Cathodoluminescence Microspectroscopy as a New Method in the Study of Art Pigments

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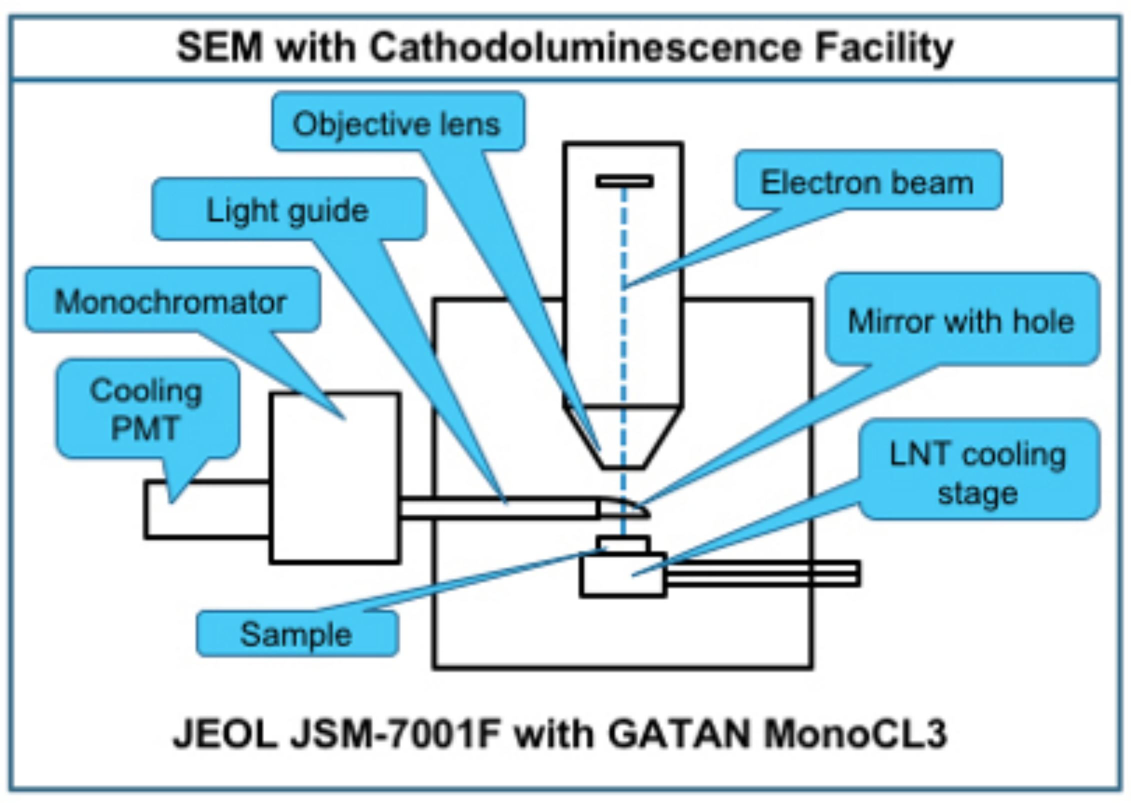
Introduction

Today a range of methods such as Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray fluorescence analysis (XRF), X-ray microscopic analysis (EDX) and, X-ray phase analysis (XRD) are used for studying the artistic materials of artworks. However, the methods of photo- and cathodoluminescence which are widely used in various fields of science, such as electronics, materials science, geology [1], etc., in the field of cultural heritage research it is used extremely rarely [2]. This is primarily due to the lack of required standards and thus reference CL spectra of numerous pigments used in painting, so, the creation of a database of characteristic CL spectra of art pigments is evidently required.

Cathodoluminescence (CL) is a physical phenomenon in which luminescence of a substance, impacted by fast electron beam (cathode rays), is observed. During the interaction of the electron beam with the sample material, electron-hole pairs are generated, which, recombining, emit photons in the ultraviolet, visible or infrared range. Analyzing CL spectra, researchers get a lot of useful information, such as phase composition of the sample, its electron-optical properties, the presence and nature of defects in the crystal lattice. Thus, the method may increase the reliability and accuracy of the study of works of painting and solve many problems in their investigation, restoration, and storage.

