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XRD characterization of cobalt-based historical pigments and glazes

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This article covers the results of application of X-ray powder diffraction (XRD) in assessing the chemical and phase composition of historical pigments and their glazes. In order to demonstrate the reliability of the above technique, XRD analyses were performed on representative samples of the cobalt-based pigments and glazes. Ten individual pigments (Kremer Pigmente) were used for X-ray diffraction characterization: cobalt yellow, cobalt violet brilliant light, cobalt violet dark, cobalt cerulean blue, cobalt blue dark, cobalt blue light, cobalt blue greenish, cobalt green bluish, and two specimens of smalt with different grind. The same pigments, along with lead oxide (Pb_3O_4) and silica (SiO_2), were used for the preparation of cobalt-based glazes. XRD analysis has proven to be a useful tool for the qualitative determination of the composition of glazes. However, in some cases many problems concerning the identification of separate phases are still to be solved using other analytical techniques.

Key words: pigments, glazes, cobalt-based, X-ray diffraction characterization

INTRODUCTION

Cobalt-based ceramic pigments are widely used for coloured glazes in the ceramic industry for floor or wall whitewares, and also in the bulk coloration of polished, unglazed, porcelainized stoneware. They are characterized by a high resistance with respect to light, environment, high temperature and chemicals. These pigments are also used in many industries because of their different colour, fine particle size, good hiding power, acid acceptance and compatibility with many organic and inorganic systems. The pallete of their colours is very large: blue, green, yellow, violet, brown and black [1–3].

Recently, new cobalt-based ceramic pigments have been synthesized using different synthetic approaches. A polycrystalline material with the qualities of a blue pigment has been obtained at low temperatures in the CoO–ZnO–SiO_2 system by the sol-gel technology [4]. The classical Co olivine blue pigment (Co_2SiO_4) and Co-doped willemite ($Co_{0.05}Zn_{1.95}SiO_4$) were prepared by the traditional solid state reaction method [5, 6]. Blue cobalt aluminate ($CoAl_2O_4$) and purple pyroborate ($Co_2B_2O_5$) were prepared by the solution combustion method [7]. Recently, a blue pearlescent pigment was obtained by coating microemulsion-synthesized $CoAl_2O_4$ nanoparticles onto mica titania [8]. Cobalt-doped alumina powders were synthesized by the polymeric precursor method to obtain a ceramic pigment [9]. The $Co_3(PO_4)_2$ and $FePO_4$ solid solutions ($Co_{3-x}Fe_xP_2O_{8+x/2}$) were synthesized by the chemical coprecipitation method [10]. The possibility of using cobalt molybdophosphates as pigments was also demonstrated [11].

There is a wide range of various historical cobalt pigments. Some of them were more important in the history of painting, others were more often used for decorating ceramic works or producing ceramic glaze [1, 3, 12–18]. For example, cobalt yellow (aureolin, $K_3[Co(NO_2)_6]$) appeared in trade as a pigment in 1860. In those years it was the only steady bright yellow glazing colour used in the colour assortment together with the Indian yellow. Because of the remarkable effect this pigment is perfectly suitable for various painting techniques:

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aquarelle, tempera and oil. Also, it is used in glass, porcelain painting, and enamel. The most important violet cobalt pigments are different phosphates: cobalt violet brilliant light ($CoNH_4PO_4 \cdot H_2O$) and cobalt violet dark ($Co_3(PO_4)_2$). These pigments have been known since the end of the 18th century. Cobalt cerulean blue ($CoO \cdot nSnO_2$) was discovered in 1789. This pigment was used in enamel art and porcelain painting. Cobalt blue dark and cobalt blue light ($CoO \cdot Al_2O_3$) pigments were already used in ancient Egypt for decorating pottery. Cobalt blue greenish ($Cr_2O_3 \cdot CoO \cdot Al_2O_3$) was produced in the middle of the 19th century and used for decorating porcelain. The colour of pigment varies from bluish green to greenish blue depending on the molar ratio of aluminium and chromium. Cobalt green bluish ($CoO \cdot ZnO$) was synthesized in 1778 and became more widely used in the 19th century. The pigment is resistant to light and suitable for all painting techniques. The blue cobalt pigment smalt ($CoO \cdot nSiO_2$) is also of significant importance in art history. It was known and used as a pigment already in the ancient world, in Egypt and Mesopotamia. In the 17th century, the smalt became one of the basic blue pigments in baroque style painting.

Recently, in order to demonstrate the reliability of the X-ray powder diffraction (XRD) technique, XRD analyses were performed on representative samples of lead oxide (Pb_3O_4 or $PbCO_3 \cdot Pb(OH)_2$) based pigments and glazes [19]. The glaze compositions contained silica and calcite as the main constituents and pigments lead-tin yellow, smalt, Verona green, manganese black, Naples yellow and malachite as secondary phases. XRD analysis has proven to be a useful tool for the qualitative determination of the composition of glazes. In the present study, attention has been focused on the characterization of cobalt-based pigments and glazes using X-ray diffraction analysis. The identification of pigments in their mixtures or on unknown ceramic samples is very important not only for the characterization of materials, but also for non-destructive conservation and successful restoration, dating and authentication [20–22].

