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The application of modern analytical techniques to the examination of the Henryk Siemiradzki's large-size painting „Nero's Torches"

ABSTRACT

Nero's Torches by Henryk Siemiradzki is one of the most important and the largest in size paintings in the collection of the National Museum in Kraków. In 1879, the painter donated his famous work to the nation. It was assigned to the Cloth Hall. By this act the artist initiated the start of the first national museum in Poland.

The painting was thoroughly examined in order to identify the technology and technique of its production, elements of the creative process and the use of materials. Tests *in situ* of such a large work (3.76 m x 7.11 m) were possible thanks to the use of modern techniques and mobile analytical equipment.

X-ray, IR and UV photos of the painting were taken. In view of the large size of the painting, 236 snapshots using X-ray radiography (DX) equipped with CARESTREAM DRX-1 System detector were needed to obtain an X-ray image of the entire painting. Then pictures obtained from individual snapshots were put together using Photoshop CS6 computer programme to cover the entire painting. UV and IR images consisted of 26 snapshots. Pictures in analytical radiation and visible light helped to better understand the painting technique, the method of painting individual parts, preparatory drawing and the creative process. Numerous changes of the painting concept (*pentimenti*) were revealed.

In order to identify pigments used by the painter, non-invasive XRF spectroscopy technique was applied using two spectrometers of Bruker AXS Microanalysis manufacture. Eighty measurements were taken in the lower part of the painting using portable spectrophotometer µXRF ArtTAX®, other parts were examined using handheld spectrometer Tracer III and working on the scaffolding (165 measurements). Non-invasive tests were complemented by other methods using sampling (XRPD, microscopy and microchemical analysis, SEM EDX, FTIR, HPLC). Data obtained allowed to identify pigments applied and the way they were bound in the painting. In view of the large size of the painting, the scope of the analysis can be considered unusual or even record-breaking.

Keywords: Siemiradzki, technology and painting technique, XRF spectroscopy, analytical radiation photograpy, IR, UV, X-ray

Nero's Torches – the fundamental meaning of the painting for Henryk Siemiradzki and for the collection of the National Museum in Kraków

Henryk Siemiradzki, who lived in the second half of the 19th century (1843–1902), was one of the most famous Polish painters of his time. He is known for his academic depictions of ancient and biblical themes. He was admired in Poland and in Europe. Siemiradzki spent most of his artistic life in Rome, but he was constantly interested in Polish affairs and closely connected to the country. We must remember that at that time Poland was occupied by three empires and thus absent on the map of Europe.

The *Nero's Torches* painting, the subject of this research, is probably the most important work of Siemiradzki's career. It was painted when the artist had already settled in Rome. The painting aroused interest among other artists and journalists before it was even finished. Because of the large scale of *Nero's Torches*, it took Siemiradzki over two and a half years to complete. He finished the painting in 1876. When *Nero's Torches* was finally exhibited, it achieved great success. The painting was on display in many European cities, and it won accolades everywhere. Moreover, the artist was awarded a gold medal for his work during the Paris International Exposition in 1878, adding to Siemiradzki's fame.

The painting illustrates the scene of the first Christians' martyrdom (Fig. I). Nero accused the Christians of setting fire to the city of Rome, regardless of the truth. As a cruel punishment, he put on a show in his palace gardens, where the Christians were tied up to wooden pillars, wrapped with straw and hemp, and set alight like torches.

The painting's significance extends beyond the development of the painter's career. In 1879, Siemiradzki donated it to the nation, "to the country" as he said, to be displayed in Sukiennice. As a result of this generous gesture, *Nero's Torches* gave rise to the founding of the National Museum as his example was followed by several Polish artists. The creation of the collection of Polish national art was particularly important for Poles during the time of partition.

The examination and research into the famous work was an integral part of a large scale project, concerning the analysis of Siemiradzki's painting technique which is being carried out in the National Museum in Kraków. Up until now, 56 oil paintings by Siemiradzki have been investigated, one of which is *Nero's Torches*.

Record breaking large scale, non-invasive, analytical radiation examination of the painting

The painting is unusually large. The dimensions are 376 cm high, and, over 7 meters long, at 711 cm. The painting's large size meant that it could not be taken into a laboratory. Carrying out the investigative work *in situ* was only possible thanks to the use of modern methods and mobile equipment. Mobile spectrometers, a digital X-ray system, and special lamps designed to take photographs in various types of radiation, were utilized. Furthermore, mobile scaffolding was used in order to perform the research.

Despite the large scale of the painting, the images of the whole picture were taken in three kinds of radiation: infrared (IR), ultraviolet (UV) and X-ray radiation.

The infrared image was executed under radiation of 1000 nm wavelength, using a Sony DSC – F828 camera equipped with a Heliopan filter RG 1000. Two 500 W halogen lamps were used as the radiation source.

