Identification of CaCuSi$_4$O$_{10}$ (Egyptian blue) in the “Birch. Spring” painting by Robert Falk (1907) using photoluminescence

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Abstract

We have detected Egyptian blue pigment in the paint layer of the “Birch. Spring” painting by Robert Falk (1907); we have also found this pigment in the paints of the sketch drawn on the canvas back side. This is probably the first discovery of Egyptian blue in a 20th century work of art. We have analyzed a modern commercial Egyptian blue pigment (Kremer) and found it to be suitable as a standard for photoluminescence spectral analysis. The characteristic photoluminescence band of CaCuSi$_4$O$_{10}$ reaches maximum at the wavelength of about 910 nm. The luminescence is efficiently excited by incoherent green or blue light. The study demonstrates that the photoluminescence spectral micro analysis using excitation by incoherent light can be efficiently used for the identification of luminescent pigments in paint layers of artworks.

Keywords: Egyptian blue, Photoluminescence, Polarizing microscopy, Elemental mapping, Paints analysis, Russian avant-garde painting

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Preprint submitted to Elsevier
Graphical abstract
Research highlights

- Egyptian blue is identified in “Birch. Spring” painting by R. Falk (1907)
- CaCuSi$_4$O$_{10}$ emission band is centered at the wavelength of 910 nm
- The luminescence is efficiently excited by incoherent green or blue light
- Luminescence enables detecting some pigments in paint layers of artworks
- Commercial Egyptian blue (Kremer) fits as a standard for spectral analysis
1. Introduction

1.1. Egyptian blue from the antiquity to the present: a brief historical reference

Egyptian blue, also known as calcium copper tetrasilicate or calcium copper phyllo-tetrasilicate (CaCuSi$_4$O$_{10}$), Alexandria frit or Pompeian blue, is one of the earliest synthetic pigments first obtained in Egypt no later than the 4th dynasty (ca. 2613–2494 BC) [1][2][3] and widely used in the antiquity [1][4][5] by different names [2][1]. Ancient Romans, e.g., knew this substance by the name Caeruleum aegyptium [2][8][9][10]. Also, it was extensively produced throughout ancient Western Asia and the Mediterranean Region (Mesopotamia, Persia, Assyria, Urartu, Parthia and Greece) [2][3][7][11][12][13][14][15][16][17][18][6][19][20]. It was found out as one of the main blue pigment in the Fayum mummy portraits (1st to 3d centuries AD) [6][19] and in the paint layer of the early Christian encaustic icons “Male and Female Martyrs” and “Sergius and Bacchus” [21]. By the 3rd century, Egyptian blue spread in the Roman Europe (see Ref. [4] and references therein) and even in Norway [22].

Egyptian blue related to the early medieval period was reported to be detected in the mural painting of a church of the 9th or 10th century AD (Lombardy, Italy) [23][24] and in an 11th century mural altarpiece of the church of Sant Pere (Terrassa, Spain) [25]. Later, in the Middle Ages, Egyptian blue, as considered, was lost [2]. However, CaCuSi$_4$O$_{10}$ was unexpectedly identified using optical and scanning electron microscopy, photoluminescence, and Raman microspectroscopy in the painting of St. Margaret by Ortolano Ferrarese (Giovanni Battista Benvenuto) made in Italy in 1524 [26].

The natural form of calcium copper tetrasilicate, cuprorivaite, was described as a new mineral from Vesuvius in 1938 [27]. Its structure is presented, e.g., in Refs. [28][29][30][31][32][33]. However, it is a rarely met mineral usually intimately mixed with quartz [33]; it is mainly distributed in Italy, Germany, USA and South Africa [32][33].

Nowadays, calcium copper tetrasilicate, due to its unique luminescence characteristics [34][35][36][37][38][39], has achieved increasing importance in science

$^{1}$Remind that, in antiquity, owing to the imperfection of the production processes, Egyptian blue pigment was frit that, apart from calcium copper tetrasilicate, comprised appreciable quantities of numerous impurities such as, e.g., wollastonite (CaSiO$_3$), Cu-rich glass, cuprite (Cu$_2$O), tenorite (CuO) [6], cassiterite (SnO$_2$), malayaite (CaSnSiO$_3$), quartz and free lime [7]. At present, the term of Egyptian blue usually relates to CaCuSi$_4$O$_{10}$ itself, especially if the art pigment is concerned.
1.2. On the “Birch. Spring” painting by Robert Falk

Surprisingly, calcium copper tetrasilicate has recently been detected using energy dispersive X-ray spectroscopy and polarizing microscopy in the 20th century painting “Birch. Spring” (oil on canvas, private collection, see Fig. 1) [47].

