

MATERIALS OF THE EARLY ETUDES BY RUSSIAN AVANT-GARDIST PAVEL FILONOV

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Abstract

Pavel Filonov is one of the most famous representatives of the Russian avant-garde. Nevertheless, before he found his recognizable style, he had created some etudes during his travels and studies in 1905-1907, which are especially rare and little known because he destroyed most of his early paintings. We studied the paint layers and grounds of nine etudes by Pavel Filonov created at the beginning of the 20th century. The micro-samples were analyzed by polarizing microscopy (PLM), Fourier-transform infrared spectroscopy in the attenuated total reflection mode (μ -ATR-FTIR), energy dispersive X-ray spectroscopy coupled with scanning electron microscope (SEM-EDX), and μ -Raman-spectroscopy. The composition of the grounds and paints had many similarities. Filonov often used zinc white, French ultramarine, viridian, red organic pigments, vermilion, cadmium yellow, yellow ochres, mares of various shades. In some of the etudes, we identified a relatively rare, for the paintings of that time, natural red dye Madder Lake that emitted intensive UV-induced fluorescence with maxima at 575 and 605 cm^{-1} . One more speciation of the studied paints was the atypical spherical shape of crystals of cadmium yellow in some of the works. The results of the research are useful for establishing Filonov's palette and understanding of the artist's path, as well as supplement the statistics of the use of the identified pigments at this time by artists who worked at the turn of the centuries.

Keywords: Pavel Filonov; PLM; SEM-EDX; Raman fluorescence; Art materials; Technical art History; Cadmium yellow; Rose Madder

Introduction

Pavel Nikolayevich Filonov (1883 – 1941) was an innovative Soviet artist who worked in between Surrealism and Expressionism and formed his own Theory of Analytical Art. He was born in Moscow in 1883 into a poor family, at the age of 13 he lost his parents and moved to St. Petersburg, where he lived until his death from starvation in 1941. He had a passion for painting since early childhood, but he took his first art course in 1897 at the Society for the Encouragement of the Arts, while attending day classes in applied painting and decorating. Six years later, in 1903, Filonov enrolled in the preparatory course for entrance into the Higher Art Institute and was expelled after a few months for the disobedience. Subsequently, he frequented the private studio of the academician Lev Dmitriev-Kavkazsky (1849 – 1916). After that, from 1908 – 10, Filonov audited classes at the Academy of Fine Arts, although he never completed a diploma course.

He had his own views on painting and developed them in his works. He tried «to express the object in its evolution both as independent phenomenon and in its relationship with the

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surrounding world, attempting to transmit energy of the individual object. He was interested in the decomposition of form and the synthesis of the evolved picture as a complex of “atoms” [1].

However, before he developed his recognizable style, he created a number of etudes in 1903 – 08, while he was studying in Dmitriev-Kavkazsky's studio (Fig. 1) [1]. Those works are especially rare and little known because he destroyed most of his early paintings [2]. Personal testimonies, notes, and diaries contain little information about his early artistic development. Investigation of the materials in the surviving works could reveal many fascinating facts about Filonov's authentic painting process in the early years: which paints he preferred, and how he mixed and put them on a canvas.

A combination of micro-invasive methods of physicochemical analysis of paints is able to provide researchers with reliable information about their composition. The implementation of spectroscopic methods such as Raman spectroscopy, Fourier-transform infrared spectroscopy in the attenuated total reflectance mode (ATR-FTIR), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) is a common practice in modern chemical analysis of objects of cultural heritage, including paintings [3]. Though polarized light microscopy (PLM) is a less popular method in such research, the method is a useful tool in identifying mineral pigments due to their unique optical properties [4].



Fig. 1. Images of the etudes *Muslim town* (a), *Arcades* (b), *Old Olive* (c), and *Landscape with a mountain village* (d) from the private collection of V.M. Fedotov.

In this paper, we present the study of art materials of nine early etudes created by Pavel Filonov at the beginning of the XX century from private collections: *Old olive* (1903-08, oil on canvas, 18.5×25.7cm), *Muslim town* (1905-07, oil on canvas, 18.9×27.5cm), *Foothills* (1903-08, oil on canvas, 12.9×26.0cm), *Arcades* (1905-07, oil on canvas, 20.2×26.9cm), *Valley* (1903-08, oil on canvas, 23.1×31.9cm), *Landscape with a mountain village* (1903-08, oil on canvas, 21.2×24.6cm), *The roof of the house* (1903-08, oil on canvas, 19.9×28.9cm), *Dam on the river* (1900s, oil on canvas, 26.5×22.6cm) and *Arab* (1905, oil on canvas, 71.7×31.1cm). In 1905 – 07, Pavel Filonov travelled to the Near East, and some of the mentioned etudes depict the obvious landscapes of it (Fig. 1). Thus, they are suggested to be created during a single journey.