The UV image was taken by means of a CANON 40D camera with a CANON EF 24–70, 1:2.8 lens. General Electric F40 Black Light Blue EX 40W operating in the range of 368 nm tubes were used as UV light source.

X-ray radiography was performed with the use of a mobile digital X-ray system consisting of an Orange 1040HF portable X-ray source, and a flexible, wireless FPS Dix-Ray® detector with matrix sized: 46 x 38.5 x 1.8 cm. A special construct was designed and assembled to position and move the detector in order to place it at the paintings verso. The X-ray source was installed on mobile scaffolding to reach subsequent parts of the painting (Fig. II, Fig. III). The exposure parameters were: 40 kV, 40 mAs.

All the individually captured images were combined using Adobe Photoshop CS6. The IR and UV images were composed of 26 exposures, which were subsequently combined to create one image. The same procedure was carried out with the X-ray radiography; unfortunately, the matrix of the detector is relatively small, (46 x 38.5 cm) as such, to create an image of the whole painting 236 exposures (!) were performed and combined, which we believe to be a record breaking number.

As a result, three images of the picture in different radiations were obtained. The analytical radiation, as well as visible light images helped us to understand thoroughly the painting technique, the execution of the particular parts of the painting, the use of underdrawing, and the creation process, including the painter's numerous local concept changes (*pentimenti*). The most interesting and valuable information was provided by the IR and X-ray images.

The IR images revealed some of the author's own overpaintings (*pentimenti*) of varying importance, as well as the underdrawing. One of the most significant changes in the artist's creative concept, was discovered in the fragment illustrating the slave setting the fire. In the visible light, it can be seen that he points downward with the torch in his hand. However, thanks to infrared radiation, it was revealed that in the first version, Siemiradzki painted the arm raised with the torch's fire burning right above the victim's head (Fig. 1). The young woman's hair was just starting to burn. It is as though the artist changed his mind, took a step back in time, and decided to depict the very moment before the tragic ceremony. This insight is essential in the interpretation of the picture's meaning. It seems as though Siemiradzki did not mean to shock and impress the audience with a bloody scene. Instead, he decided to show the quiet suffering of the innocents. This confirms Siemiradzki's first idea, which can be found in his letters[1], however the discovered *pentimenti* demonstrates the artist's hesitation.

Fig. 1. H. Siemiradzki, *Nero's Torches*, 1876, National Museum in Kraków. Fragment of the IR image. Infrared radiation revealed, that in the first version Siemiradzki painted the arm of the slave raised and the fire burning right above the victim's head. Photo by P. Frączek, M. Obarzanowski

[1] Letter to Isayev that dates from September 1873 after: T. Karpova, *Genrih Semiradzkij*, Sankt Petersburg 2008, p. 69; Letter to the artist's parents in which he comments on an article about the picture in the "Wiek" journal where in the composition's description was wrong information about burning the Christians. Siemiradzki was very upset maintaining that he depicted "the very moment before putting up the fire to the living torches"; letter not dated. After J. Dużyk, *Siemiradzki. Opowieść biograficzna*, Warsaw 1986, s. 262–263.

Fig. 2. H. Siemiradzki, *Nero's Torches*, 1876, National Museum in Kraków. Fragment of the IR image. Very accurate drawing of parts of architecture revealed by the infrared radiation. Photo by P. Frączek, M. Obarzanowski

Another change revealed by the analysis can be seen in the figure of the gladiator. Thanks to infrared radiation, the original outline of his body is noticeable. The primary shape was situated about 10 cm lower than in the final version. This decision is related to another change of Siemiradzki's idea in this section of the picture, which is visible on the X-ray image.

Apart from the changes in the concept of the painting, the IR radiation precisely showed the underdrawing made by the author. It must be emphasised that Siemiradzki did not make a thorough sketch of the whole composition on the primed canvas. Nevertheless, the artist made a very accurate drawing of parts of the architecture, as well as of the lines of perspective and the point where they meet (Fig. 2). This way of using the drawing is quite typical for Siemiradzki.

Fig. 3. H. Siemiradzki, *Nero's Torches*, 1876, National Museum in Kraków. X-ray image of the whole painting. The edges of the composition could not be analyzed because of a metal stretcher, which prevented the positioning of the detector. Photo by P. Frączek, M. Obarzanowski

The application of X-ray radiation provided a unique image of the famous painting. The X-ray radiography revealed new insight into the artist's creative process (Fig. 3). One of the most spectacular concept changes was discovered in the area of the construction of Nero's palace. Originally it had a two sided slanted roof with a tympanum on top. However, Siemiradzki later replaced it with a base carrying a sculpture of Athens' quadriga.