The author of the picture, Robert Falk (1886–1956) is one of the bright representatives of Russian avant-garde, a leading member of “The Jack of Diamonds” creative association (1910–1916) [48, 49, 50, 51]. However, the painting dates back to the early period of Robert Falk’s work, the time of his formation as an artist, and was painted in his second year at the Moscow School of Painting, Sculpture and Architecture in 1907 [52].

A two-sided image on paintings is a characteristic feature of the artist’s work at that time. Repeatedly, in need of a clean canvas, the artist turned over his work (and cut some into several parts) and wrote down the clean back of the canvas. This is exactly what he did with the “Birch. Spring” painting, when depicting a sketch of a human figure on the back of the canvas (Fig. 1). Interestingly, that Egyptian blue was identified in the blue paint layers of both images, which in-
directly supports the assumption about close time of creation of both the spring landscape and the figured sketch on the back side of the canvas.

This article presents a detailed analysis of two paint samples (Fig. 1), obtained from this painting, performed using a number of complementary analytical techniques, which has completely verified the previously reported observation of CaCuSi$_4$O$_{10}$ in blue paints of this picture [47].

2. Experimental details

2.1. Methods and equipment

We have applied the multi-analytical approach to both the characterization of the commercial Egyptian blue pigment (Kremer), used as a standard in this work, and the studies of the paint layer composition of the “Birch. Spring” painting by Robert Falk presented in this article. The following techniques and equipment were used in the research.

Mira 3 XMU (Tescan Orsay Holding) scanning electron microscope (SEM) was employed for sample imaging and elemental analysis. Pairs of SEM images were recorded simultaneously using secondary (SE) and backscattered (BSE) electrons. Elemental microanalysis and mapping was made using EDS X-MAX 50 (Oxford Instruments Nanoanalysis) energy dispersive X-ray (EDX) spectrometer.

Binder was analyzed using Tensor 27 Fourier-transform infrared spectrometer (Bruker) equipped with MIRacle attenuated total reflection (ATR) accessory (PIKE Technologies) with a ZnSe ATR crystal.

X-ray phase analysis was carried out by means of the Debye-Scherrer powder diffraction [53] using D8 Advance diffractometer (Bruker) at non-monochromatic Cu K$_\alpha$ band (Cu K$_{\alpha 1,2}$, $\lambda = 1.54184$ Å); the diffraction patterns were scanned over a $2\theta$ range from 5 to 75°. The PDF-2 Powder Diffraction Database (Joint Committee on Powder Diffraction Standards – International Centre for Diffraction Data) was used for the phase composition analysis.

For the examination of samples using polarizing microscopy (PM) a POLAM L213-M (LOMO) microscope was employed. Film polarizers rather than Nicol

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2As a rule, we record pairs of SEM SE and BSE images at each point since SEM running in the former mode it renders mainly the spatial relief of the studied surface, while operated in the latter mode it demonstrates mainly the substance density (i.e. its elemental or phase composition), whereas the information on both relief and composition of a sample is usually required for the correct interpretation of data obtained using SEM.
Table 1: Spectral data for the PE and receive paths of the PL microscope (for the spectra of the PE bands, see Fig. 2).

| Band designation | PE filter transmission band (nm) | Dichroic mirror splitting wavelength (nm) | DA filter cut-on wavelength (nm) |
|------------------|---------------------------------|-----------------------------------------|---------------------------------|
| G                | 510 to 560                      | 575                                     | 590                             |
| B                | 450 to 490                      | 505                                     | 520                             |
| BV               | 400 to 440                      | 455                                     | 470                             |
| V                | 380 to 420                      | 430                                     | 450                             |
| U                | 330 to 380                      | 400                                     | 420                             |

prisms are applied in the design of this instrument.

Micro photoluminescence (PL) spectra were acquired at room temperature using AvaSpec-2048 fiberoptic spectrometer (Avantes) connected with MIKMED-2 fluorescence stereo microscope (LOMO). Emission bands of atomic Hg and Xe of a 100-W mercury arc lamp (HBO 100, Osram) were employed for PL exciting. Five preinstalled microscope operation modes differing by the photoexcitation (PE) and data acquisition (DA) spectral ranges—designated as G (green), B (blue), BV (blue-violet), V (violet) and U (ultraviolet)—enabled varying the PE conditions. Spectral data for the operation modes are given in Table 1 and the spectral bands available for the PL excitation are plotted for each mode of the microscope in Fig. 2. The PL spectra of the samples studied in this article were generally obtained at the microscope magnification of 500×. However, the magnification of 250× or 125× was also used sometimes.