A madder lake pigment, which was found in one of the paintings, was compared to eight historical paint samples by Winsor & Newton and Lefranc. The composition of the grounds, as well as pigments and binding media were analysed using a multianalytical approach.

The research aims to reveal the palette and technology of Pavel Filonov's early artworks. This, as well, would add to the statistics of the usage of certain pigments and mixtures at the beginning of XX century.

Experimental part

Materials

The paints of the main colours (7-12 samples) were sampled under a binocular stereoscopic microscope MBS with 25× magnification. For the PLM, samples were placed on microscope glass slides with a drop of balsam of fir (Khimzavod «Balzam», Russia) diluted in 1,2-dimethylbenzene (analytical grade) (Khimmed, Russia) and topped with a cover slip.

Fluorescence spectra of red organic paints were registered using Raman spectroscopy. The samples were placed on an aluminium holder with a carbon tape. For the SEM-EDX analysis a graphite holder with a carbon tape was used for the preparation of samples.

Cross-sections were prepared in Sorel cement: mixture of MgCl (pure) (Boris Avogadro, Russia) and MgO (analytical grade) (Mosreaktiv, Russia) according to the method described in [5].

As reference samples of Madder dyes, we used seven paints manufactured by Winsor & Newton and one of Lefranc: four from paint charts of the 1930s that are stored in the archive of the Laboratory of Physicochemical Research of the State Research Institute for Restoration (GOSNIIR), and four paints produced no later than 1960 from the collection of The Nevskaya Palitra Paint Factory (formerly *the Leningrad Factory for Artistic Paints*).

Methods

The inorganic pigments and fillers were identified by PLM, based on the optical properties of crystals, and the results were confirmed and clarified by SEM-EDX and ATR-FTIR. Binders were identified using infrared spectra. Paint samples containing organic colourants were additionally investigated using Raman spectroscopy. The method was also applied to acquire fluorescence spectra of luminescent Madder lakes.

PLM

Glass slides with paint samples were investigated by the polarized microscope LOMO POLAM L-213M with 720× magnification. Photos of the pigments were taken with the CCD camera LOMO.

ATR-FTIR

Infrared spectra were acquired in the attenuated total reflection mode using spectrometer LUMOS (Bruker Nano GmbH) with a Ge ATR crystal within the range from 4000 to 600cm⁻¹. The time of acquisition of one spectrum was 1min, spot size 100x100µm, with a resolution of 4cm⁻¹. The resulting FTIR spectra of paint samples were compared with the IRUG (Infrared and Raman Users Group) database.

SEM-EDX

For the elemental analysis and high-resolution images of the samples we used electron microscopes Mira 3 XMU (Tescan Orsay Holding) coupled with X-MAX 50 (Oxford Instruments Nanoanalysis) energy dispersive X-ray spectrometer and TM4000 Plus (Hitachi) with Quantax 75 spectrometer (Bruker Nano GmbH). The accelerating voltage was 15kV, working distance varied in the range 5.5-6.5mm.

Raman

Raman spectroscopy was performed using Renishaw InVia Qontor Raman microscope equipped with a linearly polarized laser 785±0.5nm, 1200 lines/mm diffraction grating, and 50x objective (N.A. = 0.8). Raman spectra were recorded with incident power from 8 to 80 mW, spot

size of $\sim 1,2\mu\text{m}$. Parameters of acquisition: measurement range $50 - 2000\text{cm}^{-1}$, integration time 1-10c at each point, 3 spectra accumulations.

As both Raman and fluorescence spectra can be obtained using the same detector, the spectrometer was also used to collect fluorescence emission spectra of red fluorescent dyes ($\lambda_{\text{ex}} = 325 \pm 0.5 \text{ nm}$) in the range from 350 to 800nm. All of the resulting fluorescence spectra of reference samples consisted of several unresolved peaks. Their maxima were identified by deconvolution using Origin 8.5 software; peaks were considered Lorentz or Gaussian.

