RAMAN SPECTROSCOPY OF THE WORKS OF SZYMON CZECHOWICZ (1689-1775)

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1. Introduction

The Polish and the Ukrainian collections of Szymon Czechowicz's works are the subject of this study. The artist (Figure 1) was born in Cracow in 1689 and made his first steps in the profession at the court of Maximilian Franz Ossoliński under the supervision of an anonymous painter. Ossoliński perceived the talent of his pupil and sent him to continue his studies in Rome around 1711 where he spent around twenty years. In 1716 he took part in the prestigious Clementine competition of the Academy of Saint Luke. He won the third prize of the second grade in the painting category for the drawing entitled *The victorious return from the war expedition*. This enabled him to become acquainted with the paintings of artists such as Raphael, Reni, Baraccio, Rubens, van Dyck and others, whose pictures he copied. The best known and archivally certified work of the artist from this period is the image of Saint Jadwiga, made for the Polish church of Saint Stanisław in Rome. In the Eternal City, the artist also painted for other Polish churches; among them the Piarist church in Cracow and the *Assumption of the Blessed Virgin Mary* for the Cathedral in Kielce.

Around 1731, Czechowicz returned to Poland and tried to gain the title of court painter but was unsuccessful. In the 1750s he had a studio in a tenement house in the Old Town in Warsaw, together with the painter Łukasz Smuglewicz (1709-1780). He trained numerous students who, after his death, reproduced the composition schemes and technique learned in the master's studio. Their studio was recognized as the first Polish school of painting. Czechowicz's best and most well-known students included Antoni Albertrandi, Jan Bogumił Plersch and, related to him, the famous family of artists, the Smuglewicz, among them the especially outstanding Franciszek Smuglewicz.

Czechowicz was an independent artist who worked for various church and secular contractors. His paintings are mainly focused on religious themes, but he painted portraits as well. His patrons were high priests and Polish magnates such as Ossoliński, Tarło, Sapieha, Sułkowski, Branicki and the Rzewuski family. He was commissioned to

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paint art works by the Piarists nationwide. He also painted for the Jesuits, the Capuchins, the Carmelites, the Visitants and others. He worked in many localities then belonging to the Polish-Lithuanian Commonwealth, located in today's Poland, Lithuania, Ukraine and Belarus: in Warsaw, Cracow, Poznań, Podhorce, Polotsk, Vilnius and many others [1]. In all he left several hundreds of paintings and dozens of drawings.

Figure 1. "Portrait of Szymon Czechowicz", by an unknown 19th-century painter (The National Museum in Warsaw/ Poland)

This paper presents the results of Raman spectroscopy (RS) examinations of dozens of the works painted by Szymon Czechowicz (1689-1775) and his workshop, the most outstanding and prolific Polish artist of the late baroque. The studies are part of a large project concerning the characterisation of his oeuvre, techniques, and the technology used by Czechowicz. It also includes, conservation research on the paintings that have been attributed to the artist, selected works by his students and a comparative study of those paintings whose authorship is uncertain. The importance of the artist made this research necessary, as well as the fact that numerous works have been falsely attributed to him. This erroneous information is popularised by websites with their extraordinary power of dissemination, often resulting in mistaken assessments of his artistic achievements, especially from the perspective of Polish art. For these reasons, in the period from 2012 to 2017, the paintings of the artist from the Polish, Lithuanian and Ukrainian collections were subjected to invasive and non-invasive tests. Before the chemical analysis, a series of photographs of the paintings were taken in different ranges of electromagnetic radiation: ultraviolet light, near infrared and X-radiation. An elemental, non-destructive analysis of the paint layers was carried out using a portable X-ray fluorescence spectrometer (XRF). Samples were also taken for specialist examinations such as X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD) and ATR infrared (FTIR) tests. In addition, an analysis of the elemental composition was performed for the cross-section samples using Scanning Electron Microscope coupled with an EDS electron microprobe (SEM-EDS). If any of the analyses gave ambiguous results, RS was employed for clarification. In this paper we present the results concerning only the pigments and the fillers of the paint and ground layers, as these results were the most significant.

2. Experimental

Raman spectra were recorded using a SENTERRA Micro-Raman spectrometer equipped with two lasers, providing excitations at 532 nm and 488nm. The confocal microscope with objectives of 50x magnification assured the spectral footprint of the sample surface area down to about 5x5 μm^2. Detection was provided by a Peltier-cooled CCD detector operating at -65 ^oC. The spectrometer calibration was performed using the polystyrene standard. Spectra were acquired over a range of 50–4000 cm^{-1} at a resolution of 3 cm^{-1}. Depending on the signal intensity, up to 20 spectra of individual samples (5s acquisition) were accumulated and averaged. Pigments and paint components were identified based on the reference spectra from digital Raman libraries [2, 3, 4, 5].

Elemental analysis of paint layers was carried out using a portable X-ray fluorescence spectrometer (XRF) constructed in the Department of Photophysics of the Polish Academy of Sciences in Gdańsk. This spectrometer was equipped with an X-ray excitation source operating at 55 kV (Oxford Instruments) and a sensitive SDD type detector (Ketek) with an energy resolution of 155 eV for the Mn Kα line (5.9 keV). Detection depended on the elemental atomic mass and ranged from 50 to 340 ppm. Since the measurements were conducted in regular air atmosphere, the measurement range was limited to elements with the atomic number Z: $19 \leq Z \leq 92$. The research was conducted on the objects *in-situ* in museums and churches [6-8].

