

Pigment Composition in the Privilegio Rodado of Juan the Second

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The article examines the pigments used in the design of the privilege of King Juan II of Castile and Leon to his favorite Alvaro de Luna for a third part of the city of Arevalo. The charter comes from the collection of Academician Nikolai Petrovich Likhachev (1862–1936), held in the St. Petersburg Institute of History of the Russian Academy of Sciences. The document belongs to the most solemn type in the Royal Chancellery of Castile; its formula was extremely stable, while its exterior design was dynamic. The design consists of three parts: the initial, the *rueda*, and the border. The study of pigments was carried out by optical microscopy, multispectral imaging and X-ray fluorescence analysis. It was found that, contrary to the prevailing opinion in the literature, the pigments were placed on the parchment without any ground or pre-drawing. The analysis also revealed that both mineral and organic pigments were used. Different pigments were used in different elements of the decoration of the charter. The *rueda* and initial formed one group, the border — the other. In the first group, red was obtained with the use of pure cinnabar or a mixture of it and red lead. Blue and pink were formed by organic dyes in combination with lead white. The traditional Western European azurite and lapis lazuli were not used. Green was most likely a mixture of orpiment and indigo. This combination was not typical of Western European illuminations of the Late Middle Ages. Copper pigments were more common during this period. Black pigment is represented by soot, white by white lead. Green, on the other hand, is represented by copper pigments in the border, while blue and pink contain no lead. The difference in pigments set may indicate two different stages of the creation of the charter, different in time and place. A study also confirmed the use of natural gold, which is consistent with the high status of the recipient of the privilege, Alvaro de Luna, who played an important role in the Castilian court.

Keywords: Juan II, King of Castile and Leon, diplomatics, pigments, XRF, optical microscopy, multispectral imaging, privilege, Alvaro de Luna.

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Состав пигментов в привилегии короля Хуана Второго

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В статье исследуются пигменты, использованные в оформлении привилегии короля Кастилии и Леона Хуана II его ближайшему сподвижнику Альваро де Луна на третью часть города Ареvalo. Грамота происходит из собрания академика Николая Петровича Лихачева (1862–1936), которое хранится в Санкт-Петербургском институте истории РАН. Документ относится к числу бумаг, оформлявшихся в кастильской королевской канцелярии наиболее торжественно. Его формуляр был чрезвычайно стабилен, тогда как внешнее оформление отличалось динамичностью. Оформление состоит из трех частей: инициала, руэды и бордюра. Исследование пигментов проводилось методами оптической микроскопии, мультиспектральной съемки и рентгенофлуоресцентного анализа. Было выявлено, что вопреки сложившемуся в литературе мнению пигменты были положены на пергамен без грунта и предварительного рисунка. Установлено, что использованы как минеральные, так и органические пигменты. В различных элементах оформления грамоты они были разными. Руэда и инициал формируют одну группу, бордюр — другую. В первой группе красный цвет получен с помощью чистой киновари или ее смеси со свинцовым суриком. Голубой и розовый образованы органическими красителями в сочетании со свинцовым суриком. Не использованы традиционные для Западной Европы азурит и лазурит. Зеленый, по всей вероятности, является смесью аурипигмента и индиго. Такое сочетание не было характерно для западноевропейских иллюминаций Позднего Средневековья. В этот период чаще употребляли медные пигменты. Черный пигмент представлен сажей, белый — свинцовыми белилами. В бордюре зеленый, наоборот, представлен медными пигментами, а голубой и розовый не содержат свинца. Различие в наборе красок может свидетельствовать о двух стадиях оформления грамоты, различающихся по времени и месту. Также исследование подтвердило использование натурального золота, что согласуется с высоким статусом получателя привилегии Альваро де Луна, игравшего важную роль при кастильском дворе.

Ключевые слова: Хуан Второй, король Кастилии и Леона, дипломатика, пигменты, РФА, оптическая микроскопия, мультиспектральная съемка, привилегия, Альваро де Луна.

Studies on the technology of handwritten book production have been carried out for a considerable period of time. They have enabled to accumulate a solid knowledge of the materials of the support, inks, pigments of miniatures, bindings, and other components of codices. In contrast, charters seem less promising for the study of historical technology of manuscripts monuments because of their poor and homogeneous nature in general. Meanwhile, this part of the handwritten heritage represents a considerable volume of sources on human activity. Just as the study of materials and technology of handwritten books elucidates the process and peculiarities of their production, division of labor in scriptoriums, modification of books (their division or, on the contrary, binding into a convolut, borrowing sheets with miniatures, insertion or removal of sheets), and other subjects, the study of technology of charters production provides much information about the organization of the chancellery, the procedures of creating documents, the means of transmitting information, protection, and about many other subjects.

