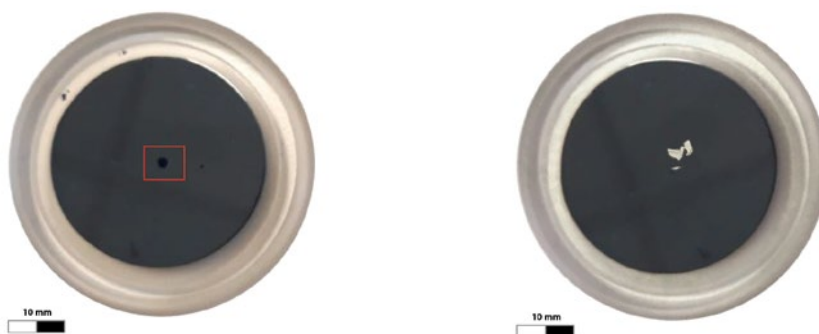


Application of XRD phase analysis and Rietveld refinement to the technological diagnostics and dating of paintings

Mineral composition of paints used for creation of artworks can be a reliable indicator for their dating and help to find authentic analogues for their restoration. Therefore, the identification of minerals in old and modern paints is one of the important analytical tasks in art science.

Here we consider the particular example of phase identification and quantification of ultramarines and zinc white of different origin and age with DRON-8 X-ray diffractometer and analytical software developed by “Bourestnik” Innovation Center, JSC. The collection of paints was kindly provided by Sergei Sirro, the curator of the State Russian Museum.

XRD measurements were complicated by minor quantities of paints. Sample weights usually did not exceed 1 mg. To get reliable diffraction data for analysis we used linear stripped position-sensitive detector for measurements and low-background polished substrates to mount paint particles. (Fig. 1).



Ultramarine from the painting “In the room” by V.Pakulin (see Fig. 2).

Zinc white from the collection of paints dated by 1941.

Figure 1 – Samples of paints mounted on low-background polished substrates cut from silicon single crystals.

Ultramarines and zinc white of Russian, Soviet and of European origin produced in the different periods of 20th century (in 1906 (Fig. 3), 1941, 80’s and 90’s), and also modern ultramarine have been analyzed and compared by their mineral composition.



Figure 2 – «In the Room» by V. Pakulin. Collection of the State Russian Museum.

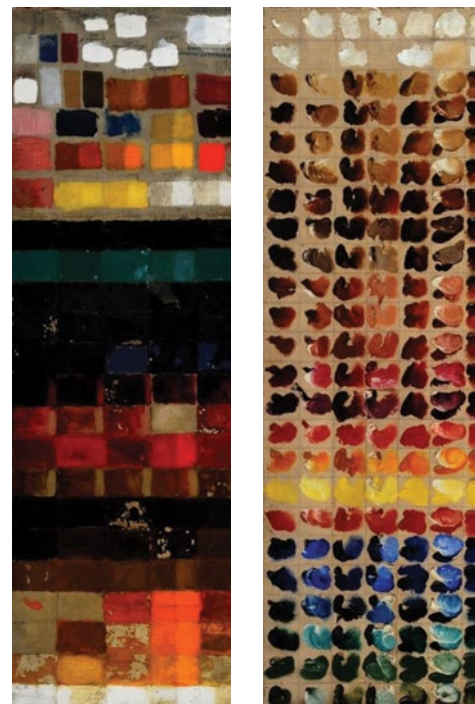


Figure 3 – Collection of Russian and Soviet paints produced in 1906 (left) and in 1941 (right), from which the particles of ultramarine and zinc white have been taken for study.

Identification of minerals has been performed with PDF-2 database (see Fig. 6 for example).

For quantification of mineral composition of paints Rietveld refinement has been successfully applied (see Fig. 7 for some examples).

Ultramarines of different ages showed lazurite $(Na,Ca)_6(SiAlO_4)_6(SO_4,S)_2$ to be the basic blue pigment. Its concentration in the studied paints varied from 100 до 20 wt. %. Additionally, the following minerals have been found in ultramarines as fillers: barite $BaSO_4$, carbonates (calcite $CaCO_3$ or siderite $FeCO_3$), boehmite $AlO(OH)$, and also gypsum $CaSO_4 \cdot 2H_2O$ and feldspars (albite $NaAlSi_3O_8$ and microcline $KAlSi_3O_8$).

Moreover, in the majority of Russian (Soviet) ultramarines the ratio between the pigment and the filler was found to be nearly the same (appr. 2:1). Pigment content in the studied European ultramarine is lower than 20 wt. %. The content of poorly crystallized lazurite in Russian paint produced in 90's do not exceed 30 wt. %. The ultramarine includes a great variety of mineral fillers (see Figs. 4 and 7b), that shows the evidence of low quality control during production of paints in Russia in this period of time.

Zinc white paints have rather stable mineral composition independent on age. They consist mostly of zincite ZnO as a basic pigment (72-97 wt. %) and a filler consisting of boehmite $AlO(OH)$ (up to 20 wt.%) and/or calcite $CaCO_3$ (up to 14 wt. %).