In addition, an analysis of the elemental composition was performed for the cross-section samples using a JSM-6380LA (JEOL) Scanning Electron Microscope coupled with an EDS electron microprobe. *Energy Dispersive X-ray micro-analyses* were performed at the Department of Geology of the Warsaw University. The test data encompassed: – accelerating voltage: 20kV, – beam current: 60mA, – vacuum: 30 Pa, – duration of point analysis and the area: 100s – working distance: 10m. The research was conducted using the so-called low vacuum technique. The pictures were recorded in the light of reflected electrons.

The diffraction patterns of the tested samples were made by the Structural Powder Diffractometry Team from the Faculty of Chemistry of the Jagiellonian University. The samples were subjected to the non-reflective bracket for diffraction measurement. The X-ray diffraction (XRD) experiments were performed using Cu Kα radiation from a PanalyticalX'pert pro MPD diffractometer. The measurements were taken employing Bragg-Brentano geometry in the 2θrange of 4.0-60.0° with a measurement step size of 0.026°. Analysis of the obtained diffraction images was made in the X'pert HighScore program, using the PDF-4 + 2014 diffraction database [9].

For further pigment analysis, the ATR infrared (FTIR) technique was applied. The analyses were performed respectively with the Bruker Alpha FTIR spectrometer (Bruker) and IR Affinity-1 (Shimadzu), equipped with a Gladi ATR attenuated total reflection (ATR) accessory with a diamond crystal (Pike Technologies). A total of 60 scans were collected in the 4000–400 cm^{-1} spectral range, while the resolution employed was 4 cm^{-1} [10-12].

3. Results and discussion

The RS studies were performed only for those samples for which the other techniques. i.e. XRF, SEM-EDS, XRPD, FTIR, gave unclear results.

The collection of pigments in the eighteenth century was very limited. The results of the research show that Czechowicz applied only a few pigments and that they were easily available. Moreover, the complex studies of the paintings proved that he narrowed down the paint-palette used by his contemporaries to a few basic elements. In the painter's workshop, burdened with a great many orders, price certainly played a considerable role in the selection of materials. These were mainly iron oxide pigments: yellow, red, brown; lead pigments: lead white, massicot; black pigments: bone black, lamp black, and vine black. In addition, he used pigments such as Naples yellow, cinnabar, Prussian blue as well as organic reds.

The elemental analyses performed directly on the tested object with the XRF method gave a general view of the composition of the studied areas or points. Further specific information about the composition of individual technological layers and specific pigment aggregates were obtainable thanks to the SEM-EDS assays executed on the cross-sections. An unambiguous interpretation of the results is possible only for some of these, i.e. those with a very characteristic composition, such as cinnabar (HgS). However, these methods are unable to distinguish pigments with a similar elemental composition of mixtures, such as for example iron or lead pigments. Moreover, distinguishing all types of carbon blacks in mixtures is impossible. XRD can solve some problems; the main drawback of this method being the amount of the sample used for the analysis. Therefore, RS was necessary to identify the types of paint and ground layer compounds.

3.1. Grounds

Szymon Czechowicz used coloured grounds in different shades of so-called salmon, red, pink and rarely, the brown colour which is sometimes observed on the canvas edge of his paintings and on the reverse of canvases that have been improperly sized (Figure 2). The fact that the artist used such coloured grounds is not surprising, because they were the shades that were predominantly used in that epoch. Reddish grounds are commonly called *bolus grounds*. *Bolus* denotes a high-quality red hue clay. The bolus ground layer has an Italian pedigree and were in common use in the seventeenth and eighteenth centuries [12]. As the artist was active in Rome, the presence of this kind of ground in his works was to be expected. Analysing the cross sections of the pictures and elemental composition of these layers, obtained by the use of the XRF and SEM-EDS tests, in the works correctly attributed to the artist, the research revealed principal elements such as: C, O, Pb, Ca, Al, Si and Fe (seldom Mg, S, Mn, As and in traces K, Na). The XRD analysis resulted in identification of the main fillers, such as chalk ($Ca(CO_3)$), different kinds of lead whites: cerussite ($Pb(CO_3)$), and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), silica (SiO_2) and in some samples, gypsum ($Ca(SO_4)(H_2O)_2$).

The obtained results suggest that the reddish preparatory layer is mainly composed of iron oxides with aluminosilicates and white grains of lead white and chalk, sometimes gypsum. The Al, Ti, Zn, Si, Mn, K as well as the As, are the chemical elements originating from easily accessible minerals commonly present in natural earth pigments from iron oxide deposits. Raman spectra also confirmed the presence of bands characteristic of chalk − 283, 712 and 1083 cm^{-1}, lead white – 1053 cm^{-1}, as well as iron oxides (Fe_2O_3) − 670 cm^{-1}. According to the data, spectral changes such as the broadening of the bands below 290 cm^{-1} were also found; in addition there were peaks near 400 cm^{-1} (here up to 408 cm^{-1}) which are obvious for materials with substituted Al in haematite (*Al-doped haematite*) [11]. Thus, one can conclude that the ground layers contain a mixture of iron and alumina oxides (Al_2O_3 and Fe_2O_3).