EXPERIMENTAL

Ten analytical grade individual pigments (Kremer Pigmente) were used for the X-ray diffraction characterization: $K_3[Co(NO_2)_6] \cdot 3H_2O$ (cobalt yellow, Aureolin), $CoNH_4PO_4 \cdot H_2O$ (cobalt violet brilliant light), $Co_3(PO_4)_2$ (cobalt violet dark), $CoO \cdot nSnO_2$ (cobalt cerulean blue), $CoO \cdot Al_2O_3$ (cobalt blue dark), $CoO \cdot Al_2O_3$ (cobalt blue light), $Cr_2O_3 \cdot CoO \cdot Al_2O_3$ (cobalt blue greenish), $CoO \cdot ZnO$ (cobalt green bluish), $CoO \cdot nSiO_2$ (smalt with different grind: 120 μm and 80 μm). The same pigments along with lead oxide (Pb_3O_4) and silica (SiO_2) were used for the preparation of cobalt-based glazes. In all cases the same molar ratio of ingredients has been selected $Pb_3O_4 : SiO_2$: pigment = 2.85 : 1.9 : 0.25.

The pigments and prepared glazes were characterized by X-ray powder diffraction (XRD) analysis. The XRD was performed with a D8 Bruker AXS powder diffractometer using $CuK\alpha_1$ radiation.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the cobalt yellow (aureolin) pigment is shown in Fig. 1. All diffraction peaks corresponds to a standard diffractogram of $K_3[Co(NO_2)_6]$ (PDF [9–404]. The XRD pattern of cobalt yellow based glaze is shown in Fig. 2. Most of the diffraction lines seen in Fig. 2 could be attributed to the Pb_3O_4 phase (PDF [41–1493]). Besides, the most intensive line from silica at $2\theta \approx 20.8°$ (PDF [34–717]) is also seen. However, no signals from cobalt yellow (aureolin) pigment, likely at $2\theta \approx 34.6°$, 24.5° and 42.8°, could be detected in the XRD pattern of the cobalt yellow based glaze.

The X-ray diffraction pattern of the cobalt violet brilliant light pigment is a typical XRD pattern of $CoNH_4PO_4 \cdot H_2O$ (Fig. 3) (PDF [21–793]). The XRD pattern of the cobalt violet brilliant light based glaze is shown in Fig. 4. The main diffraction peak of the cobalt violet brilliant light pigment located at $2\theta \approx 10.0°$ is seen in Fig. 4.