Another change was found on the X-ray image in the background of the garden. In the first version there was a fountain with a characteristic tank in the shape of a bowl. In the ultimate version, the artist painted over the fountain and put stairs and fragments of a garden in its place. Nevertheless, another, a much bigger fountain, was placed in the left corner of the picture. More specifically, a big oval pool, and fountain with a comedy mask[2] with water streaming out of it, can be observed here. Again, the X-ray image showed that originally, there was only a decorated, rectangular base in the place of the fountain. Therefore, when Siemiradzki decided to paint the bigger form he moved the gladiator slightly to the top, and middle of the painting, just to make space for the fountain. This change was probably introduced by the artist in respect to compositional reasons. With that said, it cannot be ruled out that the painter wanted to develop the motif of water as well, which seems to be significant, as far as the painting's general idea is concerned. For Christians, the fountain and the running water have a symbolical meaning of cleansing, and the purification of sins[3].

[2] D. Gorzelany, *Zabytki rzymskie źródłem inspiracji malarskiej „Pochodni Nerona" Henryka Siemiradzkiego*, „Rozprawy Muzeum Narodowego w Krakowie", Vol. VI, Kraków 2013, p. 169.

[3] D. Forstner, *Świat symboliki chrześcijańskiej*, Warszawa 1990, pp. 65–70.

The image obtained in UV radiation shows mainly the location of retouches, and the remains of varnish, but also the distribution of some kinds of pigments, for example, copper pigments and vermilion with red organic dyes.

Modern analytical techniques for non-invasive *in situ* pigment identification

X-ray fluorescence spectroscopy (XRF) is a valuable and non-invasive method for the identification of pigments. This technique is the starting point for the investigation of the pigments and paint layers in Siemiradzki's oils. However, in the case of picture as large as *Nero's Torches*, the *in situ* measurements, performed directly in the gallery, were possible only thanks to mobile equipment. To examine the lower parts of the painting an ArtTAX® µXRF spectrometer (Bruker AXS Microanalysis) was used. This spectrometer is equipped with a Rhodium X-ray tube (50 kV), a Peltier-cooled silicon drift detector, and a set of pinhole collimators ranging from 2 mm down to 200 µm. Even though it was possible to perform analysis in the gallery, installing the spectrometer on the scaffolding was out of the question. Using the ArtTAX, only a 45 cm wide band in the lower part of the picture (it has a 50 cm wide frame, which stands on 66 cm high base) could be measured. Nevertheless, 80 measurements were taken and the analyses of a variety of colours were made. As the examinations were carried out partially during opening hours of the gallery, the researchers' activity served as a kind of attraction for visitors at the same time (Fig. IV).

In order to take measurements in the remaining, upper parts of the painting, a handheld, portable XRF spectrometer – Tracer III was used. The Tracer III-SD incorporates the proprietary XFlash® Silicon Drift Detector (10 mm^2, typical resolution 190 eV at 10,000 cps) and Rh target[4]. The device is battery operated, it is relatively small (30 cm x 10 cm x 28 cm) and weighs 2 kg (with battery). All these features enabled the use of the spectrometer on the scaffold (Fig. V, VI). The Tracer III is also equipped with 4 customizable filters to optimize analysis. However, having done some tests with the use of the filters, the decision was made to perform standard measurements (without filters) which were satisfactory enough, and enabled the conducting of more analyses in a shorter time. With the use of Tracer III 165 measurements were taken at different points of the painting. A maximum voltage of 40 kV was applied. The obtained spectra were subsequently converted into the ArtTAX software in order to compare them not only to each other but also to the ArtTAX spectra.

In summary, all the 245 analyses were done by means of XRF spectroscopy, setting another record (!) and in turn provided vast knowledge about the inorganic pigments used by the artist in this prominent work.

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[4] Data from the Bruker's web page: http://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/tracer-iii/technical-details.html [access: 23.10.2014].

Mobile ArtTAX and handheld Tracer III; two XRF spectrometers – an attempt at making a comparison

When we compare the two X-ray fluorescence spectrometers, the advantages and the disadvantages of both devices can be observed (Tab. 1). ArtTAX is moveable, which is obviously an advantage, but at the same time, quite big and cumbersome to use outside the laboratory. The dismantling and then reassembling is very time-consuming. Moreover, the time of accumulating spectra is also relatively long (approximately 300 s / 40 s each)[5] so taking measurements takes quite a bit of time as well. However, the ArtTAX is very precise – the range of the measured spot is 0.62 mm / 0.1 mm while for Tracer III it is 3.5 mm. Another advantage of ArtTAX is a CCD camera, which allows the operator to see the analysed point and its colour precisely, and record the image.