Mineral composition of paint, taken from the artwork of V.Pakulin created in 30's of 20th century, corresponds to mixture of ultramarine with minor addition of zinc white from the collection of Soviet paints dated by 1941.

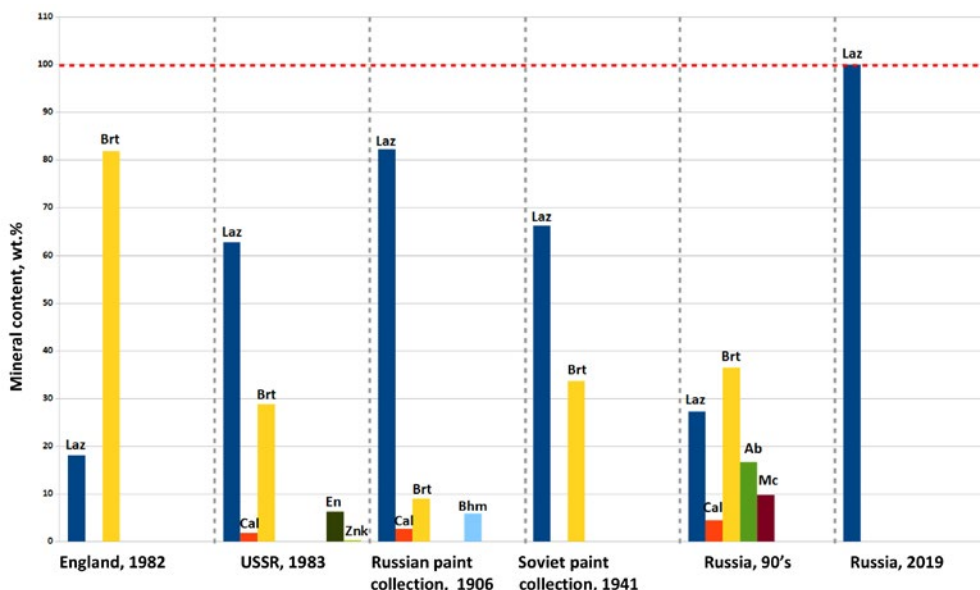


Figure 4 – Comparison of mineral composition of different ultramarines.

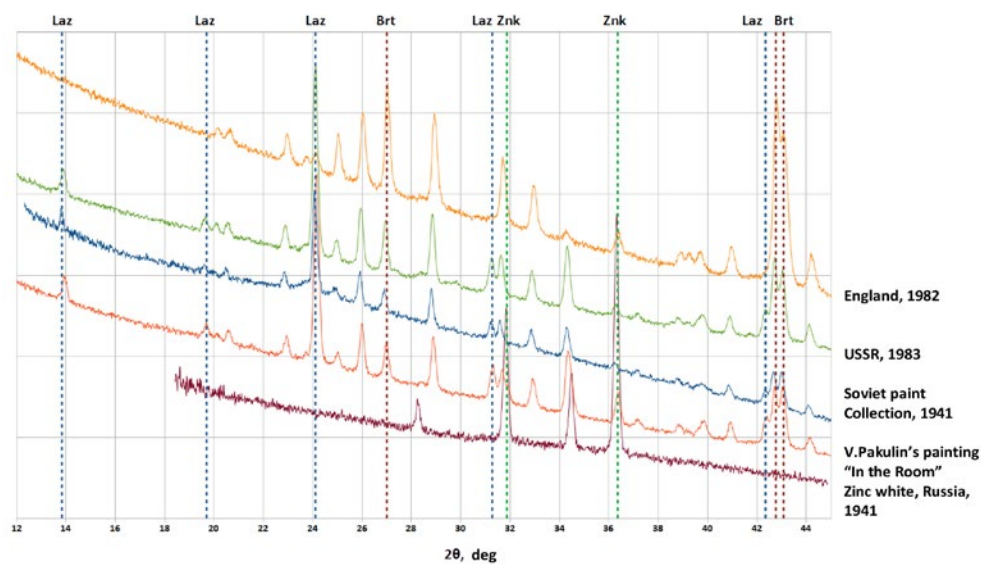


Figure 5 – Examples of XRD patterns of ultramarines and zinc white of different age. Vertical dashed lines show the analytical lines of the main minerals (Laz – lazurite, Brt – baryte, Znk – zincite).