Methods and Sampling

The samples of the selected dry pigments were pressed into small tablets. CL properties of the samples were investigated by JEOL JSM-7001F scanning electron microscope equipped by CL attachment GATAN MonoCL3 (*Fig. 1*). Some CL spectra were observed at liquid nitrogen temperature for better spectral resolution. Electron beam irradiation was carried at 15 keV electron beam energy, 80 nA current focused on less than 10 nm for about 30 minutes.



The structure of pigments were examined by μ-FTIR spectroscopy (LUMOS, Bruker), and XRF (D8 Advance, Bruker). SEM-EDX (MIRA 3 LMU, Tescan with INCA-450 energy dispersive X-ray spectrometer, Oxford Instruments)was used to determine the elemental composition and of pigments.

Figure. 1. The scheme of the experimental methods.

Materials

The samples of dry pigments from various manufacturers of artistic materials were selected for the research. Some of them are widely used in easel oil painting and icon painting in different periods of the 20th century: lead, zinc and titanium white, cobalt blue spectral ("Rublevskaya palette", "Natural pigments", "EMTI" (Russia), "Kremer", "Schmincke" (Germany) and yellow cadmium (sample of polycrystalline CdS was synthesized from the gas phase in the P. N. Lebedev Physical Institute of the Russian Academy of Sciences) (*Fig. 2*). Pigments that are more characteristic for old painting, such as Napples yellow, Egyptian blue, and massicot. were also studied

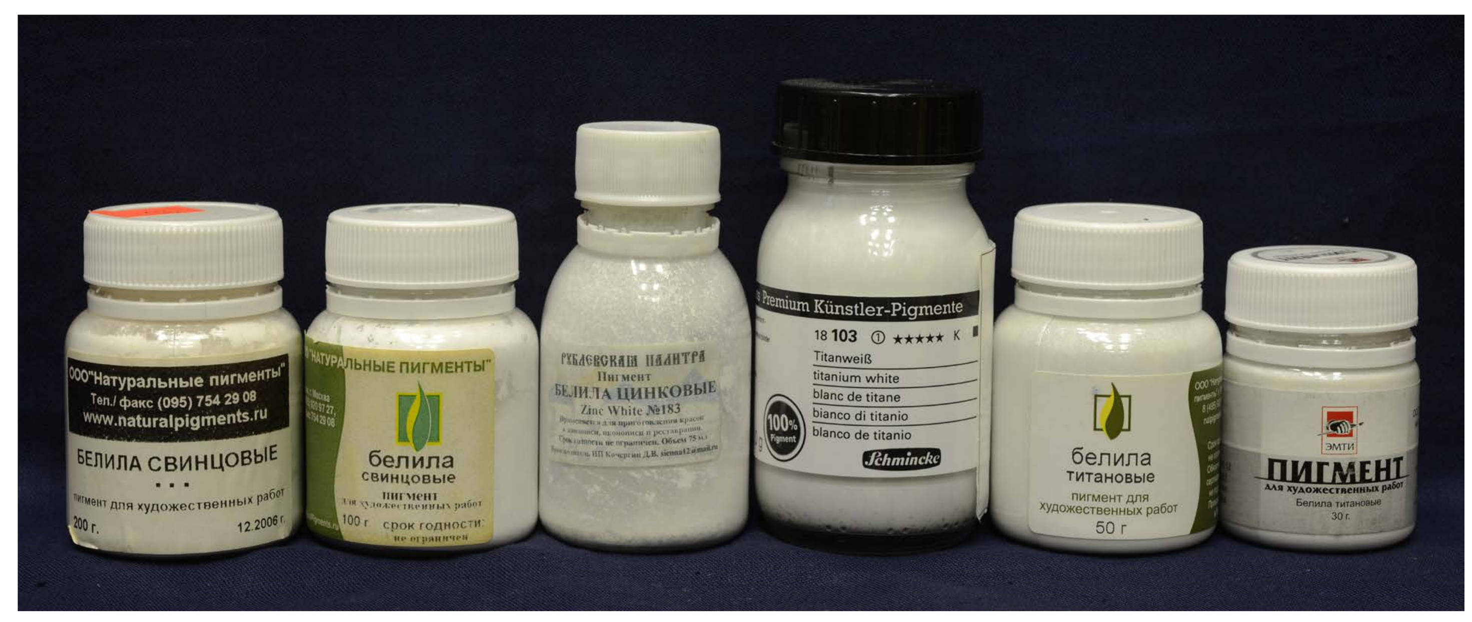


Figure. 2. Some examined dry pigments.

