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Ultramarine – not just a pigment of traditional folk architecture plasters

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Abstract

Ultramarine is a synthetic analogue of lazurite, so called lapis lazuli. It was applied first of all as a pigment of lime- and gypsum-based plasters of folk architecture. Ultramarine is still used as a pigment of building materials, and, it may act as a non-traditional pozzolanic material as well. The paper describes a laboratory synthesis procedure of blue ultramarine that is derived from historic formulas. Structural, and optical properties and phase composition of laboratory-produced samples were compared to the samples of folk houses plasters and to unused, contemporary and historic industrially-produced ultramarines. The means of powder X-ray diffraction, Raman spectroscopy, and polarizing optical microscopy were used. The properties of the laboratory-prepared samples were very close to the industrial ones. In the market, the commercially available ultramarines are blue, pink and purple. However, based on published data, it should be possible to produce green ultramarine by the modification of the production process. These colors were not reached during the laboratory experiments, even when the published formulas were precisely followed.

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1. Introduction

Lazurite $(\text{Na,Ca})_{7-8}(\text{Al,Si})_{12}(\text{O,S})_{24}[(\text{SO}_4,\text{Cl}_2,\text{(OH)}_2)]$ [1] is an aluminosilicate with sodalite structure containing entrapped sodium ions and two types of sulfur groups. Specific absorption of the part of light spectrum results in blue or other colors of the compound. It was used as a blue pigment mainly in graphic art since primordial ages. In the past, the blue lazurite pigment was obtained from the rock called lapis lazuli.

Because natural lazurite was expensive and inaccessible, the way of its artificial production was searched. Synthetic lazurite, called ultramarine, was prepared 1828 in France by Jean Baptiste Guimet. Concurrently, C. G. Gmelin prepared ultramarine using rather different formula in Germany. However, the first record of ultramarine use comes from J. W. Goethe, who observed a blue coats non-intentionally appearing on the walls of lime kilns in Sicily and which were used as a blue pigment instead of lapis lazuli [2 in 3]. Ultramarine is stable in high alkaline ambience and therefore it can be used for coloring both gypsum and lime renders and plasters. In the region of Czech Republic, lime burning is documented by archaeological finds since Neolithic period [4,5]. However, the lime application spread in the 9th century [5]. The first record of deliberate gypsum burning in the Central Europe is of a comparable age [6]. Since approximately half of the 19th century until the half of the 20th ct. ultramarine was vastly used for coloring plasters of Central European folk architecture. The evidence of its pozzolanic activity was published as well [7].

Modern production of ultramarine utilizes common cheap raw materials such as kaolin, feldspar, diatomaceous earth, zeolite, sodium carbonate, sodium sulfate, sulfur etc. The preparation proceeds in reducing atmosphere, therefore a reduction agent must be used. Coal powder, mineral oil, resin or pitch is used. Kaolin is preheated to about 550–700 °C to destabilize and dehydroxylate clay minerals structures; heated kaolin is called metakaolin. Raw mixture of metakaolin, sodium carbonate, sulfur and a reduction agent (or combinations of other components) is heated in a sealed crucible. At first, the sodium carbonate or sulfate reacts with sulfur to form sodium polysulfide. If the temperature increases, the structures of clay minerals transform to sodalite by entrapping sodium and polysulfide ions.

Technologies of ultramarine preparation were usually kept as a secret know-how of a producer. Many procedures were protected by patents [8]. Therefore, there is not much exact information on ultramarine technology.

Nowadays, the world production of ultramarine is limited [9] due to ecological reasons – extensive emissions of sulfur oxides are released during the heating. Furthermore, heavily polluted wastewater after washing the final product is the further ecological issue. Specific problem is a very fine ultramarine powder that cannot be eliminated by commercially available filters and which covers surroundings of the ultramarine plants.

2. Material and methods

To verify an old and not very well known technology, a lot of experiments of ultramarine preparation were done. The used raw materials were as follows:

- zeolite (clinoptilolite) from Nižný Hrabovec (Slovakia)
- kaolin from the Božičany site (western Bohemia)
- diatomaceous earth from the Borovany site (southern Bohemia)
- sodium carbonate and sodium sulfate (commonly available laboratory chemicals)
- powdered sulfur for medicinal purpose
- mineral oil, powder of wood coal and resin (as reduction agents)

Kaolin was preheated to 550°C with 6 hours soaking to transform to metakaolin. Zeolite was preheated to 500°C for 48 hours.

Mineral composition, lazurite crystallinity and lattice parameters were identified using powder X-ray diffraction analysis (PXRD) and Raman spectroscopy. Composition of final prepared sample was compared with commercial product made by Západočeské keramické závody n. p. Horní Bříza, plant in Břasy (Czech Republic) that was saved in sample archive since about 1960 and to two samples of historical folk architecture plasters from Eastern Moravia, Czech Republic – Lužice and Doubravy sites.