The collection of Academician Nikolai Petrovich Likhachev (1862–1936), held in the St. Petersburg Institute of History of the Russian Academy of Sciences, is particularly suitable for the study of the development of historical technology of charters due to its composite nature. Having the task of creating a “museum of historical source study”¹, N. P. Likhachev assembled an incomparable collection in terms of chronological and territorial scope². N. P. Likhachev built up his collection largely according to the material science principle³, which was extremely close to him. His doctoral dissertation “Paper and the oldest paper mills in the Moscow State” testifies to this⁴. Based on this collection, a wide variety of topics related to manufacturing of charters and the interaction of technology and the administrative process can be explored.

One of the most striking manuscripts in Likhachev’s collection is the privilege granted on January 3, 1423, in Toledo by Juan II, king of Castile and Leon (1406–1454) to his favorite Alvaro de Luna (c. 1390–1453). (Scientific-Historical Archive of the St. Petersburg Institute of History of the Russian Academy of Sciences. Western European Section. Collection 14. Cardboard 292. Storage unit No. 4). In it, the king confirms the right previously given to Alvaro (May 2, 1421) to a third part of the town of Arevalo (villa de Arévalo)⁵.

This article will outline the preliminary results of the analysis of the pigments that were used in the artwork of the privilege. Understandably, the study of a single document does not allow us to draw conceptual conclusions. However, the results obtained can serve as material for future generalizing studies.

Diplomatic commentary

The document belongs to the type of *privilegio rodado*, literally translated as “privilege with a wheel”. It is the most solemn type of document in the Royal Chancellery of Castile. The name comes from the characteristic “wheel” (*rueda* or *rota*), a sign of the king in the form of several concentric circles with inscriptions and symbolic images. This sign was placed under the main text, in the middle. It was surrounded by lists of witnesses in four columns (at first, there were no handwritten signatures). These privileges were a proof of a special royal favour, or a way of showing appreciation for services rendered to the Crown. The rights were granted in perpetuity and were hereditary.

There is a reference in this privilege to the practice established by the 1420s in the Royal Chancellery: “[line 7] Vi un[o] mi alvalá escripto [line 8] en papel e firmado de mi nombre”. Alvalá is a title document in a simple form. Such documents were always written on paper, had no seal and decorations, and the place of issue was not indicated.

¹ Klimanov L. G. N. P. Likhachev “v poiskakh zhelannykh zven’ev velikoi diplomaticheskoi vystavki” // “Zvuchat lish’ pis’mena...”: k 150-letiiu so dnia rozhdeniia akademika Nikolaiia Petrovicha Likhacheva. Katalog vystavki. St. Petersburg, 2012. P. 36.

² About the collection, see: Iz kolektsii akademika N. P. Likhacheva: katalog vystavki. St. Petersburg, 1993; “Zvuchat lish’ pis’mena...”.

³ Klimanov L. G. Muzeinye vzgliady i praktika N. P. Likhacheva // Muzeologiya — muzeovedenie v nachale XXI veka: problemy izucheniia i prepodavaniia. St. Petersburg, 2009. P. 298–305.

⁴ Likhachev N. P. Bumaga i drevneishie bumazhnye mel’nitsy v moskovskom gosudarstve: istoriko-arkheograficheskii ocherk. St. Petersburg, 1891.

⁵ Arévalo is a town 110 km North-West of Madrid. It is now part of the province of Ávila in the autonomous community of Castile and León. During the 15th century, it was a frequent seat of the Trastámara dynasty, to which Juan II belonged.

The recipient of the rights could, after a period of time, ask the ruler to confirm the royal favour — already in the form of the *privilegio rodado*⁶.

As a type of document, the *privilegio rodado* existed in the Chancellery of the Crown of Castile from the 12th century to the last third of the 15th century, and its form had been static ever since it was defined in the “Seven Partidas”⁷ (Partida 3^a, título XVIII, ley III). *Privilegio rodado* was always written on well-made parchment and on one side only. A double-sided lead seal was attached to the document on a cord of multi-coloured silk threads.

Although the *privilegio rodado* form was stable, the artistic elements of the document changed rather dynamically. In the early documents, the symbolic invocation had the form of a chrismon (with variations in the lettering). In the 15th-century privileges a decorative initial appeared in this place. The names of the king, sometimes his wife, God and the Virgin Mary were graphically highlighted in the text: these were written in capital letters, painted in different colors, or could be placed in an ornamental border. The *rueda* was retained as a compulsory requisite of the document and underwent transformations in size. From the 1320s, it began to be inscribed in a square, the space in the corners of which was subsequently filled with geometric or floral ornaments, figures of angels, symbolic image of evangelists, heraldic signs, etc.⁸ During the reign of Juan II, the margins of the pages began to be decorated with floral ornaments⁹.