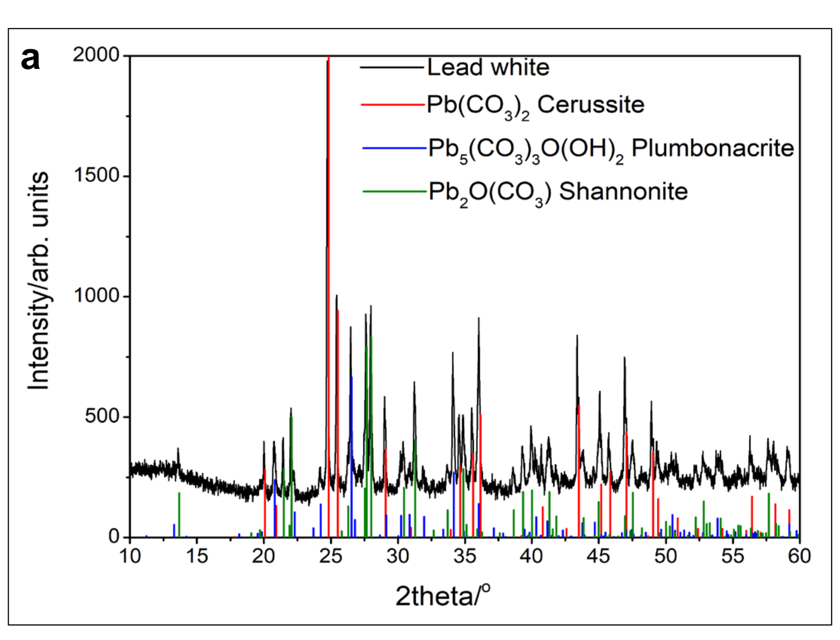
Results and Discussion

I. Standards

The problem of pigment standards is quite acute. Manufacturers of art materials, as a rule, do not indicate all the components of paints or dry pigments. These can be technological additives for imparting certain properties to paints or inert fillers to reduce the cost of dry pigments and paints. For example, it was found that the dry pigment titanium white of various manufacturers contain the small additives (up to 5%) of aluminum-based compounds (Al), silicon (Si) and/or calcium (Ca).

XRD and EDX analyses of lead white ("Natural Pigments") showed the presence of barium sulphate ($BaSO_4$), as well as a small amount (up to 1%) of titanium-based compounds. In the sample of lead white of the same company (2006 release), in addition to lead white in the form of cerussite ($Pb(CO_3)_2$), there were also other lead carbonates - plumbonacrite ($Pb_5(CO_3)_3O(OH)_2$) and shannonite ($Pb_2O(CO_3)$ (*Fig. 3*).

In the composition of Napples yellow ("Kremer") there are several crystalline phases: bindemite ($Pb_2Sb_2O_7$), lead and iron antimonate ($Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$), antimony antimonate ($Sb(SbO_4)$), some lead dimetmonate ($PbSb_2O_{2.5}$), and zinc oxide (Fig. 4). The composition of the Napples yellow ("Natural Pigments") contains lead and aluminum antimonate ($Pb_2Al_{0.5}Sb_{1.5}O_{6.5}$), lead and titanium oxide ($Pb(TiO_3)$ and zinc and titanium oxide ($Zn(Zn,Ti)O_4$) (Fig. 5). These samples of Naples yellow were studied by the CL method only as characteristic pigments of individual paint manufacturers, but not as standards.



