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LIBS, optical and multivariate analyses of selected 17th-century oil paintings from the Museum of King Jan III's palace at Wilanów

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Abstract:
The paper presents measurement results of LIBS and optical microscopy investigations applied to five 17th-century oil paintings, belonging to the collection of the Museum of King Jan III's Palace at Wilanów. The analysis devoted to ground layers at depths of about 200–300 μm (40–60 laser pulses) allowed to find stratigraphy distributions of elements characteristic for ground layers. During the latest investigations, the researchers concentrated mainly on the comparison of some specific elements like Li, Ba, Ti which could indicate the origin of the pigment and help in the process of classification of the paintings. LIBS spectra analyses were supported by statistical factorial analyses which visibly confirmed conclusions drawn from spectral and optical microscopy research.

Keywords: painting analysis, LIBS, multivariate analysis, oil paintings, ground and colour layers, Wilanów Palace Museum

1. Introduction

The Palace in Wilanów is a Polish suburban royal residence located in the south-west area of Warsaw. It was built in the years 1677–1696 as a summer residence for King Jan III Sobieski and his wife Maria Kazimiera. Designed by Augustin Locci, the building combines the character of an Italian garden villa and a French palace in the style of Louis XIV.

King Jan III was a comprehensively educated connoisseur of arts and an attentive artists' patron. He engaged foreign artists for his commissions. Among them there were French and Italian painters. Moreover, the ruler cared for national artists and funded scholarships in the St. Luke's Academy in Rome, which were dedicated to talented Polish painters. The aim of his activity was to educate and form a masterclass of artists for a planned academy, nevertheless the project was never completed. His protégés were Jan Reisner and Jerzy Eleuter Szymonowicz Siemiginowski, both trainees of the Roman Accademia. Jan Sobieski also engaged famous Polish portrait painters such as Daniel Schultz and Jan Tretko named Trycjusz. Many foreign artists worked for the Polish king, e.g. French painters: Claude Callot, Alexandre-Francois Desportes, Henri Gascar; Italian artists, e.g:

Michelangelo Palloni and Martin Altomonte as well as a Dutch painter Ferdynand van Kessel.

The erudite king was also a staunch art collector who looked for art objects all around Europe and even further. Unfortunately, after his death, the rich and valuable collection (which we know following the Inventory of 1696) was divided between his heirs. In result, along with the years passing by, it was scattered, and finally, almost completely dispersed.

Since the end of WWII, art historians have worked on determining what pieces of art were parts of the King's collection. Continuous efforts are made to recreate the royal collection. Although a lot of frescoes or ceiling paintings decorating the palace have survived until today, it is extremely difficult to find easel paintings belonging to the collection of Jan III Sobieski, including those which were created at his request. Over the years they have been subject to exchanges or trade transactions, transformation and more or less skilful conservation works. Moreover, they were usually not signed. Today, it is hard to recreate the collection.

Nowadays, the collection of paintings at Museum of King Jan III's Palace in Wilanów consists of 2291 paintings on canvas and wooden panels. Some of them could come from the royal collection.

The mission of conservators and art historians who currently take care of the collection housed at the Wilanów Palace Museum is to explain the secrets of the objects gathered there. All of them would like to discover information about the workshops in which the paintings were created as well as about their authors.

That is why in 2012 a large and interdisciplinary project entitled "Monumentum Sobiescianum" was initiated by the curators at the Wilanów Palace Museum. Its topic is in -depth research related to King Jan III and his relatives.

In the framework of "Monumentum Sobiescianum", a separate research is conducted, focusing on the recognition of the techniques and technologies of the works painted by the court painters. One part of this project is concentrated on unsigned portraits of Jan III and his family, which were probably painted during the King's lifetime and belonged to the royal collection. In the study, different methods have been used. Beside conventional micro-chemical tests and visual inspection of stratigraphic samples by light microscopy, we have applied modern analytical instrumentation, in particular LIBS but also SEM-EDS, XRPD as well as μ X-Ray Powder Diffraction analyses.

Since 2012 fifteen portraits of the King and his family have been examined – nine of them by Laser-Induced Breakdown Spectroscopy (LIBS).

We have studied stratigraphy distributions of various elements over grounds and paint layers, which allowed us to find similarities and differences of analyzed paintings.

In the current study, we have concentrated on the comparison of the composition of ground layers, essentially some specific elements like Li, Ba, Ti, and tried to classify the paintings according to their content.

2. Materials and methods

2.1. Investigated paintings

The paper describes the examinations made in 2016 on material collected during two campaigns of investigations conducted in the years 2012 [1] and 2014 [2].

In 2012 and 2014, nine oil paintings, portraits of King Jan III Sobieski and his family, were tested with the use of LIBS method and digital 3D microscopy. In 2016, we selected five of them, painted on canvas, to compare the composition of the ground layers. Results were compared with cross-sections, SEM/EDS and µXRDP data available for some paintings. The obtained results allowed us to find stratigraphy distributions of elements in selected parts of paintings as well as to identify pigments used in the tested points.