In comparison to the ArtTAX, the Tracer III is small and can be handheld, though not very light at 2 kg. The Tracer III is operated by battery so the measurements can be performed in various places, without access to electricity. This device is also equipped with an XFlash Silicon Drift Detector (SDD), which provides high speed data acquisition (eg. 6–8 s). This feature saves time, allowing for more measurements to be taken within a limited duration.. On the other hand, the Tracer III is lower precision compared to ArtTAX. Furthermore, the Tracer III has no CCD camera, which could additionally affect the accuracy of the analysis. Therefore, combining both devices optimised the effects of our investigation.

Measurements results. Pigments usage in the painting

Measurements made in 245 points across the painting, additionally supported with sample investigations allowed not only to identify the pigments used for the painting but also, to some extent, the way of mixing them by the artist in order to achieve certain artistic effects. Because of the exceptionally big size of the canvas it was not possible to analyse all its parts with great precision, but considerable knowledge was still acquired.

Firstly, it is worth noting that Siemiradzki treated each part of the painting with full artistic commitment, far from a schematic set of paints or painting techniques and their repetition in subsequent parts of the painting. Each cloth, colourful marble, jug, musical instrument or other object of craft was executed with the use of several paints and various painting methods. Despite that there are some commonalities for pigment use in certain parts of the composition, like naked bodies, white clothes, white marble, or hair. Among them, flesh colour forming pigments are most characteristic, especially emerald green[6] being an ingredient repeatedly used. Paints used in those parts contain mainly iron pigments – in bright shades ochre with vermillion and white (mainly lead but zinc

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[5] The acquisition time 300 s and spot size 0.62 mm were used during examination of *Nero's Torches*. However, in some later time ArtTAX 400 was updated, the collimators were replaced by policapilary optical system, thus the acquisition time and spot size were reduced to 40 s and 0.1 mm, respectively.

[6] Emerald green – another name: Schweinfurt green.

FEATURE	ArtTAX	TRACER
MOBILITY	mobile, heavy	mobile portable relatively light (2 kg)
ACCESS TO ELECTRICITY REQUIRED	yes	no
CAMERA	yes	no
PRECISION	0.62 mm → 0.1 mm	3.5 mm
TIME OF SPECTRA ACCUMULATION	Long (300 s → 40 s)	Short (eg. 6 s)

Tab. 1. Comparison of the two X-ray fluorescence spectrometers: ArtTAX® μXRF spectrometer and Tracer III (Bruker AXS Microanalysis)

as well), otherwise also with strontium yellow added. In dark shades also iron red, umber and (probably) copper brown are present. Both delicate shades of pale skin flesh colours, as well as the dark reds and browns are disrupted by the painter by an addition of a less obvious emerald green, giving them sometimes even greenish tint. The use of copper and arsenic compound green in flesh colours is distinctive for Siemiradzki. This pigment was identified in many paintings[7], even for dark coloured figures (e.g. *Martyrdom of St. Timothy and his wife Maura*)[8]. The colouration of the black skin of the Nubian slaves depicted in *Nero's Torches* is achieved mainly through the use of ivory black with umber. It also contains small additions of other pigments like vermilion and the aforementioned emerald green. A similar set of pigments was identified in the parts depicting dark hair, predominately ivory black, as well as umber, some ochre, vermilion, and a copper pigment[9].

[7] In the light skin flesh tones for example in the pictures: *Roman Rural Woman* (*Fishing*), *Christ Amongst Children*, *By the Source Portrait of the Artist Alexander Stankiewicz* (paintings from the National Museum in Warsaw), *In Spring* (owner: The Royal Wawel Castle Museum), *Portrait of Mother*, *Portrait of the Son Leoś* (paintings from the National Museum in Kraków) and other pictures.

[8] Collection of the National Museum in Warsaw.

[9] Basing on the XRF spectrum it is hard to explicitly determine whether, apart from copper green detected in many parts of the painting, copper oxide black (copper oxide II) or copper brown (copper oxide I – more probable) is also present. It is difficult especially because vermilion and white lead is

A very different, much softer colour scheme with a narrower set of colours, can be found in the white clothes and marbles. It has to be noted that lead white used for the roman patrician gowns is rarely pure paint from a tube. Siemiradzki differentiated its shades with minute additions of iron pigments (ochre and umber) and chromium yellow. Some additions of a copper pigment (unidentified) can be found, charcoal plant black could also be used, although it is not possible to identify it by X-ray fluorescence[10]. A similar set of lead white additions can be found in the section of white marbles.