2.2. Specimens, sampling and sample preparation

2.2.1. Samples from the painting by Robert Falk

Over 20 pigment micro samples covering the spectrum of hues used in the “Birch. Spring” painting by Robert Falk were taken under a microscope from the front and rear sides of the canvas. The samples were investigated using a set of analytical methods, such as SEM imaging and EDS X-ray elemental microanalysis including elemental mapping, PM and PL. The study showed, that the samples of the blue paint layer # 17 and # 5, which were taken at the points indicated in Fig. 1, are of topical interest.

An examining procedure of the samples was as follows. Before analyzing, every sample was divided into several portions; each portion was investigated using
a specific kind analysis. SEM imaging and EDS X-ray elemental microanalysis including elemental mapping, PM and PL analyses were routinely carried out at different portions of an original sample. The originally obtained samples evidently were inhomogeneous. However, since they were small enough to provide specimens with close properties after the division into separate portions, we consider the random variations of composition between the sample portions as insignificant. Thus, we consider each portion of the original samples as representative, in general features reflecting the properties of the whole original sample. This allows us to compare the properties of the original samples in whole based on data of a specific kind of analysis of their portions. For this reason, comparing of data obtained using specific kinds of analysis from different portions of an individual sample is also justified.

2.2.2. Commercial Egyptian blue pigment (Kremer) used as a standard

We used the commercial Egyptian blue pigment (Kremer # 10060) as a standard of calcium copper tetrasilicate for the PL investigations. Commercial art pigments are known to often be a mixture of several compounds and considerably differ in their composition depending on the manufacturer [54] that makes it difficult to employ them as analytical standards. This consideration made us thoroughly analyze the degree of purity of this commercial pigment to be convinced that it did not contain foreign admixtures and could be utilized as a reliable standard. We have investigated its elemental and phase composition using EDS, X-ray powder diffraction and polarizing microscopy. Besides, we have explored its luminescence to determine the structure of its emission band. PL spectra were acquired using exciting light of different PE bands of the microscope (Fig. 2, Table 1).

Samples of the Kremer Egyptian blue powder were not subjected to any treatment before the examinations; they were neither washed nor etched [40].

3. Results and Discussion

3.1. Examination of the commercial Egyptian blue pigment

3.1.1. SEM and EDS

SEM images of samples of the investigated powder of the commercial Egyptian blue pigment are shown in Fig. 3a–d and typical EDX spectra obtained at several points on powder particles are presented in Fig. 3e. SEM images obtained in backscattered electrons demonstrate the homogeneity of the powder composition. The EDX spectra are seen to contain only peaks of oxygen, silicon, calcium,
and copper (the intensity of the peak of carbon likely present due to a contaminant or a residual gas of the SEM chamber atmosphere is negligible). Although the elemental analysis of this powder was semi-quantitative, its data allow us to consider this substance as pure enough to be used as a reference sample in further analyses of paints.

3.1.2. X-ray powder analysis

The X-ray powder pattern of the commercial Egyptian blue pigment shown in Fig. 3 demonstrates that the phase of CaCuSi$_4$O$_{10}$ completely dominates its composition. The positions of all the diffraction maxima, except for a few very weak ones that likely emerge due to parasitic reflections, coincide with the positions of those documented in the PDF Card 01-085-0158 (ICSD Entry 402012) and Ref. [31].

We conclude that the possible content of some foreign crystalline phases is negligible in this powder that allows us to employ this commercial compound as the reference one in further analyses.

3.1.3. Polarizing microscopy

The study of samples of the commercial Egyptian blue pigment in the plane-polarized light shows optical properties, which are characteristic to Egyptian blue [55]. The thin bright blue translucent flat particles typical for Egyptian blue exhibit a very weak pleochroism [3]. Under crossed polars, the compound displays very low order interference colors and weak extinction. The shape of the particles is very diverse and characterized by irregular, angular fractures (Fig. 4). Besides, a broad particle size distribution from medium (1 to 3 µm) to very coarse (> 40 µm) is observed (Figs. 3a–d and 4).