If we assume that some time passed between the writing of the privilege (in which the date was indicated) and its decoration, then the decor could serve as an attribute to identify individual illustrators. However, only approaches to developing this problem have been outlined in the scholarship so far¹⁰. A difficult and understudied issue is the organization of the privilege design process itself. How many people were involved in the illumination process, was there any regulation, what pigments were used to mix the colors, and how were its chosen? It is not certain whether there was a symbolic meaning to the decoration.

There was undoubtedly a dynamic in the decoration of the *privilegios rodados* since the reign of Juan II, which contrasts with the state of the art of book illumination in Castile in the 14th–15th centuries. The royal scriptorium seems to have been dead for several centuries after the death of king Alfonso X the Wise in 1284. In general, very few literary or historical works on the Iberian peninsula contained extensive cycles of miniatures. The ascetic design of the Iberian codices is particularly evident in relation to the brilliant examples that were coming out of the scriptoriums in Italy, Flanders, and Burgundy¹¹. In Castile, only the “Alba’s Bible” stands out for its illuminations¹² (made between 1422 and 1430 in Toledo)¹³.

⁶ Sanz Fuentes M.J. Tipología Documental de la Baja Edad Media Castellana: Documentación concejil. Un modelo andaluz: Écija // Archivística. Estudios Básicos. Sevilla, 1981. P.253.

⁷ ‘The Seven Partidas’ (Spanish: ‘Las Siete Partidas’) is a seven-part code for the Kingdom of Castile. It was written in the 1250–1270s on the initiative of King Alfonso X the Wise.

⁸ Francisco Olmos J. M., de. El signo Rodado Regio en España. Orígenes y desarrollo. Madrid, 2017. P.59–68.

⁹ Ruiz García E. La cultura escrita en tiempos de Juan II (libros y documentos) // Documentación de la Corona de Castilla (siglo XIII–XV). Madrid, 2003. P. 154.

¹⁰ Ibid. P.149–173.

¹¹ Villaseñor Sebastian F. El privilegio rodado bajomedieval castellano como transmisor de las nuevas tendencias en la iluminación de manuscritos // Libros con Arte. Arte con Libros. Cáceres, 2007. P.705–706.

¹² A translation of the Tanakh into Castilian. Executed under the direction of Rabbi Moïshe Arragel of Guadalajara, commissioned by Luis de Guzmán, Grand Master of the Order of Calatrava. Contains over 30,000 miniatures.

¹³ Avenoza G. Biblias castellanas medievales. San Millán de la Cogolla, 2011. P.199–253.

To explain this surge in the art of decorating *privilegios rodados* under Juan II, it is necessary to undertake special research. The gradual increase in the decorative element of the privileges suggests the existence of a stable group of illustrators serving the needs of the royal court for many years¹⁴.

There are *privilegios rodados* with incomplete artwork for some reason¹⁵. These give an indication of some of the stages in the design process. The process always began after the text had been written: the places where illumination was to be carried out were marked on parchment in advance. The sketch was made with a lead pencil, then outlined with ink similar to those used in writing, but paler, diluted. Subsequently, a lead white primer could be applied to the illuminated areas to make the surface smoother. Parchment paints, whose color palette was very varied, were always made on water basis and applied with very thin brushes. The value of jewelry depended on the financial capabilities of the client. This explains the diversity in the decoration of privileges issued by the same king: from lavishly decorated to modest ones, or even left empty because the recipient of the privilege did not have enough finances. The talent of the illustrator is manifested in the technique of execution, in the choice of colors, and in the ways of combining them¹⁶.

The document we are interested in is relatively well preserved, despite some loss of the ink layer and considerable damage to the metal of the seal. The elements of the artistic design of the privilege include the following:

1. *Rueda* — three concentric circles separated by red and blue borders. In the middle there is the coat of arms of the Crown of Castile — a shield on which two lions (on a white background) and two castles (on a red background) are depicted in a checkerboard pattern. The lions rampant look to the left, their tongues hanging out. The castles are painted gold and outlined in black. The space between the coat of arms and the first circle is filled with a purple floral ornament. Inside the circles there are the names and positions of the courtiers (red and light blue letters alternate in words). Concentric circles are inscribed in a square with three frames outlined in gold, pink, and blue. The space in the four corners of the square, formed after the inscription of the circle, is filled with a repeating pattern — a flower with three petals and large leaves with white veins. In the upper left and lower right corners, the flower is green, in the upper right — red, in the lower left — blue (Fig. 1a).