The broad part of the sky is especially interesting as far as the pigments used and the painting technique is concerned. This vast plane presents a diversified colouring, and the upper, grey-blue part is built with rhythmical, slanted brush strokes laid in a way that the brown underpainting is visible from underneath[11]. These efforts cause the big area of the sky to be uneven, a little vibrant thus not flat, heavy nor oppressive. The lower parts, in high blue colour with a violet and pink hue is a typical pigment set Siemiradzki used in bright, sunny landscapes for which he was famous. Apart from lead white, cobalt blue is usually identified here, with red additions of vermilion, sometimes iron red or an organic dye[12]. In *Nero's Torches* saturated colours of the clouds at edge of tree tops are achieved by the painter by using lead white mainly with cobalt blue mixed with an iron pigment (possibly Prussian blue or/and iron red – both identified in other parts of the sky), additions of vermilion and a copper pigment (probably emerald green)[13]. In other regions of the lower sky part we find additions of zinc white, ivory black, strontium yellow, umber.

Above the dark blue clouds extends an exquisite, grey-pink blue with violet shades. The recognition of the painting technique and materials applied here, is surprising and a partially unsolved mystery. The colours in this part are very much pale, laid on dark, mainly brown underpainting. The base of the paint on the top layer building the colour of this region of the sky is lead white and a copper pigment identified (SEM EDX analysis) as emerald green (!)[14], and also cobalt blue (used in various proportions depending on the

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present in the examined points of the picture as well. However the use of brown (probably) copper pigment in the picture was proved by means of another technique.

[10] Identified in the picture with microchemical analysis.

[11] At present, the effect is probably partially intensified by the loss of opacity of the oil paint.

[12] These pigments were identified in the following pictures in the section of the sky: *Roman Rural Woman* (*Fishing*), *The Leading Light of Christianity* (oil sketch to the *Nero's Torches*), *Calvary*, *View from a Bay from a Rocky Shore* (paintings from the National Museum in Warsaw), *In Spring* (Wawel Castle), *Landscape with Figures*, *Girl at a Well* (paintings from the National Museum in Kraków) and others.

[13] It is probably Schweinfurt green (emerald green), identified in other parts of the sky. Simultaneous presence of a copper pigment together with lead and mercury, whose lines in the XRF spectrum coincide with arsenic lines do not provide a clear answer.

[14] Schweinfurt green – $3Cu(AsO_2)_2\,Cu(CH_3COOH)_2$ – "has an unusually brilliant blue-green to green hue". E.W. Fitzhugh (ed.), *Artists' Pigments: A Handbook of their History and Characteristics*, Vol. 3, National Gallery of Art, Washington, D.C., 1997, p. 219. Both XRF analysis, as well as SEM EDX analysis of individual grains showed the presence of copper and arsenic, as is also proved by microscopic observations of the samples in visible light and ultraviolet radiation. This pigment was also identified in the sky section of the following pictures: *Scene from the Life of the Early Christians*, *Ruins of a Roman Villa* (paintings from the National Museum in Kraków), *Martyrdom of St. Timothy and his wife Maura* and the copper green (possibly emerald green) in the *Christ Amongst Children* (both picures

area.). The pink hue is created by the addition of vermilion and organic red[15]. Analysis of samples (in visible light and UV radiation) taken from the upper parts of the sky do not definitely confirm visual observations (2,5x magnification) meaning the presence of a brown underpainting as a separate layer. In the cross sections, a form of a brown layer is noticeable, seamlessly transforming into a blue layer, and can be explained as a painting technique called "wet in wet". Below, on the ground layer, a very light paint layer can be found containing, apart from lead white, vermilion, ivory black, iron red, Naples yellow and intrusions of cobalt blue (Fig. VII). It was not possible to identify the brown tinting component in the lower part of the upper grey-blue layer. Basing on the SEM EDX analysis we can deduct it is an organic dye, an orange fluorescence (Fig. VIII) of amorphic particles pointing at madder lake[16]. However, this does not fully explain the colour of the underpainting visually recognized as brown. We also can't exclude that the colour is additionally created by a kind of organic medium or siccative saturating, the blue-grey paint layer, and partly the pale underpainting[17]. Other pigments were identified as additions to paint in the sky section – Prussian blue, charcoal plant black, iron red[18].

Another blue pigment was identified in the lower part of the painting. Measurements taken in the section of a group in the foreground, indicated high tin content at different points of various colours, like the violet dress, colour of carnation or the yellow paint of the sandal of the woman (Fig. IX). Because it was usually accompanied by cobalt, the conclusion was that the whole fragment was first underpainted by Siemiradzki using cerulean blue. In the final version, the painter decided to intensify the colour, so in the last layer, the artist used cobalt blue mixed with some other pigments. The conclusion, that Siemiradzki created a wider underpainting, was confirmed by the X-ray image and by the analysis of the cross-section taken from the violet dress. Cerulean blue mixed with white (lead and zinc) is also the main component of the paint that forms the light blue gown of the woman standing at the stairs.