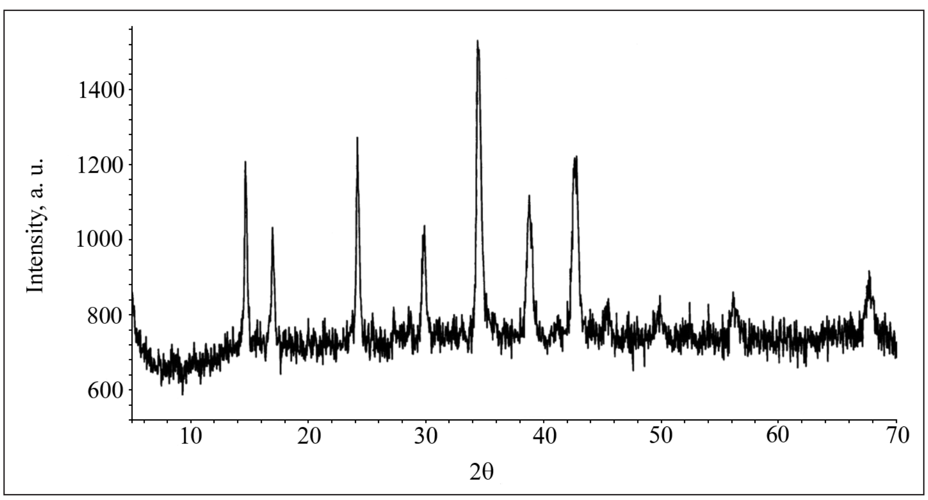

Fig. 1. X-ray diffraction pattern of cobalt yellow (aureolin) pigment

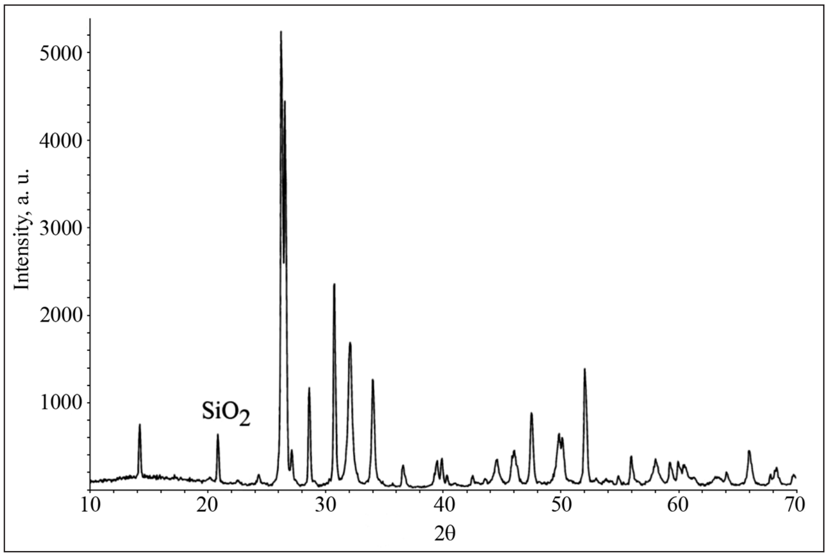

Fig. 2. X-ray diffraction pattern of cobalt yellow based glaze

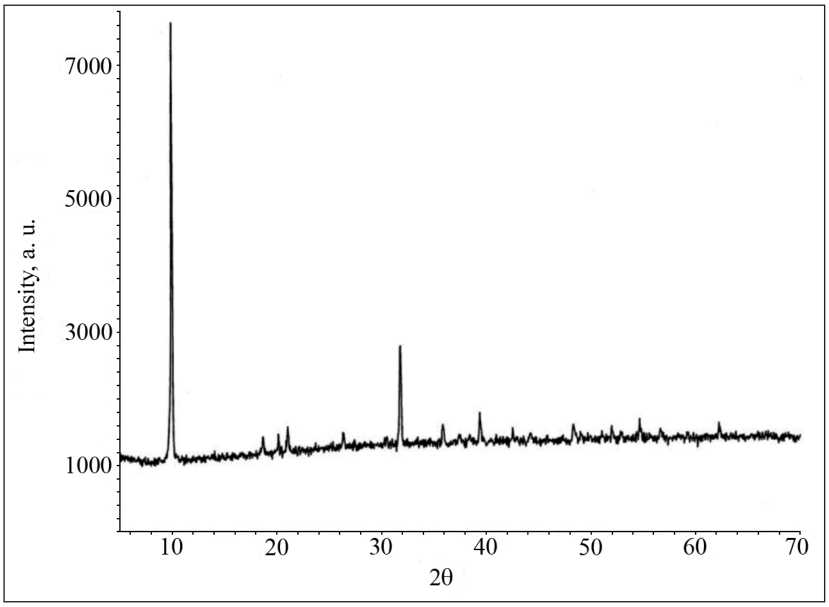

Fig. 3. X-ray diffraction pattern of cobalt violet brilliant light pigment

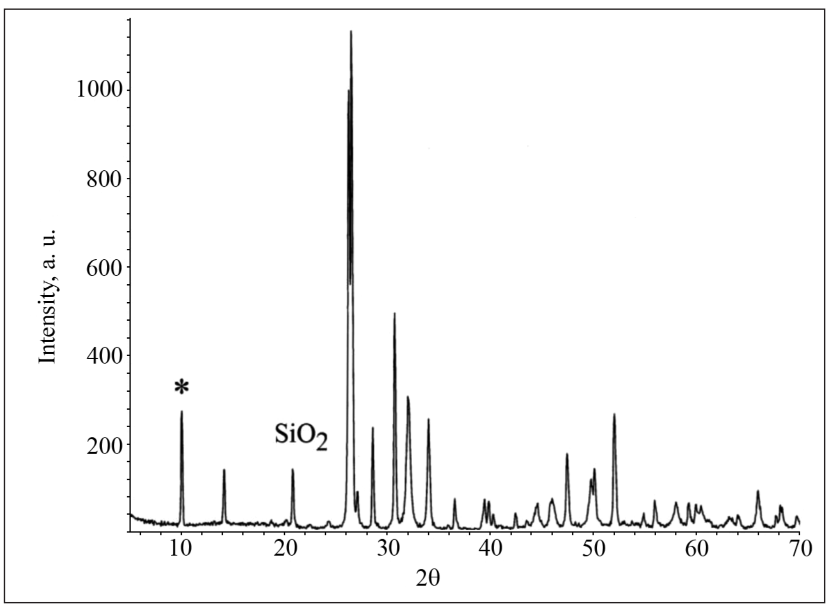

Fig. 4. X-ray diffraction pattern of cobalt violet brilliant light based glaze. (∗) – $CoNH_4PO_4 \cdot H_2O$

Therefore, we can conclude that, contrary to aureolin, the cobalt violet brilliant light pigment could be distinguished in its glaze by X-ray diffraction.

The XRD pattern of the cobalt violet dark pigment is shown in Fig. 5. This XRD pattern matches very well the XRD pattern of $Co_3(PO_4)_2$ (PDF [13–503]). The XRD pattern of the cobalt violet dark based glaze is shown in Fig. 6. Hardly distinguishable peaks of $Co_3(PO_4)_2$ phase at $2\theta \approx 21.7°$ and 23.0° are seen in the XRD pattern of the appropriate glaze. Thus, to detect the cobalt violet dark pigment in glaze by the X-ray diffraction technique is almost impossible.

The formula of the cobalt cerulean blue pigment presented in the catalogue of Kremer Pigmente is given as $CoO \cdot nSnO_2$. However, X-ray analysis data (Fig. 7) have confirmed that the purchased reagent contains cobalt stannate spinel Co_2SnO_4 (PDF [29–514]) as the main phase and the metal oxides Co_3O_4 (PDF [42–1467]) and SnO_2 (PDF [41–1445]) as secondary phases. The XRD pattern of cobalt cerulean blue based glaze is shown in Fig. 8. One can see that the most intensive lines attributable to the cobalt stannate spinel Co_2SnO_4 ($2\theta \approx 34.4°$, 17.8° and 41.8°) are visible in the XRD pattern of glaze. These results allow concluding that the cobalt cerulean blue pigment could be easily determined in glaze by XRD.

Both cobalt blue dark and cobalt blue light pigments in the Kremer Pigmente catalogue are described as $CoO \cdot Al_2O_3$ material. However, the XRD patterns of these two pigments are quite different (see Figs. 9 and 10, respectively). Surprisingly, the XRD pattern of the cobalt blue