2. The initial is the letter “E” in a golden rectangle with a blue border. The letter is pink with a white floral design that duplicates the one in the central circle of the *rueda*. The space of the rectangle is filled with floral ornaments in the same style as the corners of the square containing the *rueda* (Fig. 1b).

3. Border — a floral ornament of sharp triangular leaves, flowers with three sharp petals, flowers with alternating four sharp and four round petals, drop-shaped and spiral elements. This ornament runs along the top, left, and partly bottom sides of the document. As separate inclusions, it occurs in the middle of the left side of the document (as if separating the eschatocol from the main text), as well as above the vertical stripes

¹⁴ Yarza Luaces J. Los Reyes Catolicos y la miniature // Las artes en Aragon en el reinado de en Fernando el Catolico (1479–1516). Zaragoza, 1993. P. 64.

¹⁵ Francisco Olmos J. M., de. El signo Rodado Regio en España. P. 66.

¹⁶ Santos Navarrete M. R. et al. Privilegio rodado de Alfonso X. 1272. Privilegio rodado de confirmación de Sancho IV. 1292. Privilegio rodado de confirmación de Fernando IV. 1303. Sevilla, 2006. P. 12; Pérez del Campo L. et al. Privilegio Rodado de Jerez de La Frontera. 1268. Sevilla, 2011. P. 17–18.

that separate the space with columns of witnesses. The same stripes separate the text and border on the left side of the document (gold, pink, and blue colors), the first and second witness columns (gold and pink colors), as well as the third and fourth (gold and blue colors) (Fig. 1c).



Fig. 1. The elements of the artistic design of the privilege: *a* — rueda; *b* — initial; *c* — border [Scientific-Historical Archive of the St. Petersburg Institute of History of the Russian Academy of Sciences. Western European Section. Collection 14. Cardboard 292. Storage unit No. 4]

Historical context

Alvaro de Luna was Duke of Trujillo, Grand Master of the Order of Santiago, IV Constable of Castile¹⁷. He was an illegitimate son of Alvaro Martínez de Luna, the chief cupbearer of king Enrique III (1390–1406). Alvaro owed his career as a courtier, first of all, to his uncle, Pedro de Luna, who became Archbishop of Toledo in 1408. Alvaro managed to enter the inner circle of the young king Juan II. Until the adulthood of Juan, regents, who were antagonistic towards with each other, ruled on his behalf. They were the mother of the king — Queen Dowager Catherine of Lancaster (1390–1418), and paternal uncle — Fernando de Antequera, the future king of Aragon (1412–1416). In 1419, Juan formally began to rule independently, but in fact all state affairs were handled by his favorite, Alvaro de Luna. His influence on the king caused extreme discontent among the nobility. First of all, his rivals were the “Aragonese infantes” — the sons of the aforementioned Ferdinand of Aragon, who had claims to the throne of Castile. On the other hand, the rapid career of Alvaro gave rise to many enemies among the Castilian nobility. They grouped first around the first wife of Juan II — Mary of Aragon (1420–1445), and then around the second wife of the king — Isabella of Portugal (1447–1496). The latter convinced the king to execute Alvaro in 1453.

¹⁷ The title “constable de Castilla” was introduced by King Juan I in 1392 following the French model. The main duty of the constable was to command the army during the monarch’s absence. He also had judicial powers in relation to the soldiers, monitored the condition of fortresses and castles, had the right to wear the banner, mace and coat of arms of the king. In fact, the constable of Castile was the second person in the state. Alvaro de Luna received this title in 1423, apparently at the same time as this privilege, since in it he is already mentioned as a constable.

In addition to the fact that Alvaro de Luna for decades had been the most influential politician of the Crown of Castile¹⁸, he was a man of the Renaissance: he was well versed in art and literature and was engaged in belles-lettres.

He did much to ensure that the royal court of Castile could compete with the more brilliant Iberian courts of Aragon and Navarre. Alvaro de Luna's circle of communication included well-known intellectuals of Castile: the writer Diego de Valera (1412–1488), who became famous on the battlefield, the Augustinian monks and writers Juan de Alarcon (c. 1390–1451) and Martin de Cordova (c. 1398–1476), a royal chronicler Alvar Garcia de Santa Maria (c. 1380–1460)¹⁹.

