 \cdot 2H_2O$) [16]. The use of two types of green chrome paint indicates that the artist was looking for the right tonality for the background of the portrait.

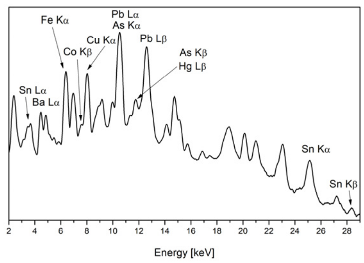


Figure 13. XRF spectra of blue paint in the painting *Portrait of Jadwiga Sapieżyna neé Sanguszko*.

Boznańska was very skilled at blurring contours and any strong accents, with paint spread in a mist-like pattern. She probably achieved delicate tonal mixtures by gently hitting the palette with her brush and the sub-painting. She also used abrasion on the dried, unevenly applied layer of paint, which produced interesting effects that can be seen when looking closely at the surfaces of the paintings.

When it came to mixing the paints, the painter chose her colors freely, not paying so much attention to chemical principles. Spectroscopic studies have shown that she mixed indelible colors with permanent ones and those which, according to the rules, should darken with each other. In Boznańska's paintings, the emerald green was mixed with both cadmium yellow and cinnabar. The strontium yellows, chromium yellows, and arsenic greens have also undergone color changes. All these less-durable paints have dimmed a little, become quieter, and harmonized. In contrast, paints such as the cinnabar, the resistant cobalt blue and cerulean blue, and the iron paints are doing well. The chrome greens also seem to be unchanged since being squeezed out of the tube. Presumably, the use of zinc white may have caused more paint layer cracks to appear in places than they should have. The canvases are definitely worse in this respect than the cardboard, where the 'cobwebs' are much more numerous and deeper.

4. Conclusions

The research into the technique and technology of Olga Boznańska's works was inspired by a monographic exhibition held on the 150th anniversary of the painter's birth. The study of both the palettes and paintings of Olga Boznańska has made it possible to gain an insight into the artist's preferences in her choice of paints throughout her career and to learn about the technology that demonstrates her individuality.

The analysis of Olga Boznańska's painting technique showed that the characteristic features influencing the reception of her works, in particular their mood, were not the result of some technological experiments but the brilliant use of basic painting means, typical of most artists active at the time. In none of the examined paintings by Olga Boznańska was the presence of preparatory drawings found. Their absence can be considered a characteristic feature of the artist's creative process. As the analyses of the composition of her paints show, Olga Boznańska used a very wide range of paints, and her palette was certainly not poor or narrow. We found several whites (zinc white, lead white, and barium white), yellows (cadmium yellow, Naples yellow, chromium yellow, strontium yellow, and synthetic iron yellow), oranges and reds (chromium orange, cinnabar, and alizarine), greens (chromium green, viridian green, and emerald green), blues (cobalt blue, Prussian blue, and cerulean blue), and several earth pigments, including umber, yellow ochre, synthetic iron red, bone black, and even organic blue. Based on the research, we can conclude that Olga Boznańska's palette was not limited. A non-invasive XRF and FTIR study of Boznańska's paintings and palettes identified 28 different pigments. These results bring new knowledge about the artist's palette and allow for a different definition of the character of her paintings, previously described as very subdued, with a limited range of colors. It turns out that the paintings, which seem to be limited to shades of silvery grays, were in fact painted with rainbow-colored paints, which the artist mixed on her palette while working on the paintings and applied to the substrate with gentle brushstrokes.

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