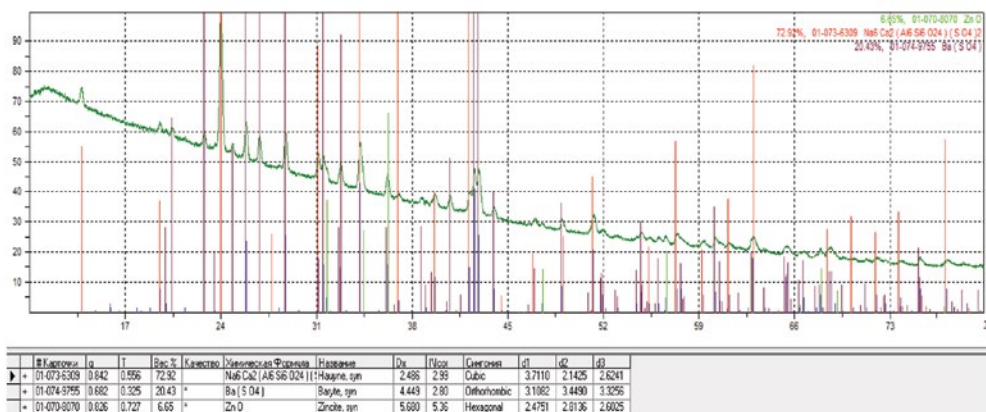


Figure 6 – Identification of minerals in the ultramarine taken from V. Pakulin's painting "In the Room".

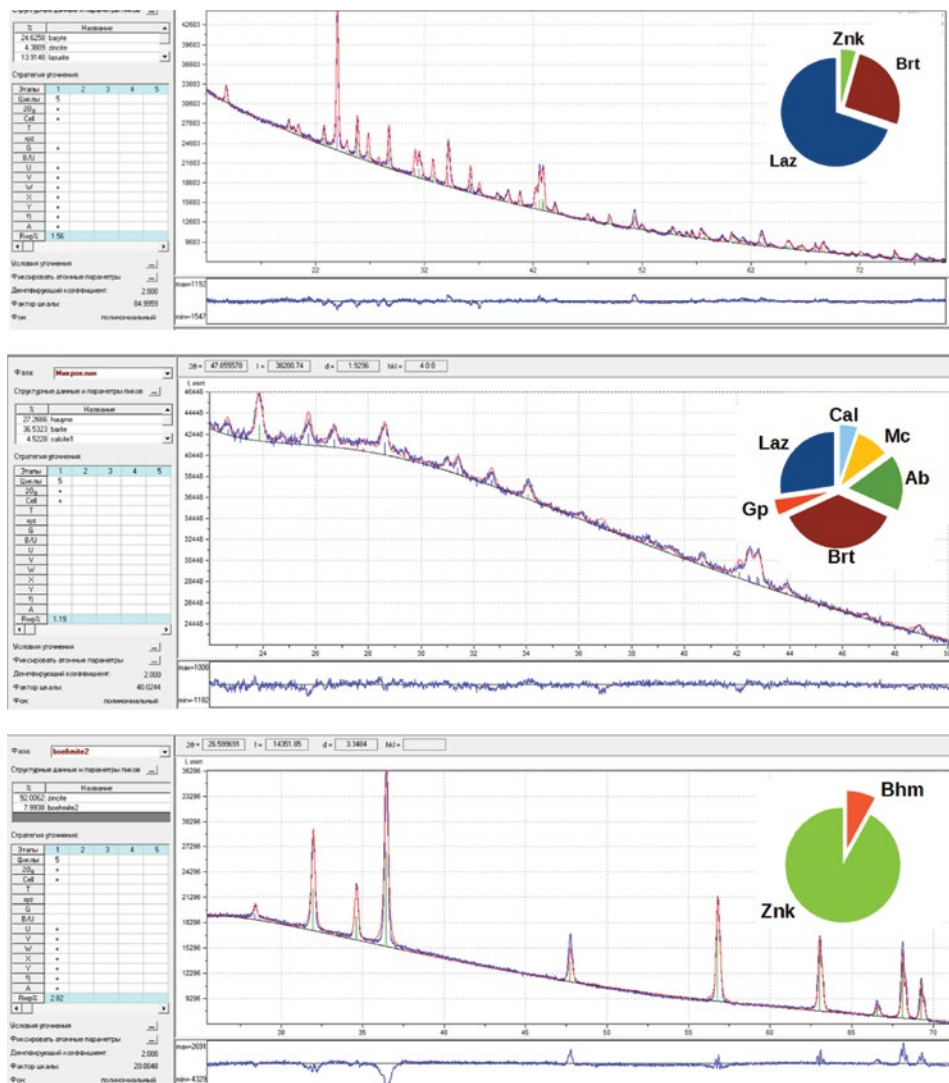


Figure 7 – Quantification of mineral composition of the following points by Rietveld refinement:
 a) ultramarine taken from V. Pakulin's painting "In the Room";
 б) Russian ultramarine produced in 90's;
 в) Zinc white from Soviet collection of paints, 1941.

To conclude, XRD phase analysis helps creating the important criteria for diagnostics of ultramarines from their mineral compositions, which can be applied to the aging of artworks and their restoration. This is especially valuable for the attribution of Russian avant-garde paintings, from which a lot of fakes have been produced in the end of 20th century.

Traditionally used analytical techniques like X-ray fluorescence give no information on mineral composition of paints to perform their aging. It seems rather interesting to apply the above experience to the other pigments from art palette of 20th century.