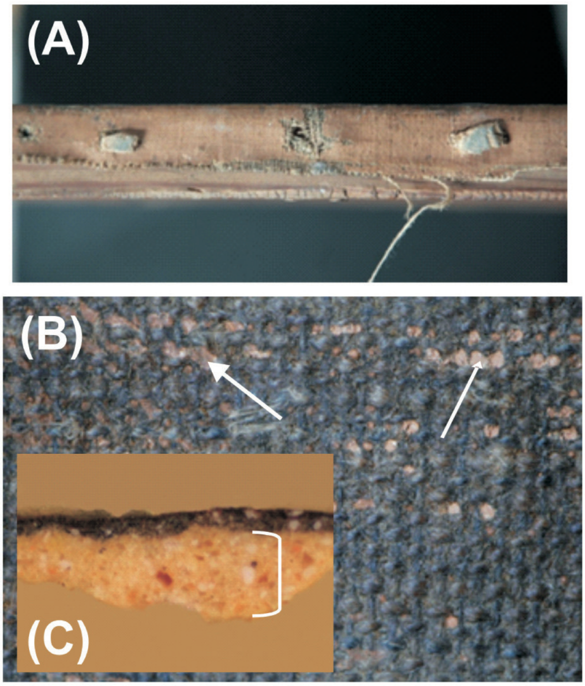

Figure 2. A: Detail of the canvas edge of the oil painting “Saint Margaret Mary Alacoque before Christ” (Lviv Museum of the History of Religion, Ukraine); B: fragment of the reverse of the “Progenitor of the Ossoliński family” (The Royal Castle in Warsaw/Poland); C: cross-section showing ground layer of the painting “Progenitor of the Ossoliński family” (The Royal Castle in Warsaw/Poland).

Raman spectra tests, moreover, surprisingly revealed bands centred at 86, 142 and 282 cm^{-1} which are characteristic for massicot (PbO) and indicated it as one of the main fillers in the layers [14], apart from another lead-based pigment – lead white (Figure 3). Yellow massicot, with a small amount of iron oxides (Fe_2O_3) tinges the grounds in all the pictures from Czechowicz's studio. Massicot can be found as a natural mineral, though it is only found in small amounts. In past centuries it was mined [15, 16]. Differentiating lead white and massicot by means of XRF or SEM-EDS in such mixtures was not possible. The presence of massicot in ground layers in that period of time was not common and unique in Polish art. For that reason, the grounds used by Czechowicz are not typical bolus grounds. Massicot is the ground filler in almost all the pictures painted by the artist and is absent in those which were pained by his followers and in the works incorrectly attributed to him. The presence of massicot in the analysed works may therefore, at times, help in determining their authorship.

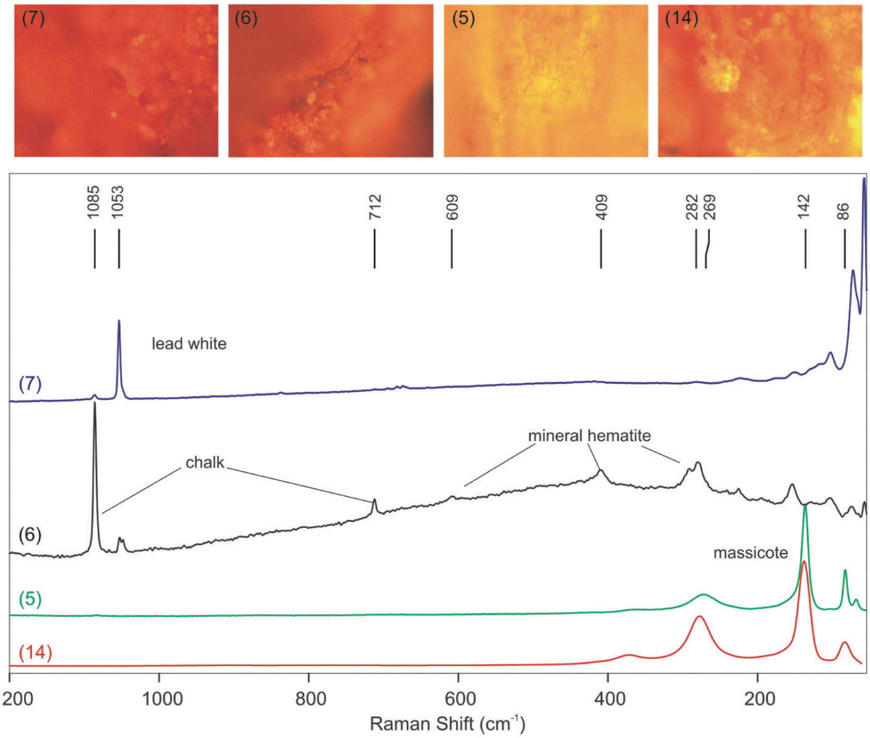

Figure 3. Raman spectra of selected grounds in the oil on canvas paintings: (5)"Saint Barbara" (Lublin/Poland; (6)"Scenes from the life of Saint Anna" (Cracow/Poland); (7)"Saint Barbara" (Drzewica/Poland); (14)"Resurrection" (The National Museum in Cracow/Poland).

3.2. Blue pigments

In the composition of the blue pigment in Szymon Czechowicz's paintings, in almost all analysed samples the SEM-EDS method (Figure 4) identified a significant presence of aluminium (Al), lead (Pb) and calcium (Ca), with a small amount of iron (Fe). This suggested the presence of Prussian blue ($Fe_4 [Fe (CN)_6]_3$) with fillers, such as chalk or lead white. Moreover, the large amount of Al in the samples could indicate an additional filler, e.g. white clay.