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from Warsaw), still in these pictures the green copper pigment was present in smaller amounts. It is also possible that Siemiradzki used another variety of copper arsenic pigment which was probably of more blue hue –Schweinfurt blue (or Reboulleau's blue). Field listed it in his *Chromatography* describing it to be the same substance as Scheel's green. G. Field, *Chromatography: or A Treatise on Colours and pigments and of Their Powers in Painting*, London 1841, p. 209; N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall *Pigment Compendium: A Dictionary and Optical Microscopy of Historic Pigments*, Routledge, 2013, p. 325, 342. However the grains of pigment observed by use of microscope look more green then blue.

[15] Organic and iron red in the sky was identified by dr P. Karaszkiewicz during examinations while the conservation of the painting in 2003–2004. E. Zygier, R. Klincewicz-Krupińska, J. Czop, *Dokumentacja konserwatorska. Henryk Siemiradzki „Pochodnie Nerona, Świeczniki chrześcijaństwa"*, Kraków 2004, p. 7 and Annex; unpublished. The presence of these pigments is partly confirmed by microscopic analysis of cross sections of samples taken from the sky and also by lack of other results in the red grain measurement SEM EDX method (towards an organic dye).

[16] *Artists' Pigments: A Handbook…*, p. 124.

[17] From Siemiradzki's notes we know that he used the siccative Haarlem, see. H. Siemiradzki, unpublished notebook (National Museum in Krakow, NI 318439, p. 15). It was produced from thickened oil and dammar varnish and doesn't include metal components. M. Doerner, *Materiały malarskie i ich zastosowanie*, Warsaw 1975, p. 78; Church claims that small proportion of that siccative doesn't affect the colour of paint. A. Church, *The Chemistry of Paints and Painting*, London 1890, p. 129.

[18] Microchemical analysis identification.

Sophisticated colour mixtures can be found in many textiles. A dark brown *pallium* with a green tint of a man adorned with a yellow flower coronet is a mixture of ochre (possibly with an addition of umber) with emerald green and a minute dose of strontium yellow and ivory black. A fancy brown of the textile is apposed with a blue trimming painted using cobalt blue with Prussian blue, locally lighted with lead white. The flowers on the Roman head are painted with the use of a deep, sculpture-like texture made of zinc white combined with zinc and strontium yellow, additional ochre brush strokes can be seen in the depressions of the texture.

The light yellow, shiny dress of a Roman woman sitting next to a gladiator is based mainly on zinc yellow mixed with lead white. Equally shiny, though more decorative Nero's vestment is lead white with strontium yellow and ochre with an addition of emerald green.

Nero's Torches is not only calm, exquisite shades. Colourful robes of the people in Nero's suite posed a good excuse to place intense patches of colour of explicit tint. These numerous, multicolour accents invigorate the painting. However, Siemiradzki painting rarely used pure paint "of the tube". Hence, the gown of the woman holding a lyre, in the foreground, owes its distinctive colour to a mix of cobalt blue with chromium pigments (chrome yellow and viridian)[19], locally with an addition of emerald green. Colourful designs on the textile present a handful of pigments – besides these forming blue we have to mention cadmium yellow, ochre, vermilion, iron red, ivory black, zinc white, an addition of strontium yellow and another chromium yellow (lead or zinc chromate).

The colour of the violet cloth hanging on the arm of the young man holding a jug, sitting next to the woman, is also based on the cobalt blue mixed with white (lead white and zinc white), as well as with a red organic dye[20]. Its shade is intensified by the brown underpainting consisting mainly of copper brown with the admixture of ivory black (Fig. X) and also of a red organic dye. There is also an addition of vermilion and emerald green in this layer[21]. The brown colour of the underpainting creates especially dark parts of the fabric's folds.

A deep red robe of a half-naked woman right behind the girl with a lyre is layer constructed. Siemiradzki laid organic red glazings (carmine lake and madder lake) especially in darker, deeper parts upon an underpainting made of vermillion mixed with an iron pigment (iron red or/and umber).

Deep greens of a textile hung on the sphinx statue and also of the *pallium* of a glamorous young man placed bellow the stairs contain apart from few other pigments (locally,

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[19] Identification of pigments in this region by XRF spectroscopy was partially supported by microchemical analysis of the sample.

[20] The conclusion about presence of the red dye is drawn on the basis of visual analysis.

[21] The SEM EDX analysis of the sample taken from the fragment of dark fold of the violet cloth provided some new information. Despite of presence of two copper pigments in the brown underpainting of the violet cloth it was possible to prove that copper brown is one of its chief components. The red organic dye is probably settled on aluminium hydroxide, which we may suppose because this element has been identified in the measure of the red grain. The microscopic and SEM EDX analyses also showed another, subsequent layers underneath the brown one: a yellow layer (ochre and strontium yellow), a blue layer (mainly cerulean blue with admixture of ivory black – already mentioned blue underpainting of the whole section), an orange-red layer (red ocher and emerald green) and a pale brownish-red layer (not analysed).

different shades) a great amount of emerald green. The colour of the textile hanging from the pedestal contains probably also another copper green without arsenic. This deep colouring Siemiradzki achieved by applying two (or more) layers of semi transparent green paint.