The privilege of 1423 is one of more than two dozen that were issued to Alvaro de Luna in the early years of the reign of Juan II²⁰. Elisa Ruiz Garcia, professor of paleography and diplomacy at Complutense University, proposed a typology of illuminated *privilegios rodados* that emerged from this Royal Chancellery. According to this typology, the privilege from the St. Petersburg Institute of History of the Russian Academy of Sciences can be attributed to the so-called “first style”. It is characterized by a relatively simple decor with a predominance of plant motifs and a border in the upper left corner²¹.

With considerable capital, Alvaro de Luna himself could sponsor the luxurious decoration of the privileges that were given to him. However, it is difficult to answer the question to what extent he himself influenced the style of illuminations. Comparison of the design of de Luna's privileges with those that were issued to other noble persons at the same time demonstrates a high degree of their similarity²². In other words, Alvaro de Luna's will as a customer was not decisive. It is more likely that he simply agreed to the use of templates available in a particular workshop. This suggests that the choice of pigments for making the colors was also determined by the traditions of the same workshop.

Materials and methods

The most effective and widespread method for elemental composition of pigments is X-ray fluorescence analysis. This method is preferable for Cultural Heritage studies because of its speed, noninvasive nature of the study (i. e., without sampling), so it does not damage the object. X-ray fluorescence analysis was carried out on a Crono (Bruker) micro-XRF analyser, silicon drift detector, Rh anode tube. Measurement parameters 20 kV, 150 µA. Collimator 0.5 mm. Measurements were made without surface cleaning. Time measurement at point is 60 sec. For optical microscopy in reflected light Olympus SZX10 stereoscopic microscope was used. Multispectral imaging: a detector of banknotes, documents, and other security printings, CmE37 (the device is equipped with sources of ultraviolet (365 nm, 254 nm) and infrared (straight 850 nm and 940 nm, oblique 880 nm) light.

¹⁸ Pérez B. Figure d'un favori exemplaire au XVe siècle: Le règne d'Álvaro de Luna, “mayor señor sin corona” // L'Espagne des validos, 1598–1645. Rennes, 2009. P. 15–44.

¹⁹ Álvarez Palenzuela V. Á. Luna, Álvaro de. Available at: <https://dbe.rah.es/biografias/12479/alvaro-de-luna> (accessed: 29.08.2022).

²⁰ Ruiz Garcia E. La cultura escrita en tiempos de Juan II (libros y documentos). P. 154.

²¹ Ibid. P. 155.

²² Ibid. P. 157.

Results and discussion

The document is written on dense parchment, with high calcium content, indicating that the parchment was probably coated with chalk according to the European tradition of manufacturing of parchment²³. An iron gall ink with a high potassium content was used to write the text. The soot is not present. The lead seal contains a small admixture of copper (less than 1 %). Also, elemental analysis of seal showed a significant amount of sulfur, which is probably contained only in the surface layers as included in the products of corrosion of the lead seal, which is strongly damaged. Of the sulfur compounds, anglesite (PbSO_4) is the most commonly formed under conditions of atmospheric corrosion²⁴. Sulfur can come either from the environment containing large amounts of sulfur dioxide gas or from crumbling iron-gall ink, which also includes sulfur.

The pigments were applied directly to the parchment, without ground, contrary to the previous investigations of Spanish researchers. No preparatory drawings could be found.

The golden items are made of natural gold with an admixture of iron; it was not imitated by substitute compositions. Such compositions, based on copper and in some cases — on lead and zinc, were sometimes used even in richly decorated manuscripts²⁵.



Fig. 2. Fragment of the charter (a) in visible light (b) in infrared light (850 nm)

The set of pigments used to make the *initial* (Fig. 3) and the *rueda* (Fig. 4) are completely the same. The black outlines were made with a composition containing soot, which strongly absorbs in the infrared part of the spectrum (Fig. 2). The most traditional

²³ Mokretsova I. P. et al. *Materialy i tekhnika vizantiiskoi rukopisnoi knigi*. Moscow, 2003. P.22–23; Reed R. *Ancient Skins, Parchments and Leathers*. London; New York, 1972. P.147.

²⁴ Burshneva S. G., Kozlova M. O. Aktivnaia korroziiia muzeinykh predmetov iz svitsa // *Arkheologiiia evraziiskikh stepei*. 2021. No. 6. P.235–241; Costa V., *Urban Fr*. Lead and its alloys: metallurgy, deterioration and conservation // *Studies in Conservation*. 2005. Vol. 50 (supp. 1). P.48–62; Tétreault J. et al. Corrosion of Copper and Lead by Formaldehyde, Formic and Acetic Acid Vapours // *Studies in Conservation*. 2003. Vol. 48, issue 4. P.237–250; Degrygn C., Guilminot E., *Le Gall R*. Faciès de corrosion développés sur des poids en plomb du Musée du CNAM de Paris // *ICOM-CC, 13th Triennial Meeting, Rio de Janeiro, 22–27 September 2002*. London, 2002. P.865–869.