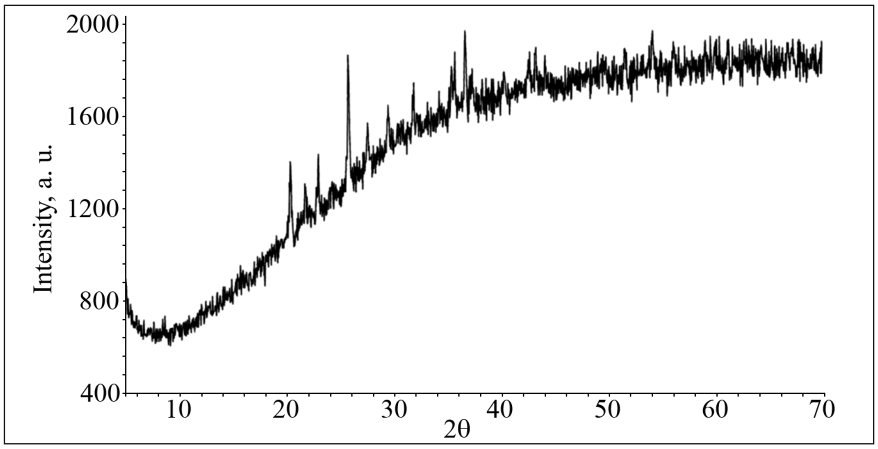

Fig. 5. X-ray diffraction pattern of cobalt violet dark pigment

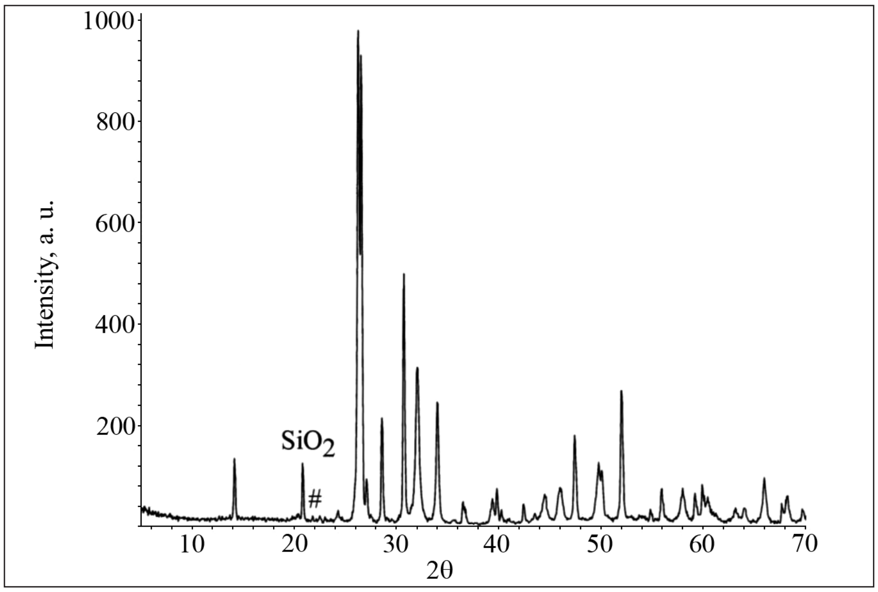

Fig. 6. X-ray diffraction pattern of cobalt violet dark based glaze. (#) – $Co_3(PO_4)_2$

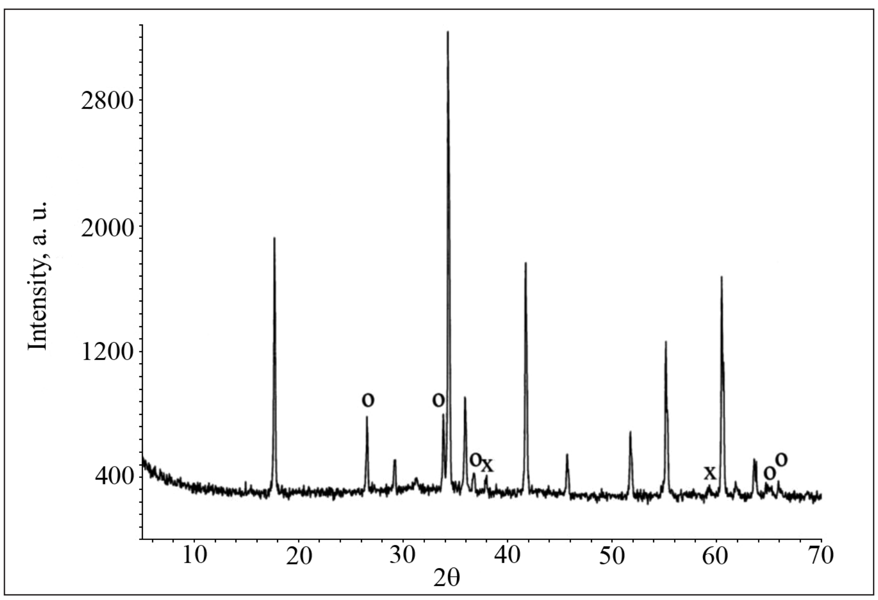

Fig. 7. X-ray diffraction pattern of cobalt cerulean blue pigment. (o) – SnO_2 and (×) – Co_3O_4