A subsequent intensively colourful place, located almost exactly at the crossing of the composition's diagonals are the yellow tunics of the slaves carrying Nero's palanquin. Here Siemiradzki used the strong colour of cadmium yellow mixed with ochre and an addition of a chromium pigment. Among other vivid colours adding distinct colourful accents to the painting, is vermilion, present in almost every patch of vivid red.

The next paint introducing vivid colouring to parts of the composition is cobalt blue. It was used in mixtures; yet, sometimes the artist applied it practically in pure form (e.g. tapestry of the palanquin, flowers on torches). In the flame of the torch, held by a slave about to emblaze the the bound victims, painted in a high impasto manner, Siemiradzki used two types of white (mainly lead but also zinc), vermillion and iron reds lighted with chromium yellow. The yellows in the flame also are: cadmium and strontium, both being of distinctively different shades. The blue shades of the fire are due to the use of cobalt blue.

In the famous work of Siemiradzki attention to detail extends beyond the masterly painted clothing. The artist was always admired for his outstanding ability in creating illusions of various textiles but also of metals, jewellery, marble, everyday life objects.

Freely, almost abstractly painted marbles of different types, including red and blue-green ones, are a mixture of patches, smears and brush touches. For red stones Siemiradzki used mainly iron reds and a copper pigment and an addition of vermillion. In dark spots bone black and a copper pigment were identified. Blue tinted marbles were painted using Prussian blue in a mixture with lead and zinc white, with additions of emerald green, cadmium and chromium yellow. Dark spots are again ivory black and a manganese containing iron pigment – probably natural umber. Green types of marble have a dominant of emerald green mixed with iron pigments (Prussian blue, umber, ochre), sometimes cobalt blue is also present.

The ochre-grey colour of the marble floor was executed with iron pigment, umber and ochre, also with an organic black (probably charcoal black) with an addition of cobalt blue and vermillion.

The signature, placed by the artist in the bottom right corner is a mix of iron pigments – burnt umber and iron red.

Complementation of non-invasive analysis with pigment identification methods requiring samples

The X-ray fluorescence spectroscopy does not allow to define, unequivocally in all cases, the kind of inorganic compounds composing the pigments in the paint layers. The results obtained by XRF spectroscopy are the elemental composition of inorganic substances, which are the subject of further interpretation. Therefore the obtained results were supplemented with data gained through methods that require the collection of samples. The following techniques were applied: optical microscopy and microchemical analysis, Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM EDX), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Powder Diffraction (XRPD), High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS), and the canvas support's fibre identification with the use of Schweizer's reagent.

Combining the microscopic analysis of the paint layers' cross-sections with the SEM EDX method allowed determining the painting method and pigment composition in some parts of the painting. Investigation of the samples' cross-sections confirmed that Siemiradzki painted most parts of his picture in several layers. Some examples have already been presented in the previous section. Thanks to combining both methods, it was also determined how the green cloth (*pallium*) of a character in the foreground was executed. The painter obtained the sophisticated colour of the fabric starting with a brown-greenish underpainting (based mainly on earth pigments, ivory black and lead white with some addition of strontium yellow and emerald green), on which he introduced thick, light impastos mostly made of white lead mixed with green earth. At the end, the artist put on a thin layer of green earth which is partly transparent (Fig. XI, XII). Examination of another sample taken from a woman's necklace revealed that to imitate its gold parts Siemiradzki painted thick impastos based particularly on zinc white with an addition of zinc yellow and ochre. Again, yellow glazing was applied over the 'white' impasto (the presence of lead and chlorine in SEM EDX analysis points at Cassel yellow). Thus the painter obtained the special brightness of the colour.

The microscopic analysis of cross-sections of other samples showed that the underpainting was often of a different colour than the final layer, and that it was frequently brown. Whereas the sample taken from the mould of the plinth, on which the artist placed the Athens' quadriga confirmed that initially a sky part was intended there (above the two sided slanted roof). The blue colour of the sky is put directly on the ground and then covered with two layers of white paint containing some admixtures of other pigments.

The microchemical analysis also resolved many doubts and clarified some of the ambiguous results obtained by XRF spectroscopy. As an example, the spectra detected in the section of the dark blue cloth of a woman standing on the stairs indicated among other elements the presence of cobalt, copper and iron the interpretation of which was equivocal (there are several pigments containing iron). Microchemical investigations proved that in this colour iron is a component of Prussian blue, as well as it confirmed presence of cobalt blue and copper green. This shows that Siemiradzki mixed different shades of blue.