²⁵ Mousavi S. M. et al. Identification and Analytical Examination of Copper Alloy Pigments Applied as Golden Illuminations on Three Persian Manuscripts // *Restaurator. International Journal for the Preservation of Library and Archival Material*. 2015. Vol. 36, no. 2. P.81–100; Aceto M. et al. Evidence for the degradation of an alloy pigment on an ancient Italian manuscript // *Journal of Raman Spectroscopy*. 2006. Vol. 37. P.1160–1170; Banik G. Green cooper pigments and their alteration in manuscripts or works of graphic art // *Pigments and colorants de l'Antiquité et du Moyen Âge: Teinture, peinture, enluminure, études historiques et physico-chimiques*. Paris, 2002. P.89–102.

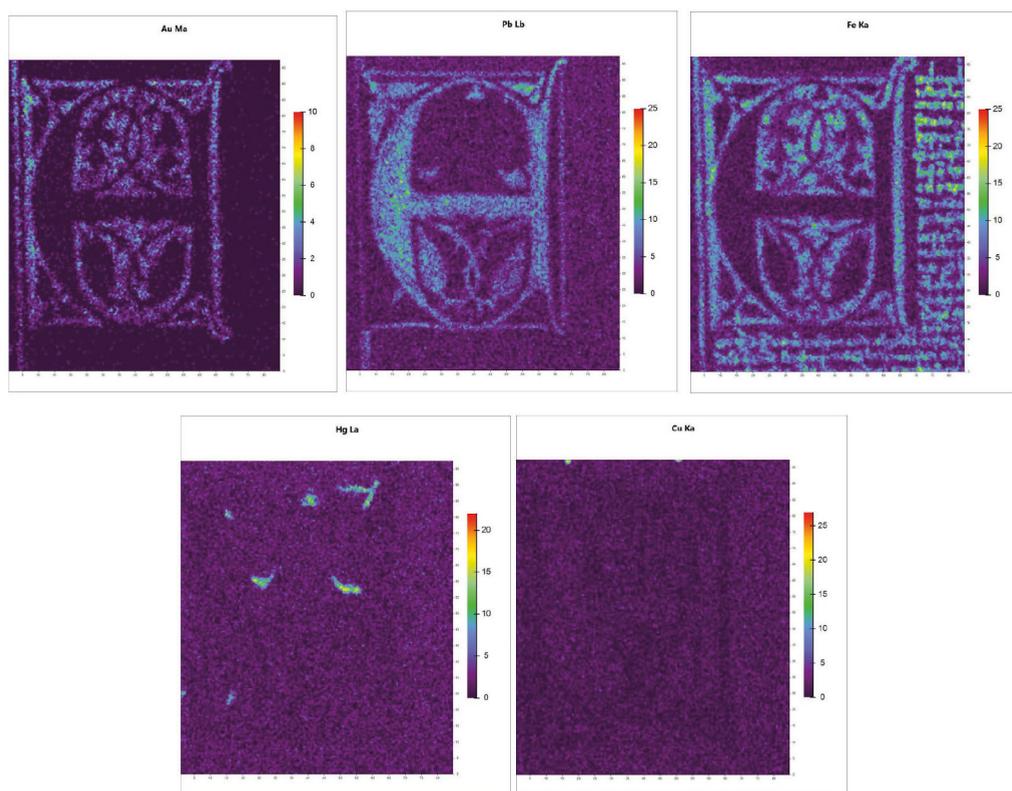


Fig. 3. Element distribution maps (initial)

blue pigments for Western Europe of the Late Middle Ages, azurite and lazurite, were not used to produce blue color²⁶. Usually during this period azurite was used for cheaper manuscripts or miniature parts, and lapis lazuli — for more expensive ones. The absence of azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) is confirmed by the absence of copper. The content of sulfur does not surpass its concentration of other points. Combined with the complete absence of aluminum and silicon, this indicates that the blue color was created without the addition of lazurite ($\text{Na}_8 \cdot 10\text{Al}_{16}\text{Si}_6\text{O}_{24}\text{S}_{24}$). The relatively rare smalt ($\text{CoO} \cdot n\text{K}_2\text{SiO}_3$) and vivianite ($2[\text{Fe}_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$) are excluded due to the absence of cobalt and iron²⁷. The blue was probably composed with the mixture of organic indigo and lead white. The pink hue was also created with organic pigment mixed with lead white. Traditional cinnabar (HgS) was not used in this case, as evidenced by the absence of mercury. The presence of organic pigments, traditionally more difficult to detect, requires further investigation. The green color used in the *rueda* and initial contains arsenic and sulfur. This can be

²⁶ Clarke M. The analysis of manuscript pigments. Why, what and how? // *Gazette du livre medieval*. 2002. No. 40. P. 36–44; Scott D. A. et al. Technical Examination of a Fifteenth-Century German Illuminated Manuscript on Paper: A Case Study in the Identification of Materials // *Studies in Conservation*. 2001. Vol. 46, no. 2. P. 93–108.