The artworks chosen for present examination are unsigned; however, we know that they were painted during the King's lifetime. All belong to the historical collection of the Wilanów palace. Two official portraits of the King wearing archaized vestments may have been created in Venice (Italy)– the bigger one is described as the original painting whereas the smaller one is considered to be a copy from the same period.

Two equestrian portraits of Queen Marie and King Jan III were attributed to the court painter Jerzy Eleuter Szymonowicz Siemiginowski and the portrait of Teresa Kunegunda, the royal daughter, is attributed to the French painter Pierre Mignard.

The ground layers in all five pictures are colourful: from yellow-orange to reddish brown, through brown-yellow, orange-red and light red. The clay-based coloured grounds are characteristic for the baroque epoch in which they replaced white grounds based on chalk and gypsum. Iron oxides and aluminosilicates dominate their chemical composition. These colourful grounds differ from each other by natural additions –products of the natural weathering of rocks. They are mainly composed of minerals rich in Fe-oxides, Si-oxides and Al-oxides (goethite, kaolinite and quartz) [3, 4]. Beside various additions of pigments like minium, calcium

Fig.1. Wil.1348, Portrait of King Jan III, unknown author, oil/canvas, 72.8 cm × 60.5 cm, photo by W. Holnicki.

Fig. 2. Wil.1197, Portrait of King Jan III, unknown author, oil/canvas, 48.0 cm × 37.0 cm, photo by W. Holnicki.

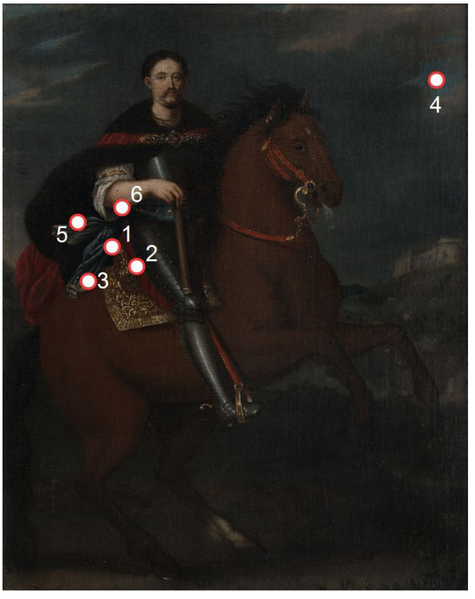

Fig. 3. Wil.1685, Equestrian portrait of King Jan III, oil/canvas, 51 cm × 40 cm, photo by Z. Reszka.

Fig.4. Wil.1686, Equestrian portrait of Queen Maria Kazimiera, oil/canvas, 51 cm × 40 cm, photo by Z. Reszka.

Fig. 5. Wil.1200, Portrait of Teresa Kunegunda Sobieska, oil/canvas, 39 cm × 30 cm, photo by A. Indyk.

carbonate, led white, iron red pigments, they can also differ from each other on deposits containing such elements as Ba, Li and Ti. For example, anatase ($Ti0_2$) was detected by X-ray diffraction in some grounds of baroque paintings by researchers from the Czech Republic [4]. That is why we selected four elements – Li, Ba, Ti and Fe for further analysis of our paintings:-Li, Ba and Ti were selected as specific additions in grounds which could help in finding differences in production materials or workshops, and Fe as a representative of elements typically present in grounds composition (like Al, Mg, Si or Ca and few others).

In the presented study we tried to classify the paintings basing on differences in Ti, Ba and Li contents in ground layers (Ca served as a reference element which allowed to carry out relative calculations and to compare results from both research campaigns

– in 2012 and 2014). We made an attempt to distinguish between investigated paintings via analysis of these additions to find clay provenance/origin.

2.2. Methodology and instrumentation

The primary analytical tool used in this study was Laser Induced Breakdown Spectroscopy (LIBS) [5], which allowed for the qualitative identification of the chemical composition and the superficial layer stratigraphy of artworks. The choice of LIBS as a primary diagnostic tool was made by the curators of the Palace Museum at Wilanów, mainly due to the low destructivity of the diagnostic method and the short time available for tests before starting conservation procedures. LIBS, in short, relies on using high power focused laser energy to cause the ablation of a small amount of surface material, resulting in plasma that emits both continuum and line radiation. Analysis of the spectra from this line radiation allows us to identify elements found in the sample, as each element emits a unique spectral signature.

A laser source in the LIBS arrangement consisted of a 266 nm UV Brio laser (from Quantel/BigSky) with 8 mJ or 10 mJ energy in 4 ns pulses. Stronger laser pulses, which would have resulted in a brighter plasma and a stronger signal, were not used in order to minimize the risk of micro-damages to oil paintings. The laser beam was directed through a 100 mm focal lens to focus the laser energy into a fine spot for ablation on painting and ground layers. The ESA 4000 spectrometer was used to collect spectral information in the 200–780 nm range during ablation. In order to capture useful line radiation, data collection lasted 5 μs and began with a 500 ns delay after the laser pulse, allowing the initial continuum emission from the plasma to disappear. For stratigraphy needs, laser pulses and spectra collection were repeated in the same area until the signal decay, which indicated that the end of a ground layer was reached. The number of laser pulses was related to a thickness of painting/ground layer and typically amounted between 25–150 pulses.