PXRD analyses were conducted on the a Bruker D8 Advance diffractometer, equipped with a copper tube ($\lambda K\alpha = 0.15418$ nm), powered at 40 kV and 30 mA at Bragg-Brentano para focusing $\Theta - \Theta$ reflection geometry; step size – $0.02^\circ 2\theta$, time per step – 188 s, angular range $5 - 80^\circ 2\theta$. Rietveld method–based quantitative phase analysis, refinement of lazurite lattice parameters, and crystallite size analysis was performed with the help of Panalytical High Score 3 plus software and ICSD 2012 database. Lazurite crystal structure information was obtained from ICSD 98-009-5459 model [10].

Raman spectra were obtained using a HORIBA LabRam HR Evolution instrument and processed using LabSpec 6 software. Measurement conditions: green laser 532 nm, 100 \times objective magnification, aperture – hole: 400, slit: 100, 600 grid, 1% filter, 2*60 s counting time, 100–1300 cm^{-1} range.

Light microscopy (LM) analysis in transmitted polarized light was performed using Olympus BX 51 microscope. Historical plasters were studied in a form of thin sections. The other samples were observed as fine powders in immersion liquid.

3. Results and discussion

A lot of unsuccessful experiments were done with various component ratios, burning temperature and soaking. The first success was recorded using a mixture of metakaolin (38.9 wt. %), sodium carbonate (30.9 wt. %), powdered sulfur (27.7 wt. %), and resin (2.5 wt. %). The mixture was heated to 750 $^\circ\text{C}$ with 8 hours soaking in a sealed platinum crucible. After this procedure, the top part of sample was grey, while the bottom part was bright blue. The desirable result was reached after reduction of the firing temperature to 730 $^\circ\text{C}$ and extension of soaking to 48 hours. The final product was of marine blue color.

The comparison of the macroscopic appearance of the experimental final product and a commercial product is shown in the Fig. 1.

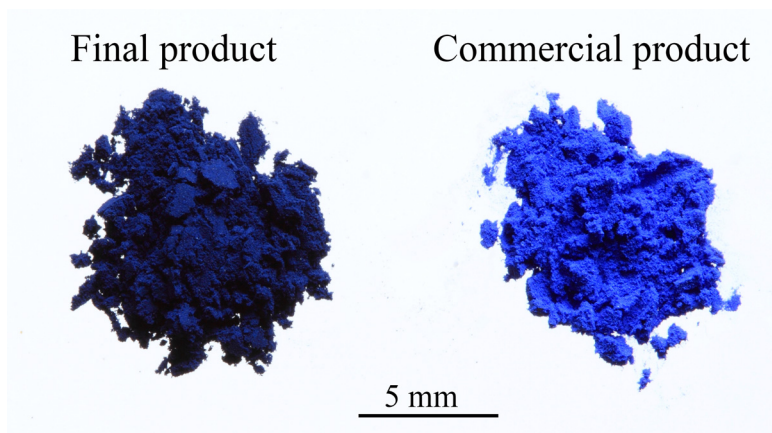


Fig. 1. Macroscopic appearance of laboratory-produced (“Final product”) and commercial ultramarine.

A microphotograph of ultramarine pigment in a layered lime plaster from a folk house from the Doubravy site – see Fig. 2. Grains of other colors than blue, violet in this case, sporadically occur in historic samples. Ultramarine of any shade can easily be optically identified due to its cubic structure, and, hence, optical isotropy. Although the production technologies of various ultramarine colors were published [3], the attempts to experimentally produce other colors than blue were unsuccessful.

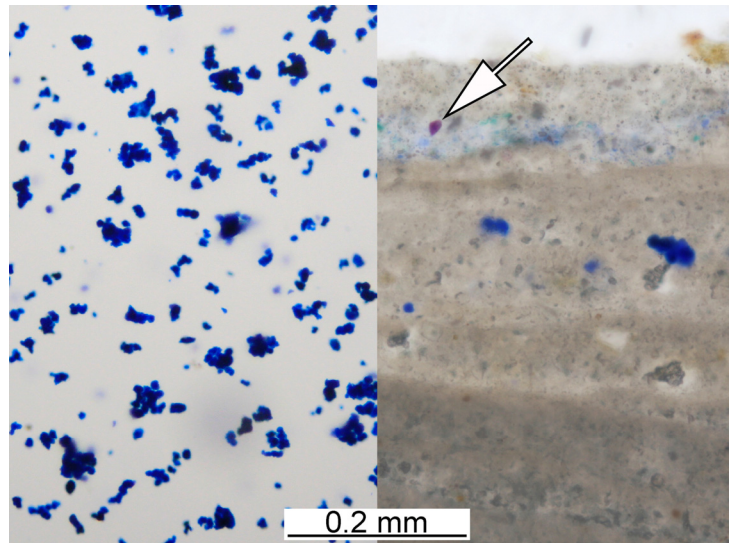


Fig. 2. Transmitted plane polarized light microphotograph of laboratory final product (left) and a thin section of lime plaster from Doubravy. Violet ultramarine grain is marked with an arrow.