Combining the results of XRF, microchemical and microscopic analyses allowed us to identify viridian and strontium yellow in the green colour of the algae growing at the stone of the fountain. A great quantity of chromium detected by XRF did not clear the type of the chromium pigment used. Microscopic observations of yellow and green particles in the powder sample and confirmation of the presence of Cr^{+3} ions (Cr_2O_3 x H_2O – viridian) and CrO_4^{-2} ($SrCrO_4$ – strontium yellow) in comparison with XRF did clarify the type. What's more, in the analysed stone area an addition of emerald green, iron pigment (probably ochre or umber) and of course a great deal of lead white were detected. Viridian and green also tints the wellhead of the oval tank under the fountain.

Microchemical analysis also helped with the detection of an organic black – plant charcoal black (K_2CO_3) – other than ivory black (identifiable by XRF) in the painting.

FTIR spectroscopy proved to be useful, especially for the identification of the paint and ground binders and expanders, as well as some of the organic pigments used by the artist. During the analysis of the sample of the ground distinctive bands for an oil medium, lead white and carbonate compounds (chalk) were detected. Examinations of this layer with SEM EDX additionally proved the presence of barium white used as filler.

Organic dyes were identified by means of HPLC-MS method. These precision analyses provided very interesting results. Two samples of green paint containing barium sulphate[22] as a substrate on which the dyes were embedded underwent the examination. Presence of the components derived from the *Rhamnaceaea* family species (kaempherol, quercetin – from Persian berries) were detected, as well as luteolin (from *Reseda luteola*) and fistein (*Cotinus coggyria* L.). These components give yellow (still de grain) or green (sap green) dyes[23]. The red organic dye[24] was identified to be a mixture of carmine lake and madder lake. The cochineal extract (carminic acid, kermesic acid), as well as purpurin and alizarin (derived from *Rubia tinctorum*) were detected[25].

A microscopic analysis of the canvas's thread sample with use of the Schweizer's reagent was performed to identify the kind of fibre. Linen was proved in the examination.

XRPD did not provide any spectacular results probably due to the fact that the samples taken from the painting were extremely minute, and too small for the X-ray powder diffraction (microdiffraction has not been executed). However, the presence of a red earth pigment in the crystalline form of hematite was confirmed.

Combining all these techniques with the non-invasive X-ray fluorescence we were able to identify the rich palette of around 25 colours that Siemiradzki used in the painting, and to determined the method of binding them by the artist. The identified pigments are: lead white, zinc white, cadmium yellow, chrome yellow, strontium yellow, zinc yellow, yellow ochre, Naples yellow[26], Cassel yellow[27], vermilion, red iron pigment, madder lake, carmine lake, cobalt blue, Prussian blue, cerulean blue, emerald green, green earth, artificial copper green, viridian, green based on organic compounds (sap green or still de grain (?) settled on barium white, umber (natural and burnt (?)), copper brown or black, ivory black, plant charcoal black. It has to be stressed here that in Siemiradzki's paintings examined until now a distinctive feature was observed – the use of many types of pigments in one work. In such a large painting as *Nero's Torches* it seems obvious

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[22] Its high content was detected by XRF measurements, presence proved by microchemical analysis.

[23] All of the berries of various species of the Rhamnacaceae family were used to produce a yellow or green dye. The color depended on the ripeness of the berries. N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall, *op. cit.*, p. 328.

[24] The sample was taken from the red cloth of a woman situated at the bottom of the picture.

[25] The HPLC-MS examination and the interpretation of the results was performed by dr hab. M. Śliwka-Kaszyńska and O. Otłowska as a part of the project: *Identification of the organic dyestuffs used by the Polish artists of the 19th century. The investigation of the influence of UV radiation on the dyes' ageing process, the identification of the degradation products* carried out under the aegis of the National Center of Science.

[26] Identified only in the underpainting of the sky in one sample.

[27] Identified in one sample in the top paint layer.

but also in other small or medium sized works repeatedly a dozen or so kinds of paints were indentified. We also managed to specify some characteristic features, like the use of emerald green in the flesh of the skin, which is not so obvious. Probably the most interesting findings, as far as the identified pigments are concerned, is that Siemiradzki used emerald green as a significant component of paint applied in the sky section, another is a very wide palette of yellow shades (7 types of yellow pigments with 3 chrome yellows among them).

Conclusions

In conclusion, the examination of the whole picture of such a large scale without removing it from exhibition was possible only thanks to the application of modern techniques and mobile equipment. Considering the exceptionally large size of the painting and the number of analyses carried out, the research may be recognized as unique and record-breaking. The achieved results are the effect of the whole team's work and commitment.

We managed to obtain most of the information about the painting by using non-invasive methods. The analyses that were carried out allowed to determine the creation process, as well as the technique and the palette used by Siemiradzki in this prominent work. The results of the examinations allowed us to complete our quest for the comprehensive knowledge of the famous artist's technique.

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