During each measurement campaign the experimental conditions were kept constant, which allowed us to compare results for different spots in all investigated paintings. Spectral line intensities of the analysed elements were used as markers representing the content of these elements. The lines selected for each element and taken for calculations were throughout the same and are shown in Table 1.

However, in the 2012 campaign the laser pulse energy was 10 mJ, and in 2014–8 mJ. In order to compare the results, we used relative contents of chosen elements (Li, Ti, Fe, and Ba) represented by selected spectral lines referred to calcium content because "absolute" (counts) and relative (for example Ti/Ca) dependencies are almost the same. Calcium was selected as a reference element

Table1. Spectral lines selected for comparisons

Element	Ca I	Li I	Ti I	Fe I	Ba II
Wavelength, nm	445.478	670.783	498.173	438.351	455.403
Transition probability, $10^7 \times s^{-1}$	8.70	3.69	6.60	5.00	11.10
Transition (upper level – lower level)	$3p^6 4s4d$ – $3p^6 4s4p$	$1s^2 2p$ – $1s^2 2s$	$3d^3(^4F)4p$ – $3d^3(^4F)4s$	$3d^7(^4F)4p$ – $3d^7(^4F)4s$	6p – 6s

since it was present over all paintings in all spots and almost in all depths.

In all stratigraphy results we present depths in terms of laser pulse numbers, since due to lack of other absolute depth-resolved diagnostics like, for example, optical coherent tomography [6], only such relative spatial resolution was possible to apply. Nevertheless, when comparing after LIBS microscopy measurements we can assume a depth of about 3–5 μm as created by one laser pulse (depending on a paint/ground layer).

The second diagnostic tool was digital microscopy. Microscopic observations were made using the digital Hirox 6700 3D microscope. Every time before the LIBS test, the surface of the painting was examined by the microscope to precisely choose the point of the laser shot (LIBS experiment). After LIBS measurement, the microscopic analysis of the surface was carried out again to find a crater profile and its characteristics (depth, size, shape, etc.) in order to evaluate the scale of surface destruction. In Fig. 7 the examination of a paint layer using digital 3D microscope is presented. The 3D microscopy reveals relatively low destruction of painting layers caused by LIBS technique. The scale

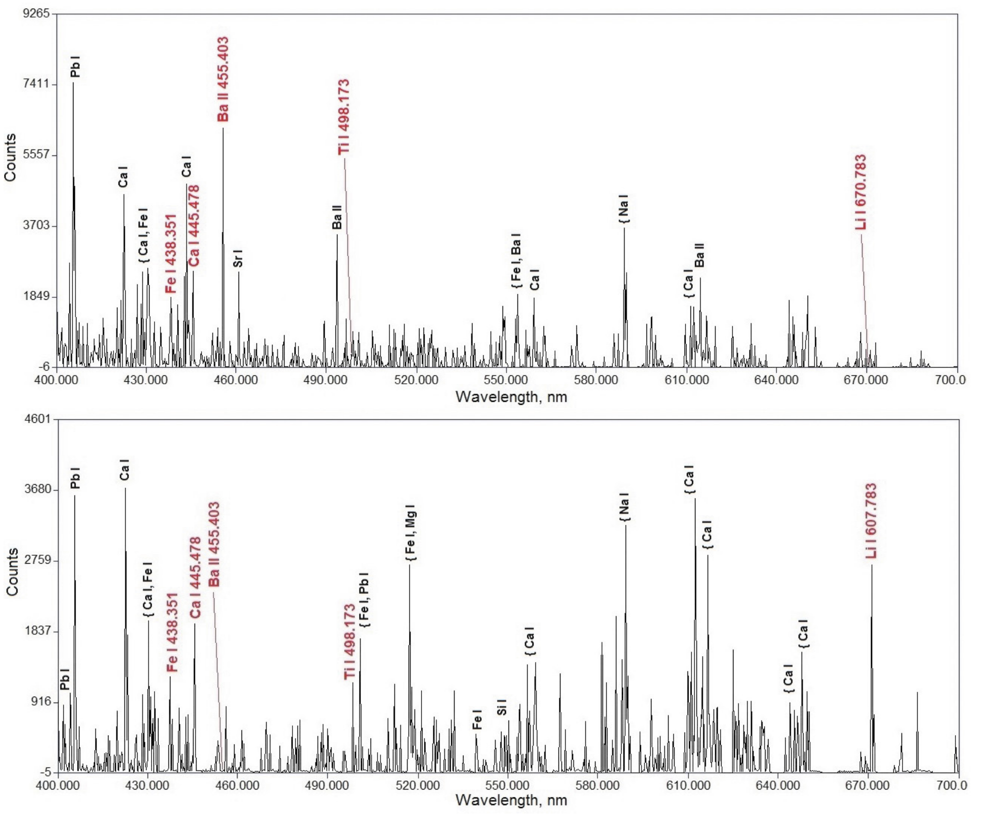

Fig. 6. Typical spectra registered during LIBS experiment: upper spectrum for painting Wil.1200, measurement point 2, depth at 54^{th} laser pulse, and lower spectrum for painting Wil.1685, measurement point 5, depth at 47^{th} laser pulse. Spectral peaks selected for calculations are marked in red, while other intense peaks – in black.

of LIBS destructiveness is shown in Figs. 7 and 8.