3.1.4. Photoluminescence

We have recorded PL spectra of the commercial Egyptian blue samples at a number of points of each sample and obtained similar results for them. Spectra of PL excited using the G and B bands (Fig. 2) nearly coincide; as it is seen in Fig. 5, they consist of the only spectral band peaking at the wavelength of about 910 nm. However, the deconvolution of this band for PL excited by the G and B bands demonstrates that they are composed of two Gaussian spectral

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3 Compare, e.g., with the Egyptian blue PM images given in Ref. [4].
4 According to Feller and Bayard’s particle size classification for pigments [56].
5 We used Voigt functions for the peak analysis.
Table 2: Content of some chemical elements in a portion of the sample obtained at the point # 5 on the painting by Falk (Fig. 1) measured using EDS analysis (at.%); the points of analysis are shown in Fig. 6a; the corresponding EDX spectra are given in (Fig. 8a); the multilayered elemental composition map is presented in Fig. 6b.

| Chemical element | Point number | Mean over the map |
|------------------|--------------|-------------------|
|                  | 51           | 52                | 53     | 54     | 55     | 56     | 57     |
| Na               | 9.53         |                   |        |        |        |        |        |
| Al               | 18.45        | 4.03              | 1.59   | 9.35   |        |        |        |
| Si               | 68.82        |                   |        |        |        |        |        |
| Ca               | 15.51        |                   |        |        |        |        |        |
| Cr               | 72.62        | 3.67              |        | 82.23  | 0.97   | 6.78   |        |
| Co               | 1.87         |                   |        |        |        |        |        |
| Cu               | 13.08        |                   |        |        |        |        |        |
| Zn               | 2.59         | 16.88             | 20.48  | 67.33  | 13.56  | 14.33  | 5.41   | 28.30  |
| Pb               | 83.12        | 6.90              | 10.55  | 4.22   | 8.30   | 1.01   |        | 22.40  |

bands peaking at about 900 and about 923 nm somewhat differing in the ratio of maximum intensities for different excitation bands (Fig. 5). PL was not detected under the sample excitation by light from the other (BV, V or U) spectral ranges. This allows us to conclude that no other luminescent admixtures emitting visible or near infrared light are contained in the examined commercial Egyptian blue pigment that enables its utilization as a standard for the PL spectral analysis in these spectral ranges.

3.2. Analysis of samples from the painting by Robert Falk

3.2.1. SEM and EDS

Specimens taken from the samples obtained at the points # 5 and # 17 on the painting by Falk were examined using SEM operated in both SE and BSE modes. Fig. 6a presents a pair of such SEM images typical for the point # 5. As it is seen from the BSE image, the paint layer specimen is composed of particles of substances differing in their composition and sizes.

Maps of spatial distribution of X-ray bands corresponding to a number of chemical elements recorded using the SEM EDX spectrometer at the same areas on the specimen are shown in Fig. 6b. The signal of the silicon K\(_{\alpha 1}\) band

\(^6\)The ratio of maximum intensities of the components peaking at 923 and 900 nm is \(\sim 3\) for the G band and \(\sim 1.5\) for the B band; the peak area ratios are \(\sim 5.7\) and \(\sim 2.3\), respectively.
Table 3: Content of some chemical elements in a portion of the sample obtained at the point # 17 on the painting by Falk (Fig. 1) measured using EDS analysis (at.%); the points of analysis are shown in Fig. 7a; the corresponding EDX spectra are presented in (Fig. 8b); the multilayered elemental composition map is presented in Fig. 7b.

| Chemical element | Point number Mean over the map |
|------------------|-------------------------------|
|                  | 171  | 172  | 173  |
| Na               | 12.58|
| Al               | 6.86 | 16.26|
| Si               | 69.45| 68.89| 44.87| 9.09 |
| Ca               | 15.23| 16.56| 12.63| 1.48 |
| Co               | 2.85 |      |      |      |
| Cu               | 12.84| 14.55| 11.18|
| Zn               | 1.22 | 10.08| 25.36|
| Pb               | 1.26 | 14.38| 32.39|

is seen to spatially correlate with the signals of the calcium Kα₁, copper Kα₁, and oxygen Kα₁ bands in these maps. At the same time, it anti-correlates with the signals of the carbon Kα₂, sodium Kα₂, and zinc Kα₁ and lead Lα₁ bands. No spatial correlation of this band was registered with the aluminum Kα₁, chromium Kα₁, and cobalt Kα₁ bands.