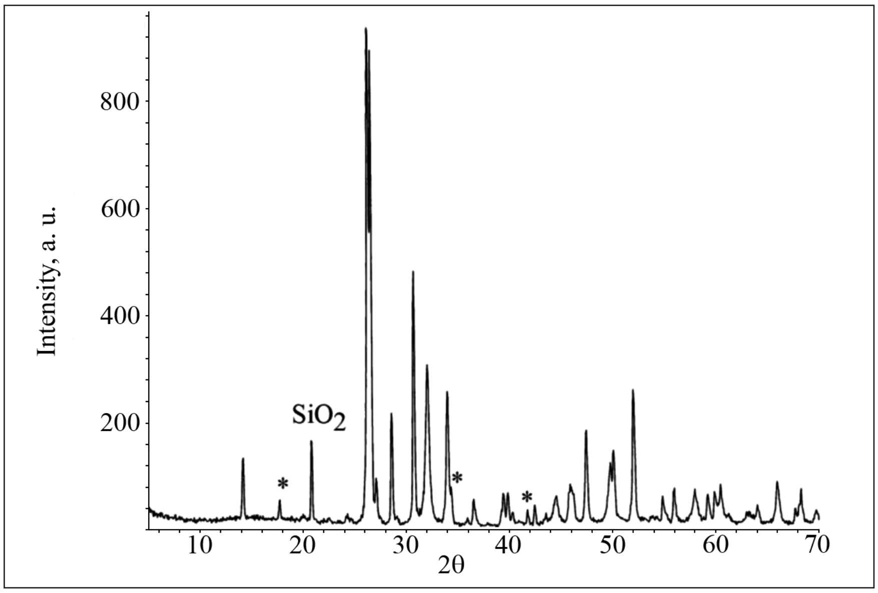

Fig. 8. X-ray diffraction pattern of cobalt cerulean blue based glaze. (*) – Co_2SnO_4

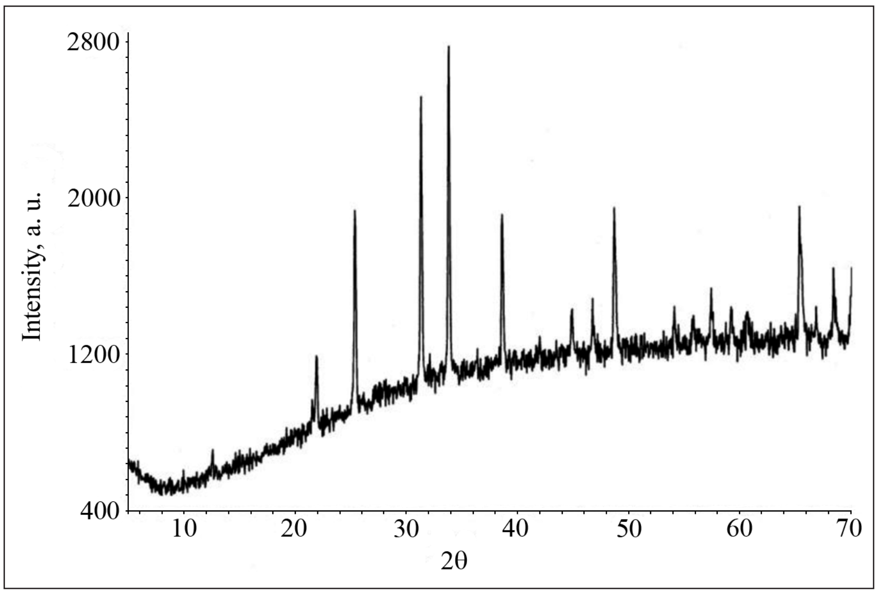

Fig. 9. X-ray diffraction pattern of cobalt blue dark pigment

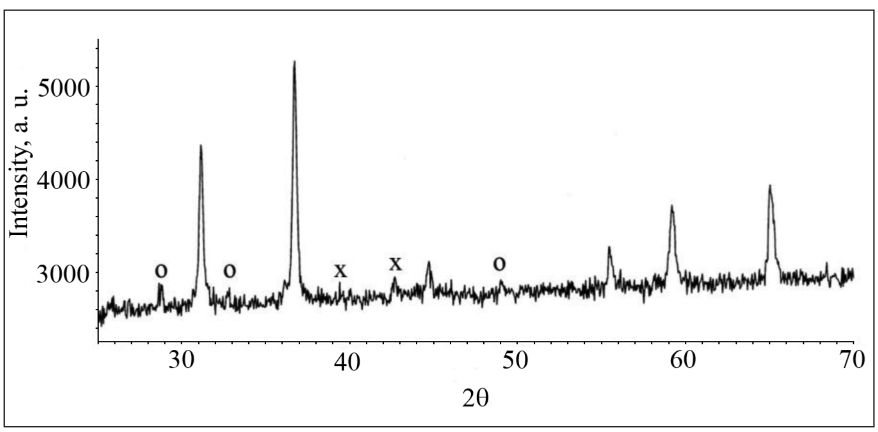

Fig. 10. X-ray diffraction pattern of cobalt blue light pigment. (o) – Al_2O_3 and (×) – CoO

dark pigment (Fig. 9) does not contain any reflections from known inorganic phases of cobalt and aluminium. Therefore, the phase composition of this pigment was not identified. On the other hand, X-ray analysis data of the cobalt blue light pigment (Fig. 10) have confirmed that the purchased reagent contains cobalt aluminate spinel $CoAl_2O_4$ (PDF [38–814]) as the main phase and metal oxides Al_2O_3 (PDF [35–1121]) and CoO (PDF [9–402]) as secondary phases. The XRD pattern of cobalt blue dark based glaze is shown in Fig. 11. The low intensity diffraction lines at $2\theta \approx 31.3°$, 25.8° and 49.0° attributable to the pigment phase, are visible in the XRD pattern. The XRD pattern of cobalt blue light based glaze is shown in Fig. 12. Between diffractions from Pb_3O_4 and SiO_2 phases, lines attributable to $CoAl_2O_4$ spinel are also seen ($2\theta \approx 36.9°$, 31.3° and 65.3°). So, cobalt blue pigments, especially cobalt blue light pigment, could be detected by XRD in their glazes.

The XRD pattern of cobalt blue greenish pigment is shown in Fig. 13. According to the XRD results, the cobalt blue greenish pigment is cobalt chromate spinel $CoCr_2O_4$ (PDF [22–1084]), but not a mixture of separate oxides $Cr_2O_3 \cdot CoO \cdot Al_2O_3$. Moreover, no phases containing aluminium have been determined. It is possible that alumina exists as a separate amorphous phase. This assumption is supported by a large background of the XRD pattern presented in Fig. 13. The XRD pattern of cobalt blue greenish based glaze is shown in Fig. 14. Unfortunately, no even traces of $CoCr_2O_4$ could be detected in the glaze by the XRD technique.