The results allowed us to find stratigraphy distributions of elements in selected parts of paintings as well as to identify pigments used in tested points. Finally, we selected 33 measurement points in 5 paintings. From 25 up to over 150 LIBS spectra were taken in the selected points. Totally, over 2000 LIBS spectra were analyzed. Two typical exemplary spectra with marked peaks of selected elements are shown in Fig. 6 for

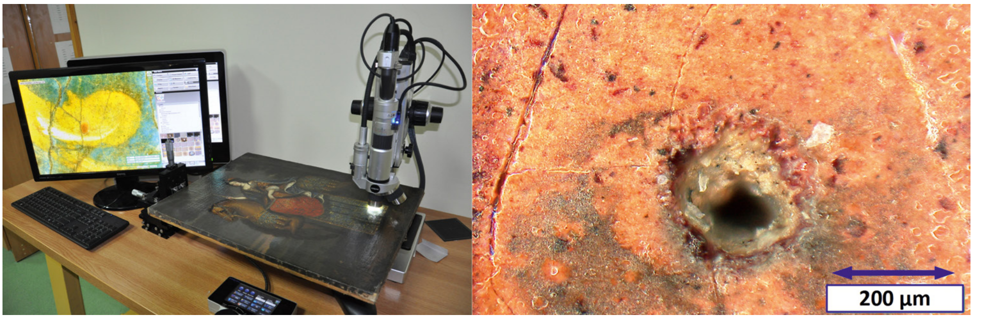

Fig. 7. Examination of a paint layer using digital 3D microscope: a) experimental stage, b) crater image showing destructive scale, photos by A. Pawlak, K. Czyż.

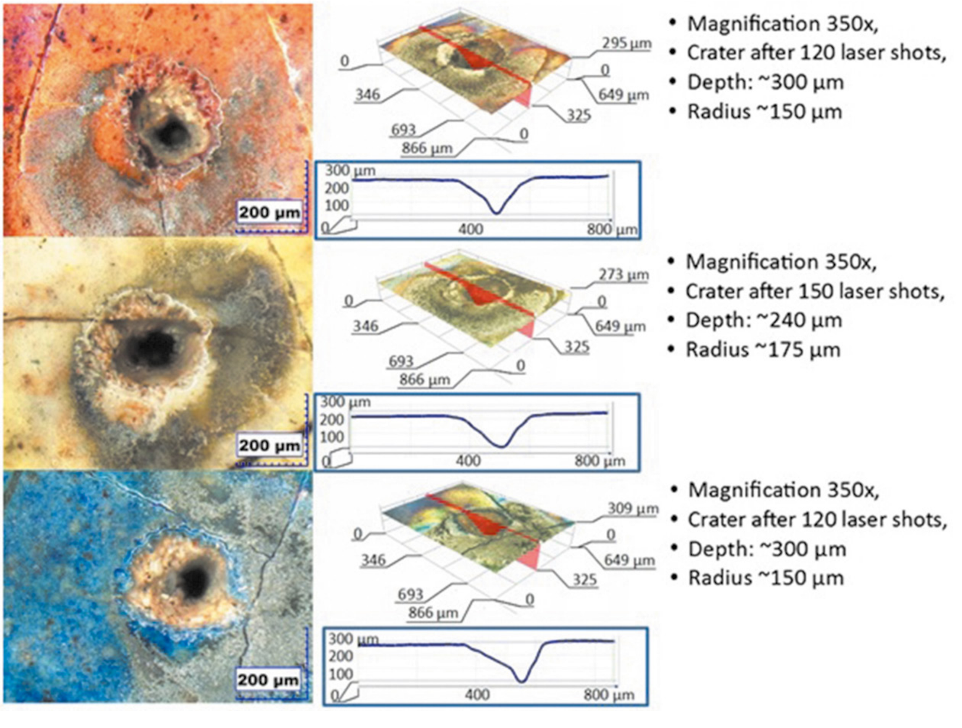

Fig. 8. Digital 3D microscopy for various paint layers and the scale of LIBS destructiveness, photo by K. Czyż.

paintings Wil.1200 and Wil.1685. The location of measurement points was shown in Figs. 1 to 5.

Evident differences and similarities were found in grounds deposited on particular paintings. During these latest investigations, we concentrated on comparison of some elements like: Ba, Li, Ti, identified in grounds layers. Basing on this, we tried to classify the paintings following the character of the ground layers. SEM/EDS and XRPD data available for some paintings were useful in aiding interpretation of LIBS spectra.