The RS studies proved the presence of Prussian blue based on the characteristic bands at 2151, 532 and 270 cm^{-1} (see Figure 5). This blue pigment was discovered in Berlin in 1704 by the dyer Jacob Diesbach and is known as a very strong dark blue colourant, which is why it was commercially available as an already lightened colour. In Czechowicz's works, it appeared around 1730 and became the main blue pigment in the painter's works. In the analysed image samples, it appears in a mixture with carbon black (the characteristic bands at 1596 and 1335 cm^{-1}) in the shadows of the dark blue robes, as well as with lead white (1049 cm^{-1}) in the lighter areas of the robes.

XRD studies showed the presence of cerussite ($Pb (CO_3)$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and calcite (CaCO3) in the blue layers. The same components were identified in the whites used by the artist by XRD which may suggest the whitening of Prussian blue with the artist's white paint. Both Raman studies and XRD did not confirm the presence of white clay. Analysis of the literature on the subject, describing the methods of obtaining Prussian blue in the eighteenth century, informs us that Prussian blues containing a significant amount of aluminium were produced using alum. Aluminium is a by-product of the reactions occurring in the manufacturing process of Prussian blue and is not related to the structure of the pigment [17, 18].

3.3. Green colour

Studies of samples taken from the greens of both draperies and landscape elements of the analysed works revealed the presence of Fe together with Pb, Al, Ca, and Si (Figure 6). The elements, present in low concentrations, were Mg, S, Na, Hg, K, As, P and Sb. The artist obtained the green colour by mixing several pigments. This effect is visible in the cross sections, suggesting the presence of green earth in the samples. However, the RS analyses clearly show that the iron identified in the green layers originates from Prussian blue, which is very easily identified by this method (Figure 7). In the RS analyses of the green pigments, the bands characteristic of Prussian blue appeared each time: at 2153, 534 and 272 cm^{-1}. To obtain the green colour, Czechowicz mixed Prussian blue with yellow pigments, which were most probably composed of Naples yellow ($Pb_3(SbO_4)_2$) (135, 326, 708 cm^{-1}), iron oxide and hydroxide compounds such as burnt sienna (292, 408, 466, 610 cm^{-1}), raw sienna (300, 391, 555 cm^{-1}), yellow ochre, as well as bone black (1603, 1354 cm^{-1}), lamp black (1585, 1348 cm^{-1}), vine black (1265, 1353, 1602 cm^{-1}) and chalk (1084 cm^{-1}). In some samples bone black or lamp black were identified with yellow pigments – Naples yellow and the above-mentioned iron-based pigments.

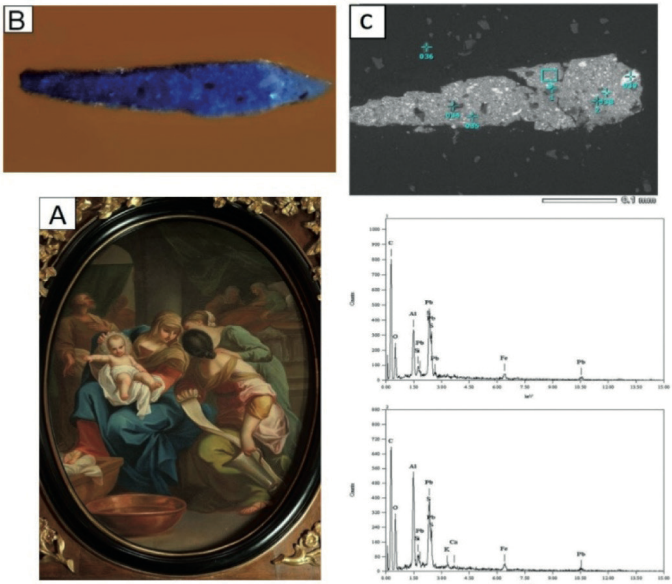

Figure 4. A: Oil on canvas "Scenes from the life of Saint Anna" (Cracow/Poland); B: cross-section showing the blue paint layer of the painting; C: Energy Dispersive X-ray microanalyses results of the cross-section of the blue paint layer sample using an electron microprobe (SEM-EDS).

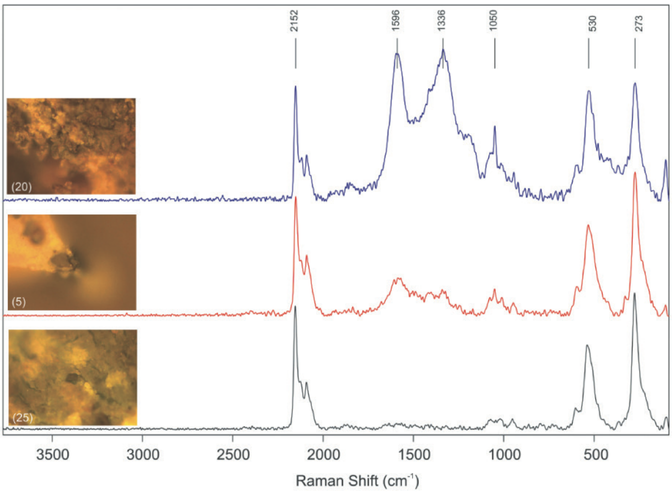

Figure 5. The Raman spectra of selected blue paint layer samples confirming the presence of Prussian blue ($Fe_4[Fe(CN)_6]_3$): (20)"Way of the Cross" (Lviv Museum of the History of Religion, Ukraine); (5) "Saint Barbara" (Lublin/ Poland); (25)"Saint Joseph" (The National Museum in Warsaw/Poland).