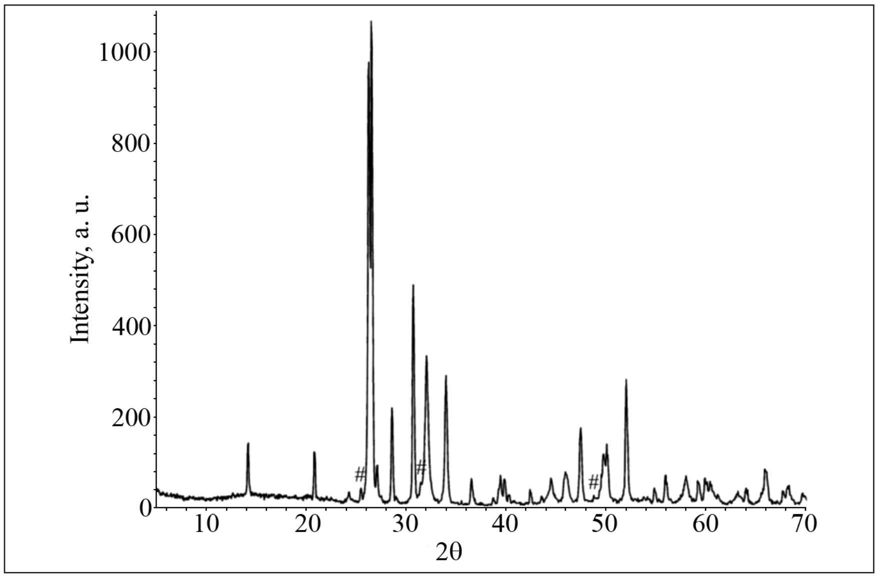

Fig. 11. X-ray diffraction pattern of cobalt blue dark based glaze. (#) – cobalt blue dark pigment

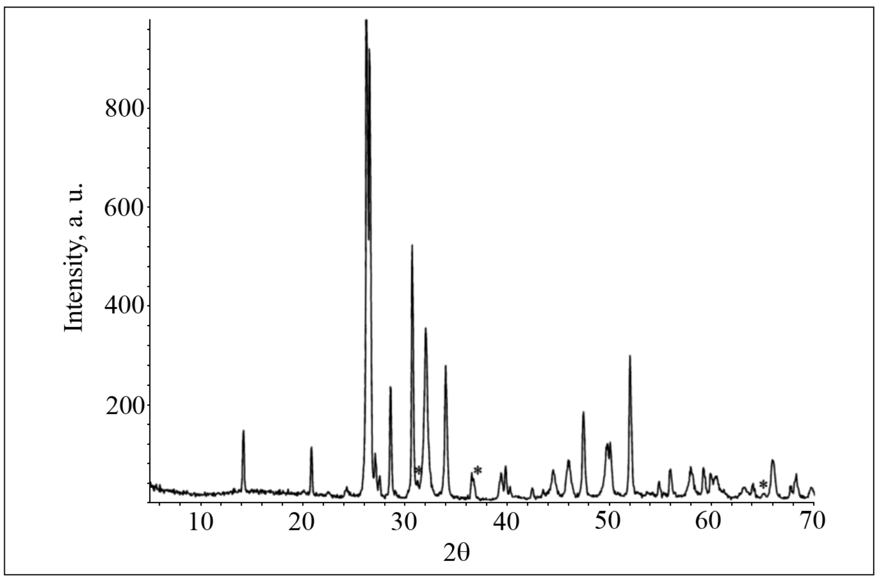

Fig. 12. X-ray diffraction pattern of cobalt blue light based glaze. (*) – $CoAl_2O_4$