The analysis was additionally supported by statistical analytical techniques- in particular, a multivariate factorial analysis(FA).

The FA involves the reduction of a number of input variables, which may be correlated in a variety of ways, into a lower number of sometimes unobservable variables called factors. The reduction of variables results in the loss of some information from entry data, meaning that the first most important factors cannot account for all changes in the data. Nevertheless, the method provides a good analysis of entry data, simplifies complex sets of data and finds relationships in the data that may not be obvious or even have a physical interpretation. Moreover, it still provides a greater understanding of probabilities and correlations. It is commonly accepted that in order to assure an accurate analysis of the data, the first two factors should account for about 70% of the variance in the entry data [7, 8]. The FA analysis was conducted with the STATISTICA ver.10 software [9] by entering a matrix of data constructed from several dozen modified LIBS spectra, from which stratigraphic information was previously obtained. A similar approach to the 17th-century paintings research was published in [10].

3. Results

3.1. Stratigraphy results

We compared ground layers in five paintings in terms of presence of such elements as barium (Ba), lithium (Li), titanium (Ti)and iron (Fe), which is the main component of all these ground layers (see Fig.9). The presented results are an average of all measurement points selected for the paintings and are shown as ratios of these four elements to calcium. Error bars are standard deviations of peak intensity ratios of specified element pairs (Li/Ca, Ti/Ca, Fe/Ca, and Ba/Ca).

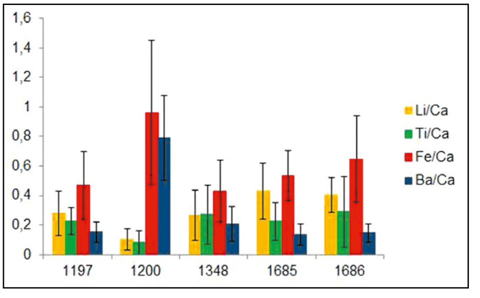

Fig. 9. Relative Li/Ca, Ti/Ca, Fe/Ca and Ba/Ca content for 40–60 laser pulse depth.

The charts show the similarity of grounds in terms of Li and Ba content in both equestrian portraits of the king and the queen (Wil.1685 and Wil.1686). Barium content in the ground layers of the portrait of Teresa Kunegunda (Wil.1200) is completely different. The barium signal is several times stronger from that recorded in the equestrian portraits of the king and the queen, and in the two portraits of the king (Wil.1197 and Wil.1348), which could mean that its barium content is much higher than in the other paintings. Lithium (signal) content, on the other hand, is several times higher in the equestrian portraits, and in the king's portraits as compared to the image of Teresa

Kunegunda. But if we compare this Li signal in equestrian portraits and in the king's portraits, we can observe that we obtained comparable values in both equestrian portraits of the king and the queen (Wil.1685 and Wil.1686), and in both portraits of the king (Wil.1197 and Wil.1348), but the Li signal in equestrian portraits is stronger than the same signal in portraits of the king.

Regarding the titanium signal, it is almost the same in four portraits except for Teresa Kunegunda (Wil.1200) where both Ti and Li signals were weak.

We can note that the Teresa Kunegunda portrait (Wil.1200) undoubtedly differs from the other four pictures by higher content of barium and low contents of Li and Ti. The details of these differences are shown in Figs. 10–12. It can be seen in these figures that after stronger signals from shallow superfi-

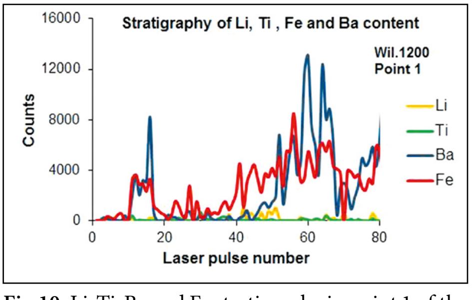

Fig.10. Li, Ti, Ba and Fe stratigraphy in point 1 of the painting 1200 (Teresa Kunegunda)

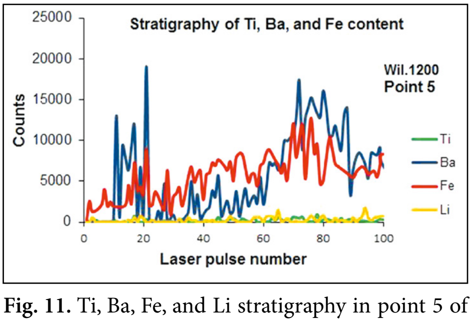

Fig. 11. Ti, Ba, Fe, and Li stratigraphy in point 5 of the painting 1200 (Teresa Kunegunda).