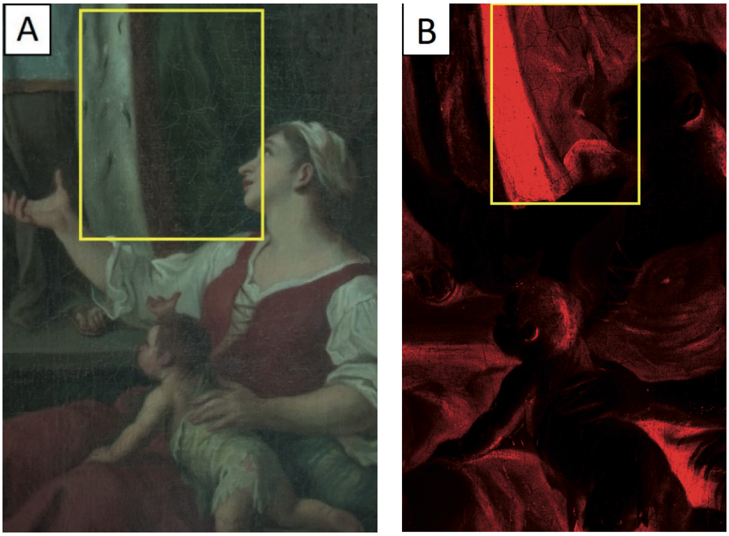

Figure 6. "Saint Elisabeth" (Tykocin/Poland), fragment. A: photo in visible light; B: and in macro-XRF with the iron (Fe) distribution map. A green fragment is marked by a yellow rectangle

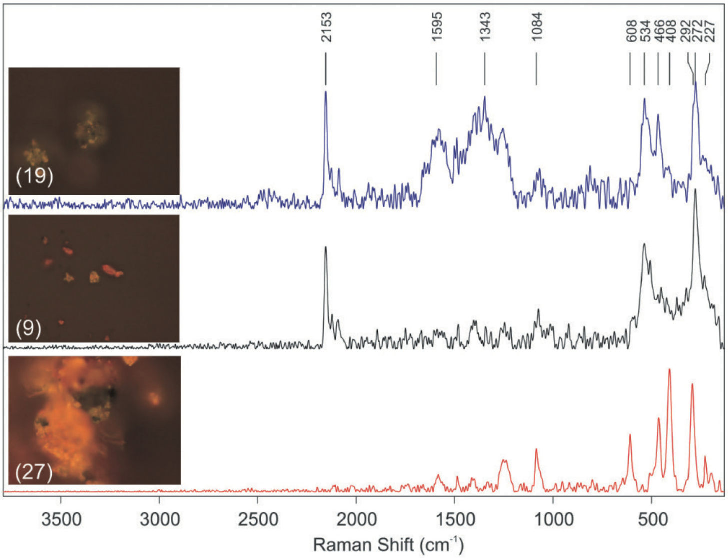

Figure 7. Raman spectra of selected green paint layers, samples: (19)"Saint Benedict" (Lviv Museum of the History of Religion, Ukraine); (9)"Annunciation of the Virgin Mary" (Lubartów/ Poland); (27)"Christ Giving the Keys to St. Peter" (The National Museum in Warsaw branch in Łowicz, Poland).

3.4. Iron pigments

The results of the study of the paint layers in Szymon Czechowicz's works show that the natural iron pigments are the basic ones used by the artist (Figure 8). The results from the SEM-EDS and XRF studies of the brown and yellow layers very often reveal the presence of iron (Fe) with elements such as: Mg, As, Ti, Al, Si, Ba, Mn, Zn, which are present in the accompanying minerals commonly found in natural pigments with an iron oxide or hydroxide base. The iron compounds were identified in the layers of yellow, where different forms of Fe_xO_y with a different degree of hydration, are also very common. Yellow ochre ($FeO(OH)\cdot nH_2O$) was mixed by the artist with white lead, as well as Naples yellow ($Pb_3(SbO_4)_2$). Chalk was also identified in the yellow layers, as well as silica. In the picture *Scenes from the life of St. Anna* (Cracow), limonit ($2Fe_2O_3 \bullet nH_2O$) was identified, as well as warm ochre. In the yellow samples taken from the paintings in the Church of the Holy Trinity in Tykocin, arsenic (As) was identified by the use of SEM-EDS tests, while in the pictures painted in Lwów, magnesium (Mg) and titanium (Ti) were identified in the yellow layers, indicating the different sources of natural yellow pigments used by the artist.

As mentioned above, iron pigments were recognized also in the greens (mentioned above, burnt and raw sienna, yellow ochre) and in the grounds (mentioned above, Fe_2O_3). All shades of brown, both dark and bright, were obtained by the artist using a mixture of iron pigments with cinnabar (HgS), lead white, chalk, Naples yellow, carbon black (C), bone black ($Ca_3(PO_4)_2 + CaCO_3 + C$) and sometimes Prussian blue. The precise assessment of the type of iron pigment in the brown layers was possible only through the RS analysis (Figure 9) [19]. The brown layers revealed the presence of characteristic bands of mainly burnt (292, 408, 466, 610 cm^{-1}) and raw sienna (300, 391, 555 cm^{-1}), as well as warm ochre (608, 408, 293, 226 cm^{-1}). Burnt sienna dominated in the browns of Czechowicz's pictures. The artist mixed it with cinnabar and lead white with chalk. In order to obtain darker shades of brown, he mixed it with black pigments, mainly bone and lamp black. Using non-invasive XRF tests for the brown colour of the paintings from the Church of the Holy Trinity in Tykocin, in addition to iron (Fe), manganese (Mn) was identified, suggesting the presence of raw umber.