However, some domains of the map of the oxygen Kα₁ band are seen to correlate with the map of the chromium Kα₂ band. Besides, O Kα₁ signal is seen to be distributed quite uniformly across the map as well as that of C Kα₂, Zn Kα₁ and Pb Lα₁, and all these signals correlate well with one another. Additionally, some bright features of the O Kα₁ map coincide with some bright features of the C Kα₂ map.

The signals of Al Kα₂ and Co Kα₂ also strongly correlate with one another. The Na Kα₂ band is distributed quite homogeneously across the map with numerous tiny bright spots that are also spread rather uniformly in the map. The uniformity of the Na Kα₂ distribution and the smallness of sizes of its bright features make it difficult to detect any correlation between this map and the rest ones. Nevertheless, some bright points in the Si Kα₁ and Na Kα₂ maps are seen to coincide (e.g., a couple of small bright spots at the center of the left edge of the Si Kα₁ map and a pair of similar spots at the same place of the Na Kα₂ map).

The multilayered map of the spatial distribution of the Cu, Co, Ca, Al, Cr and Si Kα₁ X-ray bands clearly demonstrates the presence of compounds, which contain a combination of Co and Al and a combination Cu, Ca and Si, gathered in
particles in this specimen. Besides, separate areas containing Cr are also seen in the map.

A pair of SEM SE and BSE images typical for the point #17 is shown in Fig. 7. In general features, the composition of this paint layer specimen (see the BSE image in Fig. 7a) looks similar to the composition of the specimen taken at the point #5 (the BSE image in Fig. 6a) with the exception of the sizes of most particles, which look somewhat smaller than those in the sample taken in the point #5.

Maps of the X-ray bands distribution (Fig. 7b) also demonstrate the same regularities as the maps of the sample from the point #5. The maps of the Si Kα, Ca Kα and Cu Kα lines demonstrate coinciding features. Some features in the map of O Kα coincide on the specimen surface with the analogous features in the maps of Al Kα1, Co Kα1, Si Kα1, Ca Kα1 and Cu Kα1. Distributions of Zn Kα1 and Pb Lα1 are quite similar; they are distributed quite uniformly.

The multilayered map of the specimen from the point #17 shows that, judging from the spatial distribution of the Ca Kα1, Al Kα1, Si Kα1 and Pb Lα1 X-ray bands, grains containing Si and particles of a substance containing Al are included in a quite uniformly distributed mixture of fine grains of compounds containing Pb or Zn.

EDX spectra recorded at the points, indicated in Figs. 6a and 7a, are shown in the panels (a) and (b) of Fig. 8 for the points #5 and #17, respectively. They evidence the presence of C, O, Na, Al, Si, Ca, Cr, Co, Cu, Zn and Pb in detectable quantities in the point #5 and the same set of elements except for Cr in the point #17 on the painting by Falk. Semi-quantitative estimates of their content in the samples from both points are given in Tables 2 and 3. It is seen from the spectra and tables that different compounds are detected in different points of the elemental analysis.

They can be easily identified if elemental mapping and EDS analysis are combined with the polarizing optical microscopy.

3.2.2. Polarizing microscopy

Preliminary studies of the samples #5 and #17 by PM microscopy show the presence of blue crystals, which optical properties correspond to Egyptian blue (see Section 3.1.3). However, in contrast to the commercial pigment, its color is much less intense (Fig. 9), likely due to thinner flakes. The particle sizes vary from large (3 to 10 µm) to coarse (10 to 40 µm) (Fig. 6 and 7). In addition, zinc white (ZnO), lead white (2PbCO3·Pb(OH)2 + PbCO3), synthetic ultramarine (Na7Al6Si6O24S3), cobalt blue (CoO·Al2O3) were identified in both samples, and
viridian (Cr\textsubscript{2}O\textsubscript{3}·2H\textsubscript{2}O) in sample #5. The ratio of these pigments in each sample is diverse and regulates the hue of the blue paint layer.

3.2.3. Photoluminescence

PL spectra recorded from different portions of the paint layer samples obtained at the points #5 and #17 of the painting by Falk (Fig. 1) demonstrate similar sets of features specific for each PE band (Fig. 10). The spectra obtained under the G-band PE (Fig. 2, Table 1) in the range from 590 to 1100 nm demonstrate a single band, peaked around 906 nm, which coincides with the band of the reference sample (Fig. 5) and for this reason is unequivocally attributed to Egyptian blue (Fig. 10a).