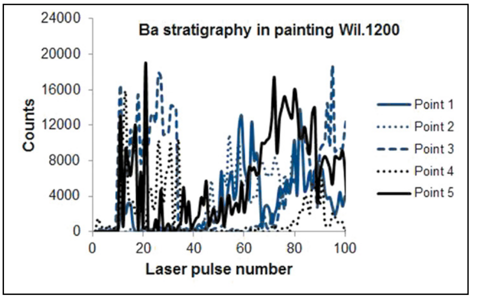

Fig. 12. Ba stratigraphy in various points of the painting Wil.1200 (Teresa Kunegunda portrait).

cial paint layer (typically within 1–30 laser pulses) a certain signal fall is observed, next followed by gradual increase of the analysed signal intensity (usually from 30th-40th laser pulse), which sometimes spreads over 200–300 laser pulses. This signal rise can be interpreted as a start of a ground layer. Since in some measurement points both painting and ground layer are very thin (see Fig. 17), we selected for a further analysis signal depths between 40 and 60 laser pulses as representatives of upper parts of ground layers. Similar signal behaviour is visible in Figs. 13–15, 16 (left) and 17 (right).

The stratigraphy distributions in Fig. 12 reveal that the barium content in points 1200.1, 1200.2, 1200.3, 1200.4 and 1200.5, shown in Fig. 9 as an average factor for the entire painting for depths 40–60 laser pulses, can be clearly observed outside the depth of 40–60 pulses, and show a clear barium signal in the surface parts for all tested points of the painting. Moreover, in this painting the Ba signal is stronger than Li one.

Synthetic barium sulfate ($BaSO_4$) has been used since the earlier 19th century as a white pigment but Ba was identified by Alain R. Duval in coloured grounds of paintings created by French artists between 1620 and 1680 in Paris [11, 12]. The author of that study argued that it was used as an

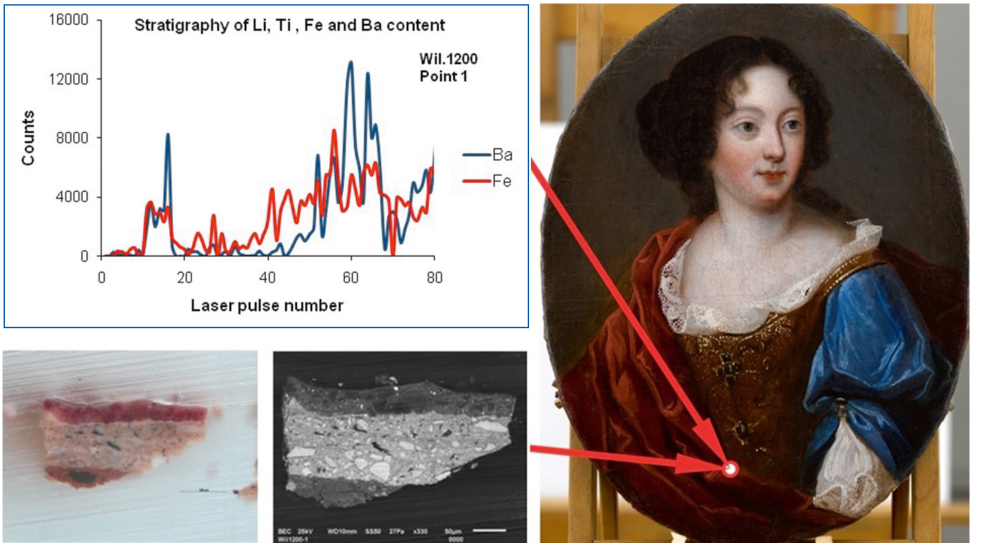

Fig. 13. Ba stratigraphy in point 1 of the painting 1200 (Teresa Kunegunda portrait), photos of cross-sections by Z. Cermakova, J. Hradilowa ALMA laboratory.

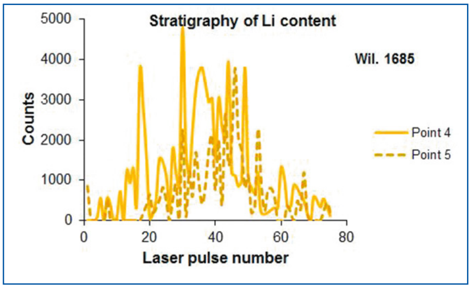

Fig. 14. Li stratigraphy in points 4 and 5 of the painting Wil.1685 (equestrian portrait of the king).

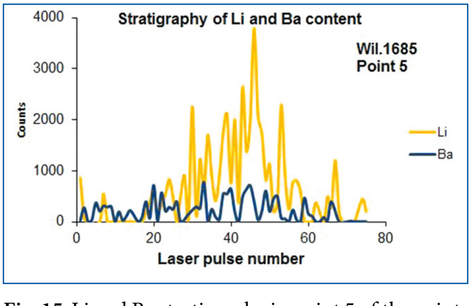

Fig. 15. Li and Ba stratigraphy in point 5 of the painting Wil.1685 (equestrian portrait of the king).

extender in grounds supplied by an unidentified dye provider operating in Paris in the 17th century. Having examined grounds in 155 paintings by 17th and 18th century French painters, the study further established that barite was present in grounds layers prepared on the basis of earth pigments rich in iron oxides. It could have been added to increase the weight of the merchandise (in oil binding agents, $BaSO_4$ is completely colourless) or probably as a natural impurity. SEM-EDS analyses of Teresa Kunegunda Sobieska's portrait [13] confirm these observations, as in this portrait Ba was identified within a particle surrounded with a red particle of red iron. Examples of SEM-EDS analyses for point 1 in the Teresa Kunegunda portrait are shown in Fig. 13.