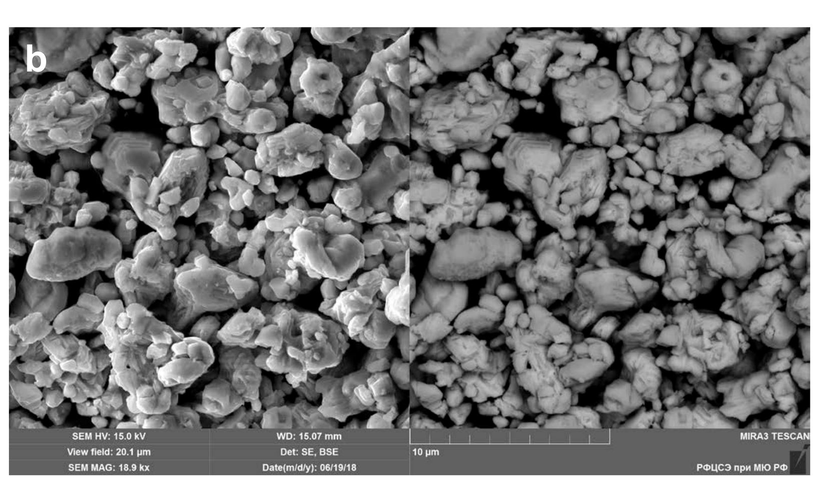


Figure 3. XRD-pattern of the sample of lead white, "Natural pigments" (a) and SEM image of the sample (b).

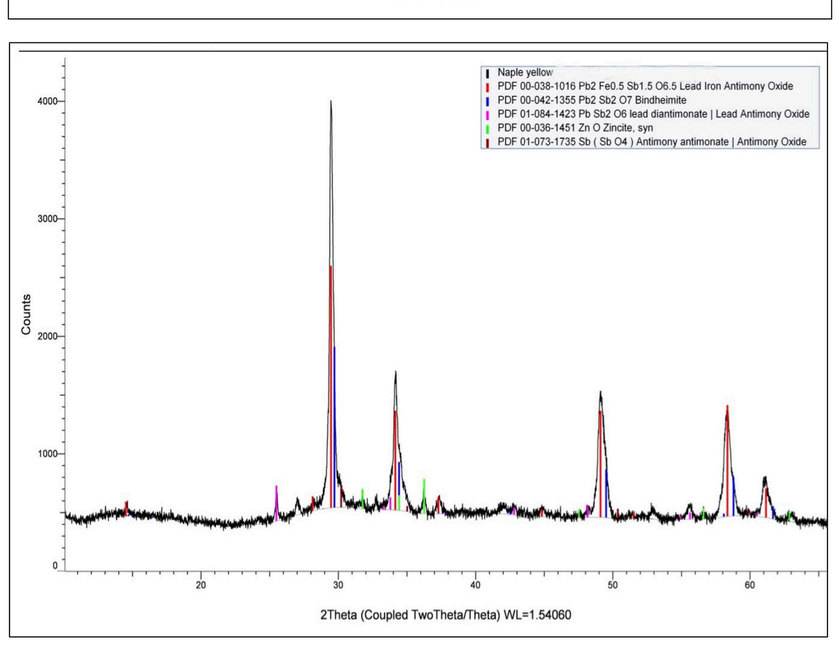


Figure 4. XRD-pattern of the sample of Napples yellow, "Kremer".

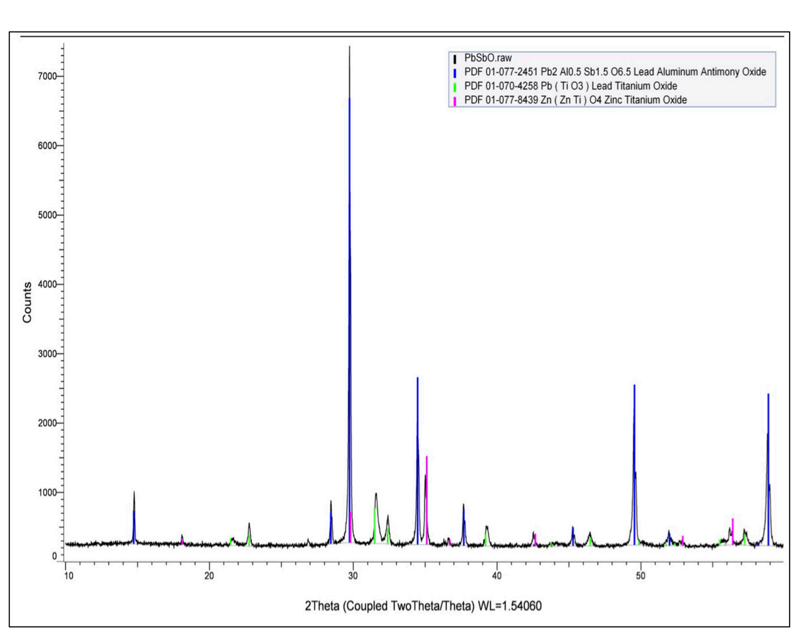


Figure 5. XRD-pattern of the sample of Naples yellow, "Natural pigments".