²⁷ Grenberg Iu.I., Pisareva S.A. *Maslianye kraski XX veka i ekspertiza proizvedenii zhivopisi*. St. Peterburg; Moscow; Krasnodar, 2020. P. 125–127.

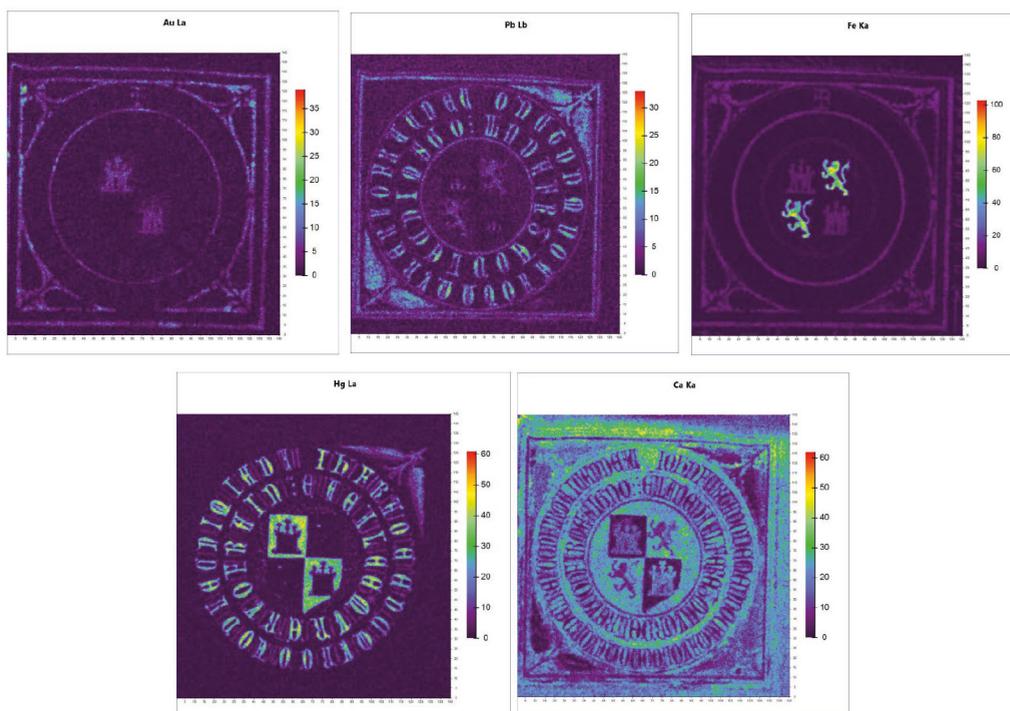


Fig. 4. Element distribution maps (*rueda*)

interpreted as a mixture of orpiment (As_2S_3) or realgar (As_4S_4)²⁸ with indigo. This recipe for green paint was advised by Cennino Cennini in his famous manual²⁹. This mixture was more gentle for the support of the manuscript than copper pigments, which had a negative effect on paper and parchment. Medieval artists were well aware of this effect of copper pigments on the support of the document³⁰. On the other hand, Cennino Cennini specially recommended verdigris for parchment and paper³¹. The red color used for the floral motifs has a gradual transition from red to orange. This effect could have been obtained with cinnabar and red lead: this is evidenced by the higher mercury content in the red hue and the higher lead content in the orange. The field of the Castilian coat of arms, the letters in the *rueda* and the tongues of the heraldic lions are painted in pure vermilion. The figures of the lions are made with iron pigments. The white touches contain lead and may be interpreted as white lead.

As for the border, the set of pigments is divided into two parts: a vertical triple line of gold-pink-blue and colored touches accentuating the floral ornamentation. The colors used for the vertical lines correspond in elemental composition to the other two compositional parts of the charter. The gold on the leaves of the border contains a significant amount

²⁸ Realgar is quite rare, but its use as a pigment in manuscripts is attested (*Mokretsova I. P. et al. Materialy i tekhnika vizantiiskoi rukopisnoi knigi*. P. 32), so it cannot be excluded without further research.