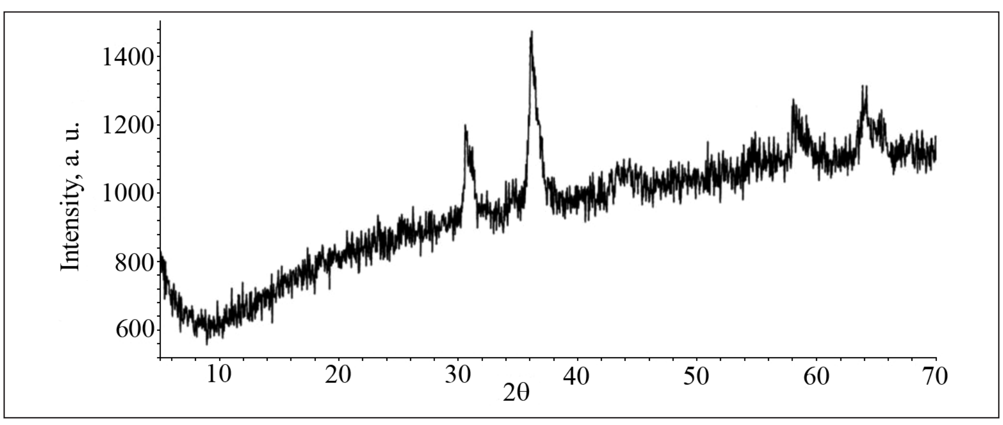

Fig. 13. X-ray diffraction pattern of cobalt blue greenish pigment

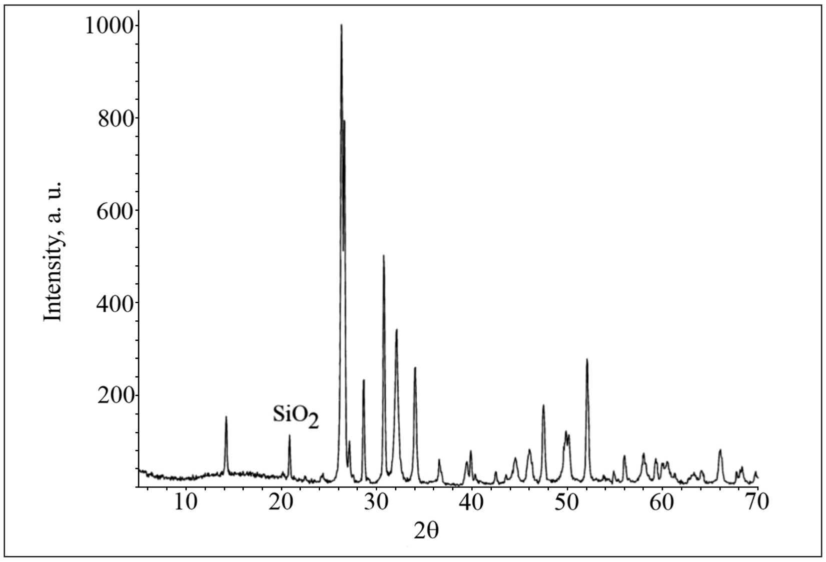

Fig. 14. X-ray diffraction pattern of cobalt blue greenish based glaze

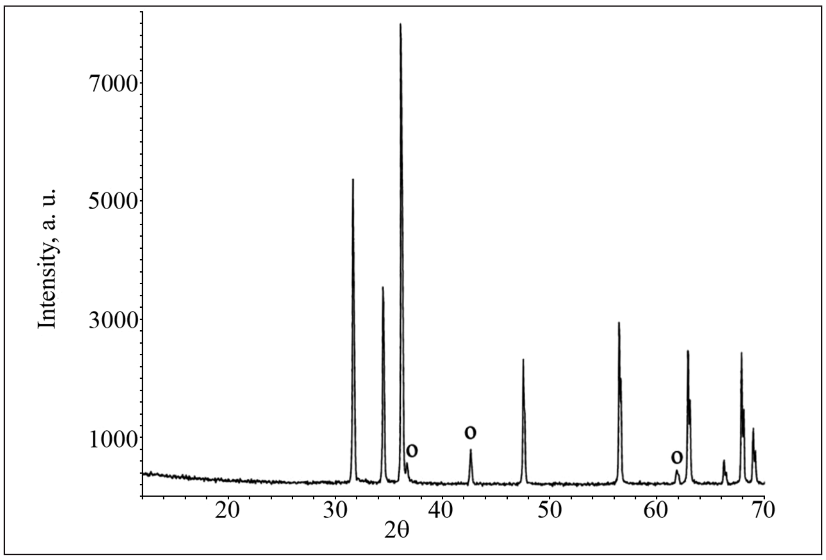

Fig. 15. X-ray diffraction pattern of cobalt green bluish pigment. (o) – CoO

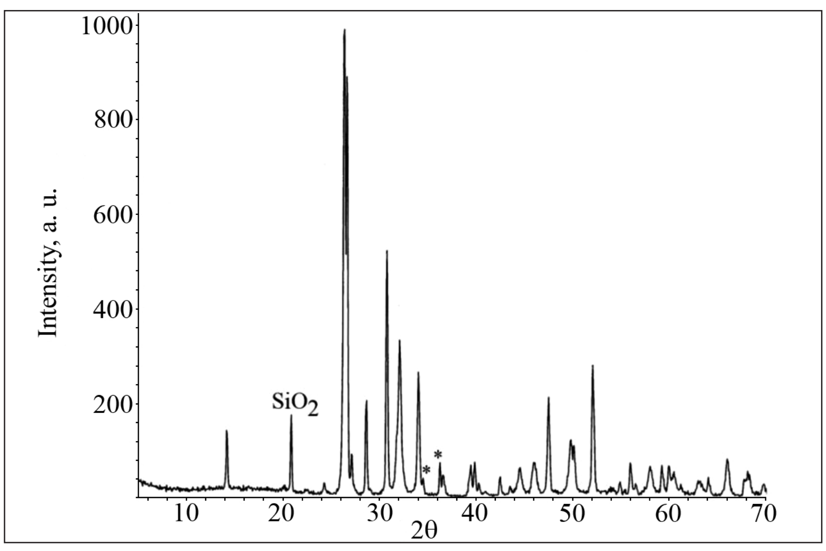

Fig. 16. X-ray diffraction pattern of cobalt green bluish based glaze. (∗) – ZnO

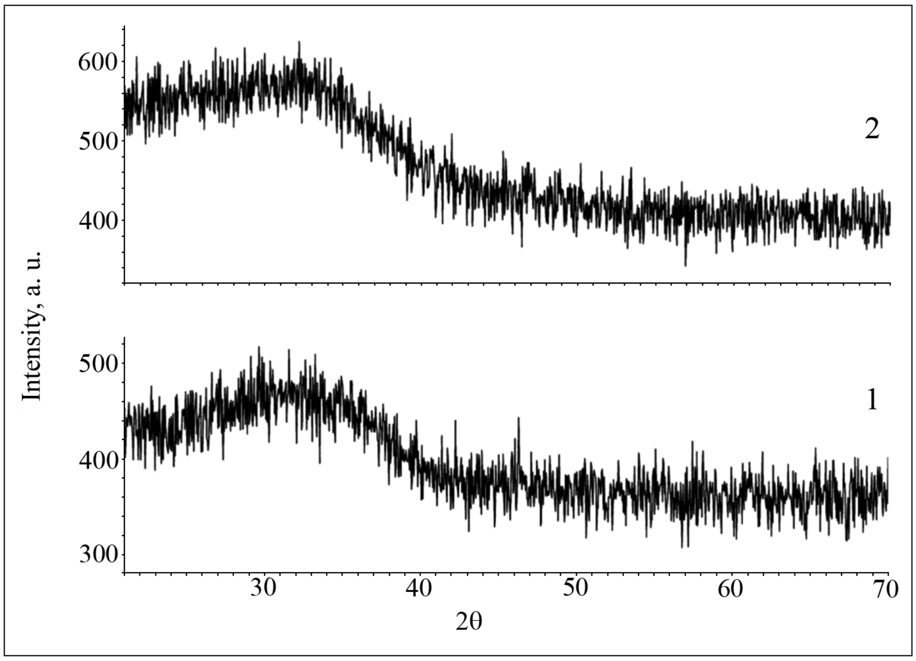

Fig. 17. X-ray diffraction pattern of cobalt smalt pigments having different particle size: (1) –120 μm and (2) – 80 μm

The XRD pattern of cobalt green bluish pigment corresponds to the XRD pattern of ZnO (PDF [36–1451]) as the main phase along with diffraction lines from the CoO (PDF [43–1004]) phase (Fig. 15). These results are in good agreement with the nominal composition of the pigment (CoO · ZnO). The XRD pattern of cobalt green bluish based glaze is shown in Fig. 16. The marked diffraction lines at 2θ ≈ 36.3° and 34.4° correspond to the ZnO phase. These results suggest that, contrary to the cobalt blue greenish pigment, the cobalt green bluish pigment could be distinguished in its glaze by X-ray diffraction.

Finally, Fig. 17 represents two XRD patterns of the smalt pigment (CoO · $nSiO_2$) having a different particle size – 120 μm and 80 μm. We see that both XRD patterns show only an amorphous character, and no any crystalline phases could be identified. Therefore, no further experiment with smalt based glazes were undertaken.

CONCLUSIONS

Cobalt-based pigments and glazes of different chemical composition were characterized by XRD analysis which has clearly showed that the chemical composition of some purchased pigments (cobalt yellow, cobalt violet brilliant light, cobalt violet dark, cobalt green bluish) corresponds to the one given in the Kremer Pigmente catalogue. However, the chemical composition of several pigments has been slightly corrected. The cobalt cerulean blue pigment contains cobalt stannate spinel Co_2SnO_4 as the main phase and metal oxides Co_3O_4 and SnO_2 as secondary phases. The cobalt blue light pigment contains cobalt aluminate spinel $CoAl_2O_4$ as the main phase