The study of other pigments showed that their elemental composition corresponds to the pigments indicated by the manufacturers, however, in some cases, minor impurities of some elements were also recorded.

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II. SEM Cathodoluminescence Microspectroscopy

A distinctive feature of the SEM microcathodoluminescence method is the combination of high spatial resolution typical to SEM with spectral analysis capabilities typical to photoluminescence and other methods of optical spectroscopy. Since electron beam can be focused in the area with less than 10 nm diameter size, this technique permits high resolution luminescence measurements of different materials including multicomponent. The report presents some CL spectra of pigment standards that can be used to study the paintings (*Figs. 6 to 9*).

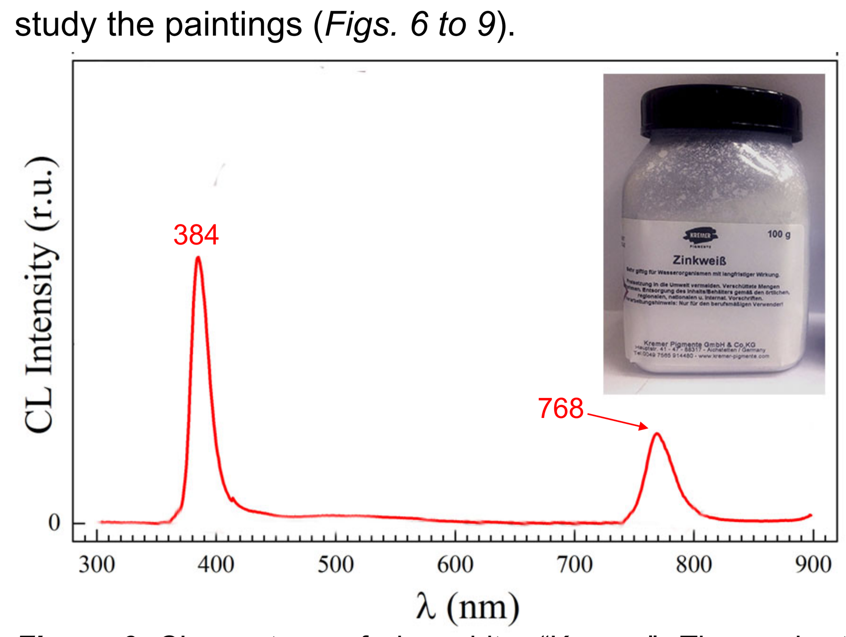

Figure 6. CL-spectrum of zinc white, "Kremer". The peak at twice the wavelength is the second order of the diffraction grating associated with the design of the instrument.

In the CL spectra of samples of dry zinc white, an intense exciton peak at 384 nm is observed (Fig. 6). In the study of samples of oil paints using the CL method, the indicated peak with high intensity was present both in oil paint based on zinc white (1967, "Lefranc") and in oil paint based on titanium white (1967, "Lefranc"). The characteristic bands of titanium white observed in the CL-spectra of the standards (*Fig. 7*) in the CL-spectrum of the oil paint were not observed. It may be due to the different luminescence capacity of zinc and titanium oxides. Thus, in complex mixed paints, zinc white can be easily identified even if the pigment present in insignificant amounts. Identification of titanium white is difficult.