PL spectra obtained using the other PE bands are presented in Fig. 10b. For each PE band, the spectra were recorded in the specific spectral range presented in Table 1. All the spectra consist of a broad spectral band peaked at \( \sim 500 \text{ nm} \) composed of a predominating strong line and five weak lines on both sides of it (the spectra excited using the B-band show only the long-wavelength wing of this strong line). The strongest band is peaked at \( \sim 500 \text{ nm} \) and the weak ones are peaked around 430, 460, 560–570, 610–620 and 680 nm (the parameters of the weak lines obtained from the deconvolution of the initial bands are determined with rather high degree of ambiguity).

Remark that only the spectra for the point #5 are presented in Fig. 10b. The spectra obtained for the point #17 are similar to them but much more noisy because of somewhat lower intensity of PL excited using all the PE bands except for the band G. However, they demonstrate the same set of spectral lines as the spectra recorded at the point #5 with a single predominating line at \( \sim 500 \text{ nm} \) and five much weaker ones on both sides of it.

Note also that the B-band-excited PL of the samples from both points, like in the case of the reference sample of Egyptian blue, also demonstrates a spectral band at \( \sim 900 \text{ nm} \), but, due to much lower intensity, the recorded signal of this PL band is too noisy and for this reason is not shown in the spectrum obtained from the sample taken from the Falk’s painting (Fig. 10b).

\(^7\)The composition was determined based on both PM and the data of SEM-EDS (Figs. 6, 7 and 8; Tables 2 and 3).
3.3. Brief discussion

3.3.1. On the paint layer composition and the nature of its luminescence

The above analyses allow us to conclude that both of the samples from the painting by Falk contain close sets of pigments. The sample taken from the point # 17 contains lead white (2PbCO$_3$·Pb(OH)$_2$ + PbCO$_3$) and zinc white (ZnO), artificial ultramarine (Na$_{8-10}$Al$_6$Si$_6$O$_{24}$S$_3$), cobalt blue (CoO·Al$_2$O$_3$), and Egyptian blue (CaCuSi$_4$O$_{10}$).

The composition of the sample taken from the point # 5 is mainly similar to that of the sample from the point # 17. In addition to the pigments found in the latter sample, this one contains also viridian (Cr$_2$O$_3$·2H$_2$O). Besides, it contains somewhat less amount of Egyptian blue. For this reason, paint in the point # 5 has somewhat greener tint than in the point # 17.

PL spectral analysis unambiguously proves the presence of Egyptian blue in the paint layer of the picture by Falk since the PL spectra obtained from the samples taken at both points (Fig. 10a) demonstrate the intense emission at the characteristic PL band peaking at about 910 nm.

It should be noticed, however, that some earlier articles reported the position of the PL band characteristic to Egyptian blue nearly coinciding with the peak position presented in this work (e.g., $\lambda_{\text{max}} \approx 910$ nm at $\lambda_{\text{PE}} = 637$ nm [34], $\lambda_{\text{max}} \approx 909$ nm at $\lambda_{\text{PE}} = 625$ nm [40]). Others, on the contrary, reported a somewhat displaced PL band for this compound (e.g., $\lambda_{\text{max}} \approx 950$ nm at $\lambda_{\text{PE}} = 632.8$ nm [39], $\lambda_{\text{max}} \approx 932$ nm [38]). Nevertheless, all those articles assigned these PL bands to the $^2\text{B}_2g \rightarrow ^2\text{B}_1g$ transition in Cu$^{2+}$ ions.

Moreover, the authors of Ref. [37], when investigated Ca, Ba and Sr copper silicates pigmented acrylic coatings, have demonstrated a broad PL band for calcium copper silicate situated in the interval from $\sim 800$ to $\sim 1000$ nm. Its maximum gradually moved from $\sim 870$ to $\sim 905$ nm as the pigment concentration increased in the acrylic film. The band was obviously composed of a number of components that peaked in the range from $\sim 860$ to $\sim 930$ nm.

The issue of the characteristic peak position of calcium copper silicate and the changes in its position requires further investigations, which are, however, far beyond the scope of this article.

Besides the line of Egyptian blue presented in Fig. 10a, the spectra plotted in...
Fig. 10b show PL of some other pigments whose PL bands are peaked around 500 nm.

We ascribe this PL to mutually superimposed deep-level emission (DLE) bands in ZnO \cite{57,58,59}. The intense cyan-green emission band of ZnO centered at \(~ 500 \text{ nm} (~ 2.5 \text{ eV})\) is often attributed to the electron transitions from oxygen vacancies (V\(_O\)) to the valence band \cite{59,60,61,62,63,64}. Alternatively, it is assumed to be related to the emission of Cu\(^{2+}\) ion in a zinc lattice site \cite{64}.