In the equestrian portraits (Wil.1685 and Wil.1686) the lithium signal was much stronger than the less evident barium one, which is shown in Figs. 16 and 17 (left), and was several times higher as compared to that

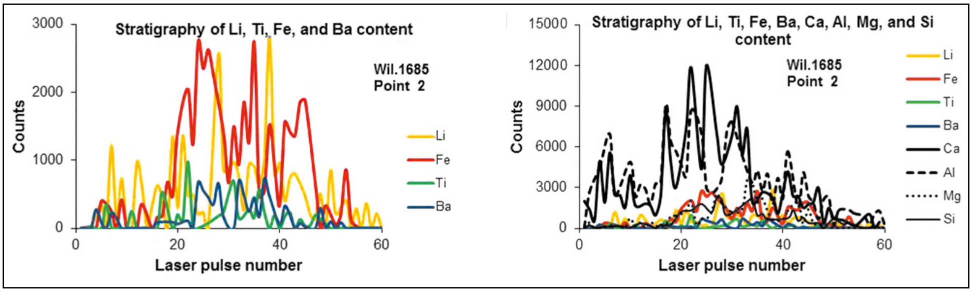

Fig. 16. Li, Ti, Fe, and Ba stratigraphy (left) and Li, Ti, Fe, Ba Ca, Al, Mg, and Si (right) for point 2 of the painting Wil.1685 (equestrian portrait of the king).

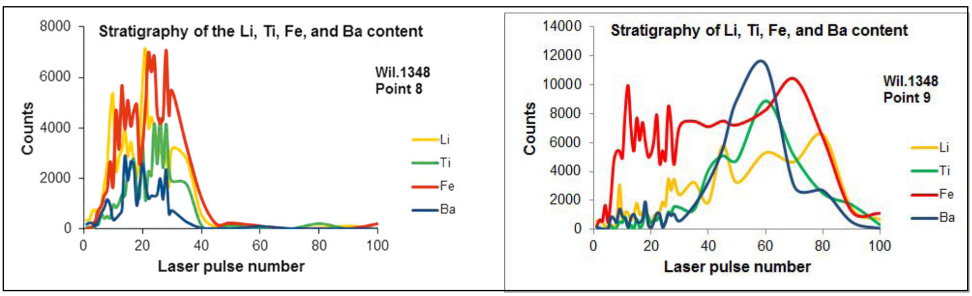

Fig. 17. Li, Ti, Fe and Ba stratigraphy in points 8 and 9 of the painting 1348 (portrait of the King, points 8 – left cheek and 9 – neck refer to carnations).

found in the portrait of Teresa Kunegunda (Wil.1200) – we can see this in Figs. 14 and 15.

Lithium, on the other hand, could be an element found, e.g., in a mineral known as spodumene ($Li_{0.85}Mg_{0.24}Fe_{0.91}Si_2O_6$), which had been identified during a previous study conducted using μ-XRPD [14, 15] on samples taken from the painting *Lato* (Summer) plafond by Jerzy Eleuter Szymonowicz Siemiginowski. In Fig. 16 (right) it is shown that the signals from all elements of spodumene like: Li; Si; Mg; Fe were identified in paint and ground layers in the equestrian portrait of the king (Wil.1685).It is not out of the question that, if found in subsequent studies, this mineral content could be a benchmark that could help in painting classification. The same applies to barite content in the grounds and painting layers.

A clear Ti signal was identified in the ground layers of the two portraits of the king. It was not so evident in the case of Teresa Kunegunda portrait and a bit weaker in two equestrian portraits. At the present stage of our study it is not possible to identify the compound being a source of Ti in these grounds. In the paper by T. Grygar [4] Ti was identified in red-orange bolus grounds found in four baroque paintings. In the 17th century synthetic pigments containing titanium oxide (titanium white) were yet not known, that is why we can suppose that the presence of titanium compounds in grounds can be related to natural admixtures to clays, which are the major components of bolus grounds. These clays can be products of the intense weathering of laterite rocks, rich in aluminium and iron compounds, containing, among others, titanium oxide – the anatase. Laterite rocks arise in result of weathering of silicate rocks in a hot and humid climate. This can be an indication for searching such materials among painting products. The authors of the study [4] claim that *Ti-contents must be a "fingerprint" of the individual ochres and characteristic of their mineralogical origin*.

Moreover, during our work we noted a few unexpected facts. For example, we observed significant differences in the characteristics of painting layers that seemed very similar at first sight. This is shown in two different points for carnations in the bigger painting of the King (Wil.1348), where the paint layer is two times thicker in the neck than in the cheek (see Fig. 17). Additionally, one can observe a significantly higher Ba signal in the thicker layer (point 9), even stronger than the Li signal. This was not observed in other measurement points in the King's portraits.