The darker marine blue color of the final laboratory product may be caused by significantly higher lazurite concentration in the final product (84.8%) than in the commercial one (67.9%). Although a better crystallinity (crystallite size) may play a role as well. The next abundant mineral in both the samples is nepheline. Low contents of quartz and the presence of albite in the commercial product can be considered as residues of unreacted raw material. Thenardite is the last mineral identified in both samples. The thenardite presence can be easily explained by the raw mix composition and production procedure. The occurrence of very low amounts of sodalite is possible as well. The complete phase analysis, lazurite crystallite size analysis, and lattice constant refinement – see Table 1. The properties of lazurite from two samples of historical plasters of folk houses calculated from powder X-ray diffractograms are also given in the Table 1. The commercial product exhibits the lowest crystallinity of lazurite. It may be due to fastening the industrial production process or extensive milling process. The lattice constant and, hence, the unit cell volume, is the largest in the laboratory final product, which could be caused by larger sulfur content per formula unit. However, the differences in the lattice constants are not very significant.

Table 1. Phase composition of laboratory-produced (“Final product”) and commercial ultramarine and lazurite properties in the examined samples.

	Mineral	Chemical formula	Final product	Commercial product	Lužice (gypsum plaster)	Doubravy (lime plaster)
Phase analysis (wt.%)	Lazurite	$((\text{Na,Ca})_{7-8}(\text{Al,Si})_{12}(\text{O,S})_{24}[(\text{SO}_4)_2\text{Cl}_2(\text{OH})_2])$	84.8	67.9		
	Nepheline	$\text{NaAlSi}_3\text{O}_8$	14.2	25.2		
	Quartz	SiO_2	0.3	2.4		
	Thenardite	Na_2SO_4	0.7	1.6		
	Albite	$\text{NaSi}_3\text{AlO}_8$	-	2.9		
	Lazurite Crystallite size (nm)		68.1	51.6	65.3	64.1
	Lazurite lattice parameter a (Å)		9.1012 (5)	9.0725 (5)	9.0744 (5)	9.0902 (9)
	Rwp		8.635	7.932	8.265	7.428

Lazurite structure was also compared by the means of Raman spectroscopy. The obtained spectra are compared in the Fig. 3. Apparently, the lazurite structure is nearly identical in all the examined samples.

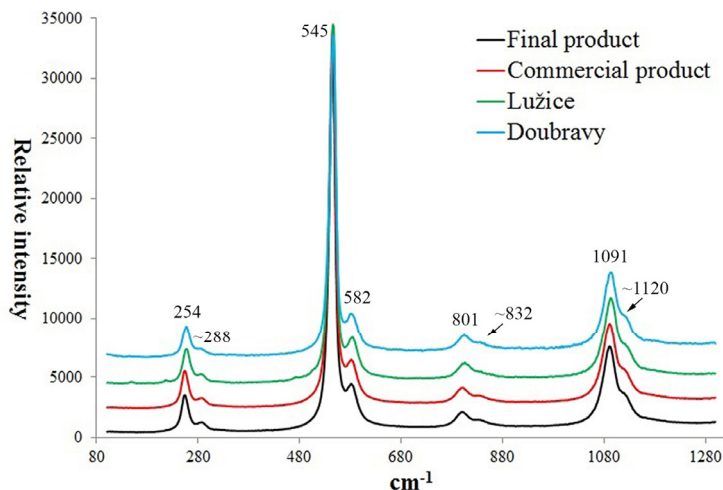


Fig. 3. Raman spectra of the analyzed samples.

4. Conclusion

The old technology of ultramarine production was successfully reconstructed. Ultramarine (lazurite) of the same crystal structure as found in the ultramarines of examined historic samples and in the examined commercial product was synthesized. The obtained sample can serve as reference standard for old paints and plaster research. The successful technology can be used for ultramarine production for restoration purposes.

Grains of other colors than blue also occur in “imperfect” ultramarine pigment of historic plasters. However, the experimental laboratory preparation of these pigments (green, violet, and pink) was not successful.

Acknowledgements

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