The weak DLE bands seen in Fig. 10b are also described in the literature. The violet-blue emission band at \(~ 430 \text{ nm} (~ 2.85 \text{ eV})\) may be associated, e.g., with the electron transition from the zinc interstitial (Zn\(_i\)) level to that of zinc vacancy (V\(_{Zn}\)) \cite{59,63}. The DLE related blue band at \(~ 460 \text{ nm} (~ 2.7 \text{ eV})\) has not assigned thus far. However, since a considerable red shift of the deep-level PL maximum from \(~ 2.7 \text{ to } 2.5 \text{ eV}\) was observed with the growing sample temperature up to 150 K, the authors of Ref. \cite{59} supposed that the deep-level related band was composed of two peaks, blue and cyan-green, with the former one dominating at the temperature \(T < 150 \text{ K}\) and the latter one at \(T > 150 \text{ K}\). The greenish-yellow PL band peaking in the range from \(~ 560 \text{ to } 570 \text{ nm} (~ 2.2 \text{ eV})\) is likely related to the electron transitions from the conduction band to oxygen interstitials (O\(_i\)), whereas the orange band centered at 610 to 620 nm \(~ 2 \text{ eV}\) may be assigned to the Zn\(_i\) \(\rightarrow\) O\(_i\) electron transitions \cite{59}. The nature of red PL band at \(~ 680 \text{ nm} (~ 1.8 \text{ eV})\) is unknown at present \cite{63,64} although it is also assumed to be connected with defect-related DLE \cite{65}.

Note also that the emission band of hydrocerussite (2PbCO\(_3\)-Pb(OH)\(_2\)) also lies in the range 480 to 580 nm \cite{57}. This band is probably superimposed on the ZnO DLE one.

Thus we can conclude that zinc and probably lead whites also contribute to the PL spectra of the samples emitting in the visible range at the wavelengths around 500 nm under B, BV, V and UV PE.

3.3.2. A remark on the provenance of Egyptian blue in the painting by Falk

We are sure that Egyptian blue detected in this painting can certainly be only of European provenance. The case is that, from the one hand, the manufacture of art materials was limited to only a small amount of paints of a rather poor color assortment at that period in Russia, which could not include such a rare pigment as Egyptian blue. On the other hand, it is well known that Russian artists preferred

\footnote{Some other models of this emission are also reviewed in Ref. \cite{64}.}
paints produced in Europe due to their higher quality. Despite there is no reliable information about Egyptian blue manufacturing in Europe in the beginning of 20th century, the oil paint based on this pigment was mentioned as ‘Bleu de Pompéi’ in the Lefranc & Cie catalogue in 1930.\footnote{Additionally, the same dry pigment, Pompeian Blue, according to Ref. \cite{8}, was presented in Lefranc & Cie, France, in 1929.} It can be assumed that the paint was also being produced earlier, yet, it does not seem to be popular among artists. It may be the cause of the lack of Egyptian blue in artworks of the 20th century.

4. Conclusion

Summarizing the article let us present its main statements.

First, we have thoroughly analyzed the commercial Egyptian blue pigment produced by Kremer and found it suitable for utilization as a standard for PL spectral analysis. The characteristic emission band of CaCuSi$_4$O$_{10}$, which is used for the analysis, has been found to peak at the wavelength of about 910 nm. This band is composed of two components peaking at about 900 and 923 nm. The PL band is efficiently excited by green or blue incoherent light.

Second, we have detected Egyptian blue pigment in the paint layer of the “Birch. Spring” painting by Robert Falk (1907, oil on canvas, private collection). In addition, we have found the same pigment in the paints of the sketch drawn on the reverse side of the canvas. This is likely the first time that Egyptian blue has been discovered in 20th century paintings as well as in pieces of art of that period of time at all.

Finally, we should emphasize in conclusion that this study cogently demonstrates the micro PL spectral analysis to be an efficient tool for detecting luminescent pigments contained in paint layers of works of art. Excitation of pigment luminescence in paints of art pieces by incoherent light is effective. At the same time, application of light sources enabling the PE band selection in wide ranges, which are often available in PL microscopes, considerably enhances the pigment analysis possibilities that is especially important for examining compounds, which are characterized by selective PE of luminescence and their mixtures.