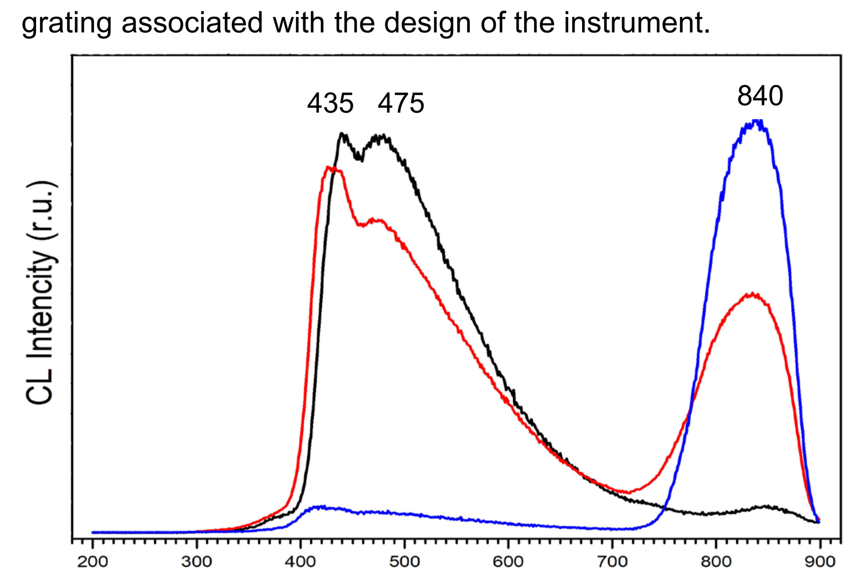

Figure 7. *CL*-spectra of titanium white, "Schmincke", registered at room temperature in different points (red and black spectra) and at LN temperature (blue spectrum).

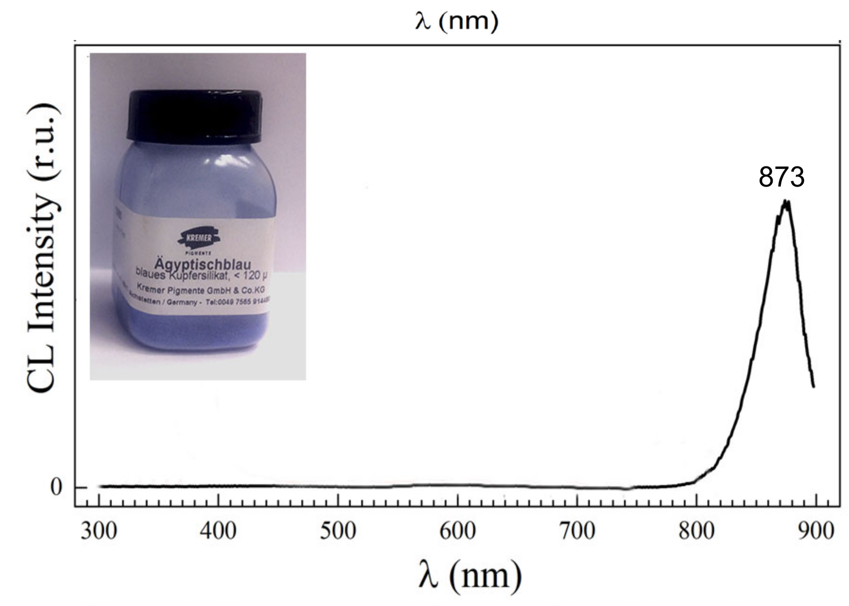

Figure 8. CL-spectrum of Egyptian Blue, "Kremer".

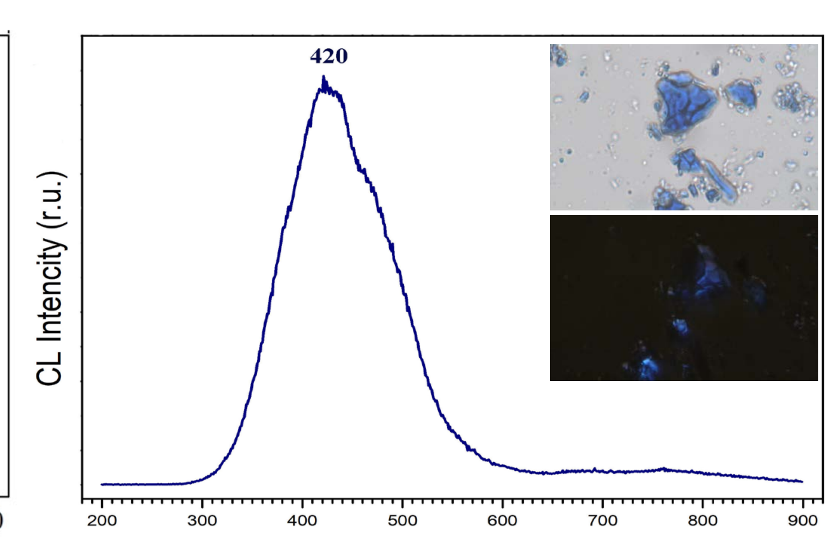

Figure. 9. CL-spectrum of cobalt blue spectral, Dulevo porcelain factory. Artistic Paints Plant.

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