and metal oxides Al_2O_3 and CoO as secondary phases. According to the XRD results, the cobalt blue greenish pigment is cobalt chromate spinel $CoCr_2O_4$, but not a mixture of separate oxides Cr_2O_3 · CoO · Al_2O_3. Besides, the XRD pattern of the cobalt blue dark pigment does not contain any reflections from known inorganic phases of cobalt and aluminium. The cobalt smalt pigment (CoO · $nSiO_2$) is a completely amorphous material. It was also demonstrated that, contrary to the cobalt yellow, cobalt violet dark, cobalt blue greenish and cobalt smalt, the cobalt violet brilliant light, cobalt cerulean blue, cobalt blue dark, cobalt blue light and cobalt green bluish pigments could be distinguished in the appropriate glazes by X-ray diffraction. Finally, we have demonstrated that XRD analysis is a significant analytical tool for the characterization of historical pigments and glazes. The results summarized in this paper are very important for developing new methods for the conservation of glazed pottery.

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KOBALTO ISTORINIŲ PIGMENTŲ IR GLAZŪRŲ APIBŪDINIMAS RENTGENO SPINDULIŲ DIFRAKCINĖS ANALIZĖS METODU

Santrauka

Parodyta, kad Rentgeno spindulių difrakcinė analizė yra pakankamai efektyvus metodas kobalto pigmentams bei glazūroms apibūdinti. Kobalto pigmentų (Kremer Pigmente, Vokietija) Rentgeno spindulių difrakcinė analizė akivaizdžiai parodė, kad kai kurių pigmentų kataloguose pateikta cheminė sudėtis skiriasi nuo nustatytosios. Kobalto pigmentas ceruleumas yra Co_2SnO_4 (pagrindinė fazė), SnO_2 ir Co_3O_4 mišinys, o ne $CoO \cdot nSnO_2$; kobalto mėlynasis šviesusis – $CoAl_2O_4$ (pagrindinė fazė), Al_2O_3 ir CoO mišinys, o ne $CoO \cdot Al_2O_3$; kobalto melsvai žaliasis – $CoCr_2O_4$ (pagrindinė fazė), o ne $Cr_2O_3 \cdot CoO \cdot Al_2O_3$. Kobalto mėlynojo tamsiojo fazinė sudėtis nieko bendro neturi su $CoO \cdot Al_2O_3$. Nustatyta, kad Rentgeno spindulių difrakcinės analizės metodas tinka identifikuoti kobalto šviesiai violetinį, ceruleumą, kobalto mėlynąjį šviesųjį, kobalto mėlynąjį tamsųjį ir kobalto žalsvai mėlynąjį jų glazūrose, tačiau netinkamas aureolino, kobalto tamsiai violetinio, kobalto melsvai žaliojo ir smaltos identifikavimui.