3.5. Black pigments

The most popular black pigments in the eighteenth century were bone and ivory black and had been known since ancient times. They generally contained calcium phosphate ($Ca_3(PO_4)_2$, calcium carbonate ($CaCO_3$) and carbon (C); vine black contained 90% carbon (C), insoluble carbon compounds and ashes and lamp black which is an amorphous carbon black made from condensed smoke from the burning of mineral oil, tar, pitch or resin. For the identification of the black pigments, point analyses were used on cross-sections using the SEM-EDS method. The black points of various painting layers were analysed, because black in its pure form does not occur in the artist's works. Very often carbon (C) and phosphorus (P) were identified in these analyses. This clearly indicates that bone black was used in the painter's works. It was also confirmed by Raman tests which revealed characteristic bands for this pigment, centred near 1603 and 1354 cm^{-1}. In a large group of images, SEM-EDS also identified pure carbon (C) on selected dark points.

Figure 8. "Saint Szczepan" (Tykocin, Poland). Fragment – A: photo in visible light; B: macro-XRF with iron (Fe) distribution map.

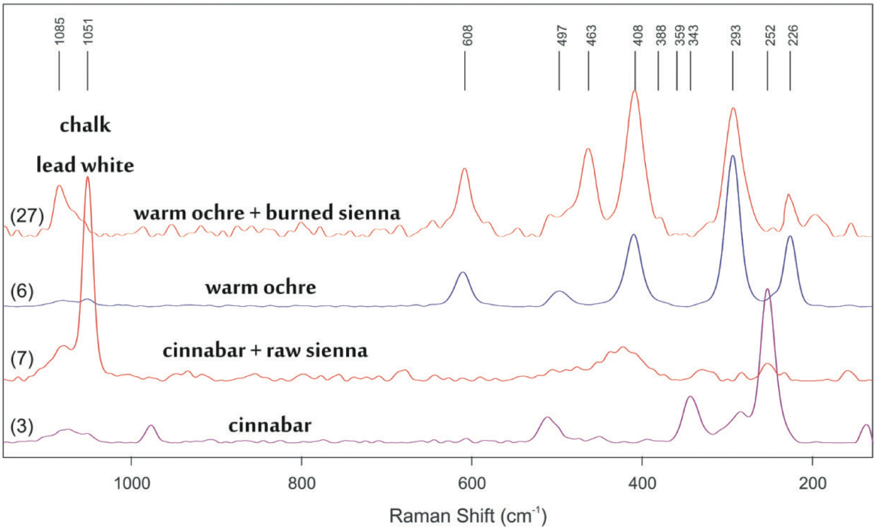

Figure 9. Raman spectra of selected paint layers containing iron oxide pigments: (27)"Christ Giving the Keys to St. Peter"(The National Museum in Warsaw branch in Łowicz, Poland); (6)"Scenes from the life of Saint Anna" (Cracow/Poland); (7)"Saint Barbara" (Drzewica/Poland); (3)"Progenitor of the Ossoliński family" (The Royal Castle in Warsaw, Poland).

RS is known as a very sensitive method for analysing carbonaceous materials; especially the I_D/I_G ratio which is mainly applied to differentiate the various kinds of carbons [20, 21]. A D band is forbidden in graphite structures and its appearance in Raman spectra is connected with double resonance Raman processes induced by lattice disorder and defects causing in-plane breathing vibrations of the aromatic ring structures (A_{1g} symmetry) while the G band is assigned to the in-plane stretching vibration of sp2 carbon (E_{2g} symmetry). The changes in the D/G intensity ratio are not only related to graphitisation of the carbon structure but also to the pyrolysis process occurring during preparation of the carbon material from different organic materials [22]. According to the above, by using the RS results it is possible to distinguish between carbon pigments prepared by means of different methods. However, precise identification of the origin of carbon pigments requires the study of documented historical sources. The mixture of different carbon pigments characterised by the different I_D/I_G ratio, even in one single sample allows us to conclude that the artist used a mixture of carbon blacks of different origin to obtain the black pigment for his paintings (Figure 10).