These occasional, specific observations made the entire analysis very time-consuming, but fortunately sometimes revealed new potential directions for our future painting research with the use of other diagnostic methods and equipment.

3.2 Factorial analysis

As it was already mentioned in subsection 2.2, the comparative study of lithium, barium, iron and titanium content in the grounds was concluded with the multivariate statistical analysis, namely Factorial Analysis (FA), which was applied to find similarities/differences between paint and ground layers and to confirm (or not) the conclusions drawn from the stratigraphy distributions. The results of this statistical approach are shown in Fig. 18. The figure represents the entire chemical composition(not only Li, Ti, Fe, and Ba) reflected by LIBS spectra in all five paintings taken from depths of 40–60 laser pulses (about 200 ~ 300 μm). Each spectrum is marked as a separate point in the chart, wherein the LIBS spectra for the individual painting are marked with the same colour. The data suggest that the paintings may come from three separate workshops. The first one for equestrian portraits of the King and Queen; the second workshop for the King's portraits and the third one for Teresa Kunegunda portrait. We can observe a certain similarity to the composition of equestrian portraits Wil.1685 and Wil.1686 and the King's portraits Wil.1197 and Wil.1348 in painting undercoats, which corresponds to the similarity of complete LIBS spectra at the depths of 40–60 laser pulses. Thus, the factorial analysis, a mathematical-statistical method, confirms the observations of ours senses and historical examinations. This can be a good point to start further classification of the paintings.

4. Conclusions

Finally, the results showed that the LIBS measurements can be used as an efficient method to complement micro-chemical analysis as well as a method to identify and examine artworks.

The presence in grounds of such characteristic elements as Ti, Li and Ba could possibly serve as a basis for classifying paintings.

It should be noticed, however, that in such complex tasks as research of complicated and ambiguous paint layers of oil paintings, the LIBS method is sometimes not sufficient -

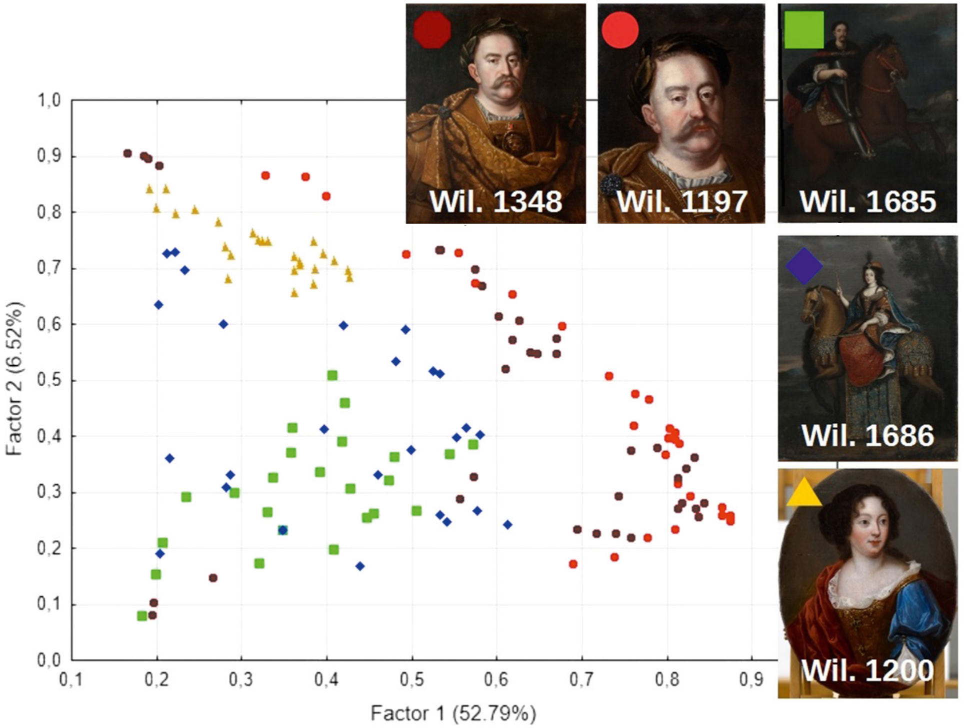

Fig. 18. Factorial analysis of LIBS spectra for depths of 40–60 laser pulses.

it should be complemented by other tests and analyses, for example SEM/EDS and XRPD.

The presented results suggest that:

- the two equestrian portraits of the King and the Queen could be painted by one author, most likely a court painter;
- the two King's portraits probably came from the same workshop but not necessarily the same one as the equestrian portraits;
- the Daughter's portrait clearly exhibits differences in chemical composition of the ground (high Ba and low Li and Ti concentration) as compared to the other artworks–it was probably created in France.

The research should be and will be continued. In the future research we, are going to expand our investigations to a new set of paintings and try to combine LIBS and microscopy measurements with Raman spectroscopy and other optical, non-destructive optical diagnostic methods (like visible fluorescence spectroscopy or XRF). This should enrich results and new data will be of significant meaning for identification and assignment of major production workshops, art schools, and/or painters performing during the epoch of King Jan III Sobieski.

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