Acknowledgments

The research was accomplished under the collaboration agreement between GPI RAS and GOSNIIR.
Electronic supplementary material

Figure S1: Photographs of pages from the Lefranc & Cie catalogue of 1930: (a) the cover, (b) the title page and (c) the page 10 that contains the record about Egyptian blue ("Silicate de cuivre et de chaux. Bleu de Pompéi").

Conflict of interest. None declared.

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Figure 2: Mercury arc lamp spectral bands used for the excitation of PL in the luminescence microscope (the band designations—U, V, BV, B and G—correspond to those in Table 1; the input flange of the spectrometer fiber-optical cable was set coaxially with the microscope objective in place of a sample on the microscope stage during the measurements; technical data for the PE and receive paths of the microscope are given in Table 1).
Figure 3: Pairs of SEM SE (a, c) and BSE (b, d) images of a sample of the commercial Egyptian blue pigment (Kremer # 10060); numbered crosses in the panel (c) indicate points on powder particles, at which the EDX spectra were obtained; EDX spectra (e) obtained at the points shown in the panel (c), the numerals correspond to the point numbers; X-ray powder pattern [Cu K\(\alpha\)] (f) obtained from a sample of the Kremer # 10060 pigment, the experimental data are shown by the solid line and the vertical bars present the diffraction data for CaCuSi\(_4\)O\(_{10}\) from the PDF Card 01-085-0158 (ICSD 402012) [31].
Figure 4: PM images of powder particles of the commercial Egyptian blue pigment (Kremer #10060): (a) parallel and (b) crossed polars.
Figure 5: PL spectra obtained from a sample of the commercial Egyptian blue pigment (Kremer # 10060); letters B and G designate the spectral ranges of light used for the luminescence excitation (Fig. 2, Table 1); the symbols present experimental points, the dotted and dashed lines show the band components derived by deconvolution of the experimental curves using Voigt functions, and the solid lines are a cumulative fit peaks.
Figure 6: A pair of SEM SE and BSE images (a) and elemental composition maps (b) of a specimen taken from the paint layer samples from the point #5 of the painting by Falk (Fig. 1); numbered crosses in the panel (a) indicate points on the specimen, at which the EDX spectra were recorded (Fig. 8a); single-colored maps represent the distributions of signals of the X-ray bands of a number of chemical elements (the bands are given in the upper right corner of each map); a multicolored map is a multilayered one composed of the X-ray band maps of several elements (the elements are shown in the lower left corner of this map).
Figure 7: A pair of SEM SE and BSE images (a) and elemental composition maps (b) of a specimen taken from the paint layer samples from the point # 17 of the painting by Falk (Fig. 1); numbered crosses in the panel (a) indicate points on the specimen, at which the EDX spectra were recorded (Fig. 8b); single-colored maps represent the distributions of signals of the X-ray bands of a number of chemical elements (the bands are given in the upper right corner of each map); a multicolored map is a multilayered one composed of the X-ray band maps of several elements (the elements are shown in the lower left corner of this map).
Figure 8: EDX spectra obtained at separate points on specimens taken from the paint layer samples from the points #5 (a) and #17 (b) of the painting by Falk (Fig. 1) and by averaging X-ray spectra over the elemental composition map of each specimen; numerals at the curves correspond to the point numbers (Figs. 6a and 7a), the letter ‘m’ designates the mean spectrum of the corresponding elemental composition map (Figs. 6b and 7b).
Figure 9: Complementary pairs of PM images [(a) and (b), (c) and (d), (e) and (f)] of portions of the paint layer samples obtained at the points #17 [(a), (b)] and #5 [(c) to (f)] of the painting by Falk (see Fig. [1]) using parallel [(a), (c), (e)] and crossed [(b), (d), (f)] polars; the numbered arrows indicate examples of particles of Egyptian blue (1), cobalt blue (2), lead and zinc whites (3), artificial ultramarine (4) and viridian (5).
Figure 10: PL spectra recorded at portions of the paint layer samples obtained at the points #5 and #17 of the painting by Falk (Fig. 1); designations G, B, BV, V and U indicate the spectral ranges of light used for the luminescence excitation (Fig. 2, Table 1).
Identification of CaCuSi$_4$O$_{10}$ (Egyptian blue) in the “Birch. Spring” painting by Robert Falk (1907) using photoluminescence

Supplementary material

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Figure S1: Photographs of pages from the Lefranc & Cie catalogue of 1930: (a) the cover, (b) the title page and (c) the page 10 that contains the record about Egyptian blue (“Silicate de cuivre et de chaux. Bleu de Pompéi”).

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