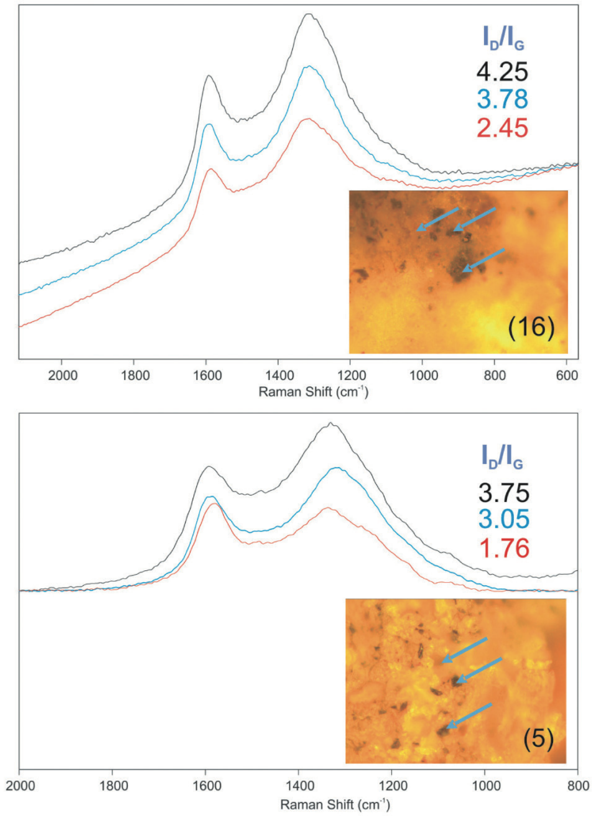

Figure 10. The Raman spectra of selected black pigments: (16)"Saint Bonaventure" (Węgró, / Poland); (5)"Saint Barbara" (Lublin, Poland).

4. Conclusions

The comprehensive study of Szymon Czechowicz's paintings presented in this work allowed the characterization of the materials used in his studio. The results from the RS analyses played a key role in this identification and made it possible to precisely identify the composition of the grounds. In particular, this applies to the indication of the presence of a massicot together with lead white used in the layers. These studies also formed a meaningful contribution to the identification of other pigments with a similar elemental composition that appeared in mixtures such as those in the iron pigments: yellow, red ochre and sienna. The results from RS confirmed the presence of Prussian blue in the layers of blue and green pigments in the analysed images.

Interestingly, the RS research on the black pigments proved that the artist used different carbon mixtures to obtain black paint. Such a diagnosis is impossible to achieve with other methods. In addition, the RS analysis confirmed the presence of pigments used by the artist, that had already been identified by means of other methods.

The main conclusion from the results presented here, is that without RS tests it would be impossible to achieve such precise research results, which are helpful in the authentication of Szymon Czechowicz's works (see Table 1).

Table 1. The Raman tests of grounds, blues, greens, iron pigments – browns and yellows and blacks in the works of Szymon Czechowicz and his workshop

Nr	Title	Year	Grounds	Blues	**Greens**	**Iron pigments**		**Blacks**
						Browns	Yellows	
1	*Saint Jadwiga* (Rome/Italy)	1725	massicot, lead white	–	–	burnt sienna	–	–
2	*The copper snake* (Lviv Historical Museum)	1714-1730	read lead, red ochre	–	–	–	–	–
3	*The Immaculate Conception* (Warsaw/Poland)	1730s (?)	massicot	Prussian blue	carbon black, Prussian blue, burnt umber, chalk	burnt umber	yellow ochre, lead white	carbon black
4	*Progenitor of the Ossoliński family* (The Royal Castle in Warsaw/Poland)	1731-1734	massicot	Prussian blue	Prussian blue, chalk, lead white, burnt umber, carbon black	burnt umber	–	carbon black
5	Paintings from the Missionary Church (Lublin/Poland)	1736	massicot, chalk, lead white	Prussian blue, lead white, carbon black	Prussian blue, chalk, burnt umber, carbon black	burnt umber	–	carbon black

6	*Portrait of the Pomeranian voivode Jakub Narzymski* (The Kórnik Library of the Polish Academy of Sciences /Poland)	1739	massicot	Prussian blue, lead white, coal black	–	–	–	carbon black
7	*Saint Francis* (Lviv Museum of the History of Religion/ Ukraine)	around 1740	massicot, raw sienna, red ochre, minium	–	–	raw and burnt umber	–	–
8	*Annunciation of the Virgin Mary* (Lubartów/Poland)	1740	massicot, coal black	Prussian blue	Prussian blue, chalk, burnt umber	burnt umber	–	–
9	*Martyrdom of Saint John of Nepomuk* (The National Museum in Warsaw/ Poland)	1740s	massicot	Prussian blue	Prussian blue, chalk, burnt umber, carbon black	burnt umber	–	carbon black
10	*Martyrdom of Saint Florian* (The National Museum in Warsaw/ Poland)	1740s	massicot	Prussian blue	Prussian blue, lead white, burnt sienna, carbon black	burnt sienna	–	carbon black
11	*Scenes from the life of Saint Anna* (Cracow/Poland)	1741	chalk, lead white, red ochre	Prussian blue	Prussian blue, chalk, lead white, burnt umber, carbon black	burnt sienna, warm ochre, burnt umber	yellow ochre, lead white, chalk.	carbon black
12	Paintings from the Piarist Church (Opole Lubelskie/Poland)	1745	massicot	Prussian blue	Prussian blue, burnt umber	burnt sienna	–	carbon black, silica
13	*Way of the Cross* (Lviv Museum of the History of Religion/ Ukraine)	1747	–	Prussian blue, lead white, chalk, coal black	–	burnt sienna	–	carbon black
14	*The Entombment* (The National Museum in Cracow/ Poland)	1747	red lead	–	–	–	–	–