²⁹ *Cennino Cennini. Kniga ob iskusstve, ili Traktat o zhivopisi*. Moscow, 1933. P. 31.

³⁰ *Mokretsova I. P. et al. Materialy i tekhnika vizantiiskoi rukopisnoi knigi*. P. 35; *Banik G. Green cooper pigments...* P. 90.

³¹ *Cennino Cennini. Kniga ob iskusstve, ili Traktat o zhivopisi*. Moscow, 1933. P. 31.

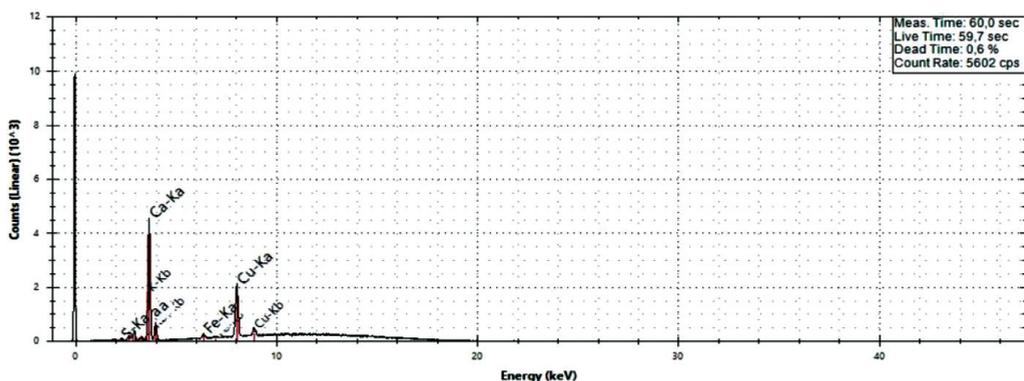


Fig. 5. XRF spectrum of the green pigment (border)

of iron, as the other gold elements of the decoration. In contrast to them, the pigments on the scrolls of the ornament differ in composition from the others. First of all, green is represented here not by a mixture of orpiment and indigo, but by copper pigment (Fig. 5). Because of large variability of copper pigments³², it is not possible to specify which pigment was used in this case based on the XRF alone. Pink and blue do not contain lead. Nor do they contain any other elements that would allow them to be attributed to the mineral group. We are probably dealing here with organic pigments without the addition of white lead. In particular, it should be noted that the touches are rather negligently applied. Taken together, these features may indicate that these color accents were added to the border later or outside the workshop where the main decoration of the charter was made. Perhaps more than one master worked on the document. Considering that the practice of decorating privileges with a border was just taking shape during the reign of Juan II, then perhaps the charter from the St. Petersburg Institute of History of the Russian Academy of Sciences reflects a phase in the formation of this tradition, when the border was originally made with soot outline and gold, and then was completed with colored touches.

Conclusion

The first attempts were made to determine the set of pigments used for the illumination of *privilegio rodado* of Juan II. This set is not quite usual for Western Europe in the Late Middle Ages. First of all, the most common azurite and lazurite were not used, and blue was created with the mixture of an organic pigment (probably indigo) and lead white. The green hues are presumably formed by a mixture of orpiment and indigo. Although Cennini gives a recipe of green dye made from orpiment and indigo, natural science indicates that this mixture is typical for earlier manuscripts³³, whereas malachite, verdigris, and other copper pigments are more common in the Late Middle Ages. For Byzantine manuscripts,

³² Pisareva S. A. Mednye pigmenty drevnerusskoi zhivopisi XI–XVII v. Moscow, 1998. P. 16–31.

³³ Bioletti S. et al. The examination of the Book of Kells using micro-Raman spectroscopy // Journal of Raman Spectroscopy. 2009. Vol. 40. P. 1043–1049; Brown K. L., Clark R. J. H. The Lindisfarne Gospels and two other 8th century Anglo-Saxon/Insular manuscripts: pigment identification by Raman microscopy // Journal of Raman Spectroscopy. 2004. Vol. 35, no. 1. P. 4–12.

by contrast, this mixture is predominant³⁴. The copper-containing pigment was used only for color accents in the border. In order to understand whether the choice of pigments is original or, on the contrary, standard, it is necessary to involve the comparative data. Such work is possible today, thanks to the development of non-destructive methods of analysis. Tracing the use of pigments systematically will help to clarify the process of document production, the participation of the client in this procedure, and the mutual influence of the different chanceries on one another.

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³⁴ Mokretsova I. P. et al. Materialy i tekhnika vizantiiskoi rukopisnoi knigi. P. 34–36.

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