15	Paintings from the Church of the Holy Trinity (Tykocin/ Polnd)	1749-1750	massicot	Prussian blue	Prussian blue, chalk, yellow ochre, carbon black	–	yellow ochre, chalk, cinnabar	carbon black
16	*Christ* Giving *the* Keys to St. Peter (The National Museum in Warsaw branch in Łowicz/ Poland)	around 1750	massicot	Prussian blue	Prussian blue	burnt sienna, lead white, chalk, warm ochre	–	–
17	*Child Jesus* (Lviv Art Gallery named after Boris Woźnicki/ Ukraine)	around 1750	massicot, raw umber, chalk, read lead	ultra-marine, Prussian blue	–	–	–	carbon black
18	*Child Jesus* (Lviv Art Gallery named after Boris Woźnicki branch in Olesko/ Ukraine)	around 1750	chalk, burnt sienna, massicot	Prussian blue, caput mortum	–	burnt sienna, chalk, raw umber	–	carbon black
19	*Saint Margaret Mary Alacoque before Christ* (Lviv Museum of the History of Religion/Ukraine)	second half of the 1750s	massicot, raw sienna, red lead	Prussian blue	Prussian blue, gypsum, chalk, lead white, burnt umber, carbon black	burnt umber	–	carbon black
20	*Saint Benedict* (Lviv Museum of the History of Religion/ Ukraine)	1756-1758	read lead, raw umber, red ochre	Prussian blue	Prussian blue, burnt umber, carbon black	burnt umber, cinnabar, carbon black, chalk,	–	carbon black
21	*Saint Scholastica* (Lviv Museum of the History of Religion/ Ukraine)	1756-1758	–	Prussian blue	–	–	–	–
22	*The Presentation of the Virgin at the Temple* (Lviv Museum of the History of Religion/ Ukraine)	1756-1758	red lead, chalk, red ochre	Prussian blue	–	–	–	–
23	*Resurrection* (The National Museum in Cracow/Poland)	1758	massicot	Prussian blue	–	–	–	–
24	*Resurrection* (Lviv Art Gallery named after Boris Woźnicki branch in Olesko/ Ukraine)	1758	massicot, chalk, red ochre	Prussian blue	–	–	–	–

25	*Communion of Saint Stanislaus Kostka* (Lviv Historical Museum)	the end of 1750s	chalk, lead white, gypsum, raw umber, massicot?	Prussian blue	–	cinnabar, carbon black, chalk	yellow ochre, lead white, chalk, raw sienna, raw umber	carbon black
26	*Saint Barbara* (Drzewica/Poland)	1760s (?)	chalk, lead white, red ochre	–	–	burnt and raw sienna, cinnabar	yellow ochre, lead white	carbon black
27	*Madonna* (Lviv Museum of the History of Religion/ Ukraine)	around 1760s	massicot, lead white, carbon black	–	–	–	–	–
28	*Saint. Bonaventure* (Węgrów/Poland)	1760s	massicot	Prussian blue	Prussian blue, chalk, burnt umber, carbon black	burnt umber, cinnabar, carbon black	yellow ochre, lead white	carbon black
29	*Saint Joseph* (The National Museum in Warsaw/Poland)	1760s (?)	massicot	Prussian blue, lead white, chalk	Prussian blue, burnt umber	raw umber, burnt umber	yellow ochre, lead white, chalk, raw sienna, raw umber	carbon black

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Summary

The paper presents the results from Raman spectroscopy (RS) analyses of the works of Szymon Czechowicz and his workshop – the most important Polish baroque painter. RS was used for clarification and supplementation of results carried out by the methods: Infrared False Colour (IRFC), XRF, XRD, SEM-EDS, GC-MS, and ATR-FTIR. A complementary analysis of the artist's work allowed the characterisation of the fillers and the binders of the grounds and the paint layers in his art. The presented results showed that RS was especially useful for identifying the pigments used in the mixtures. It allowed the presence of Prussian blue in the blue and green colours to be determined and made it possible to distinguish the types of iron pigments in the mixtures. The method was useful also for the identification of several types of black pigments in the samples and to identify the massicot in the ground layers which contained another lead pigment – lead white. Tables and figures show the summation of test results carried out by RS analysis, the indication of specific chemical compounds in the painting layers and grounds, all of which provide additional information about the workshop of the most important painter of Polish Baroque. The main conclusion is that without using RS, it would be impossible to achieve these precise research results, helpful in the authentication of Szymon Czechowicz's works.

Riassunto

Il lavoro presenta i risultati delle analisi in Spettrometria Raman (RS) dei lavori di Szymon Czechowicz – il più importante pittore barocco polacco – e del suo laboratorio. La RS è stata usata per chiarire e completare i risultati ottenuti con le seguenti tecniche: fotografia ad infrarosso a falso colore (IRFC), XRF, XRD, SEM-EDS, GC-

MS e ATR-FTIR. Una ulteriore analisi ha permesso la caratterizzazione delle cariche e dei leganti dell'imprimitura e degli strati di colore. La presentazione dei risultati ha mostrato che RS è stato particolarmente utile per identificare i diversi pigmenti usati nelle miscele. È stato identificato il blu di Prussia nei colori blu e verde distinguendo le diverse tipologie di pigmenti a base di ferro nelle miscele. Il metodo è stato anche utile per identificare i vari pigmenti di colore nero nei campioni e il massicot (monossido diossido) negli strati preparatori che contengono un altro pigmento a base di piombo – biacca di piombo (carbonato basico di piombo). Le tabelle e le figure mostrano i risultati ottenuti con il RS, i composti chimici negli strati di pittura e nell'imprimitura, fornendo dati sulla bottega del più importante pittore barocco polacco. La conclusione è che senza l'impiego della RS non sarebbe stato possibile ottenere i suddetti risultati, permettendo l'autenticazione delle opere di Szymon Czechowicz.