Results and discussion

The materials Filonov used are typical for paintings of the beginning of the XX century [7]. All of the etudes were created using oil paints and had many similarities in pigment composition. In the works we identified zinc white (ZnO), French ultramarine ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$), viridian ($\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), red organic pigments, barium sulphate (BaSO_4), calcite (CaCO_3), cadmium yellow (CdS), yellow ochre, mases of various colours¹, vermilion (HgS), cobalt green ($\text{CoO} \cdot \text{ZnO}$), cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$), glauconite ($(\text{K},\text{Na})(\text{Mg},\text{Fe}^{2+},\text{Fe}^{3+})(\text{Fe}^{3+},\text{Al})(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The results of the research of the composition of paint layers and grounds are presented in Table 1.

Table 1. The composition of grounds and paint layers of the nine early etudes of Pavel Filonov

Colours	<i>Old olive</i>	<i>Muslim town</i>	<i>Foothills</i>	<i>Arcades</i>	<i>Valley</i>
Ground	Zinc and lead whites, barium sulphate	Zinc and lead whites, barium sulphate	Zinc and lead whites, barium sulphate	Zinc and lead whites, barium sulphate	Zinc and lead whites, barium sulphate
White	Zinc white	Zinc white	Zinc white	Zinc white with barium sulphate	Zinc white with calcite
Red	Red ochre, red organic pigment	Red ochre, red organic pigment	Vermilion, red organic pigment	Mars red, red organic pigment	Vermilion, red ochre, red organic pigment
Orange	-	Red lead	Mars orange	-	Mars orange
Yellow	Cadmium yellow, yellow ochre, yellow organic pigment	Cadmium yellow, yellow ochre and mars yellow, yellow organic pigment	Yellow organic pigment, mars yellow	Cadmium yellow, yellow ochre and mars yellow	Cadmium yellow, yellow ochre and mars yellow
Green	Viridian, cobalt green	Viridian, cobalt green, glauconite	Viridian, cobalt green, glauconite	Viridian, cobalt green	Viridian, glauconite
Blue	French ultramarine, cobalt blue	French ultramarine, cobalt blue	French ultramarine, cobalt blue	French ultramarine, cobalt blue	French ultramarine
Brown and black	Mars brown, carbon black	Mars brown, carbon black	Mars brown, soot	Mars brown, soot	Mars brown, soot
Fillers in cromatic paints	Barium sulphate, calcite, gypsum	Barium sulphate, calcite, gypsum	Barium sulphate, calcite, gypsum	Barium sulphate, calcite, gypsum	Barium sulphate, calcite, gypsum

¹ Mars pigments were distinguished from ochres by the morphology of particles and degree of its dispersion by means of PLM [6].

Colours	<i>Landscape with a mountain village</i>	<i>The roof of the house</i>	<i>Arab</i>	<i>Dam on the river</i>
Ground	Zinc and lead whites, barium sulphate	Zinc and lead whites, barium sulphate	Lead white, chalk	Lead white, barium sulphate
White	Lead-zinc white, zinc whites with calcite	Zinc white	Zinc white with calcite and barium sulphate, lead-zinc whites	Zinc white
Red	Vermilion, red organic pigment	Vermilion, red organic pigment	Vermilion, mars red, Madder Lake, red organic pigment	Vermilion, red organic pigment
Orange	Orange ochre and mars orange	Red lead, mars orange	-	-
Yellow	Cadmium yellow, yellow ochre and mars yellow, yellow organic pigment	Cadmium yellow, yellow organic pigment	Cadmium yellow	Cadmium yellow, yellow organic pigment, mars yellow
Green	Viridian, glauconite	Viridian, cobalt green	Emerald green	Viridian
Blue	French ultramarine, cobalt blue	French ultramarine	French ultramarine, cobalt blue	French ultramarine
Brown and black	Mars brown, soot	Soot	Soot	-
Fillers in chromatic paints	Barium sulphate, calcite, gypsum	Barium sulphate, gypsum	Gypsum	Barium sulphate

Canvases and grounds

The canvases of seven of the nine etudes (*Old olive*, *Muslim town*, *Foothills*, *Arcades*, *Valley*, *Landscape with a mountain village*, and *the roof of the house*) were commercially primed with a white oil ground, which consisted of zinc and lead whites with an addition of barium sulphate. Furthermore, the canvasses were of a similar size ($\approx 20 \times 30 \text{ cm}$), had plane weave, and their thread density was $12 \times 12 \text{ threads/cm}^2$ (Fig. 2).

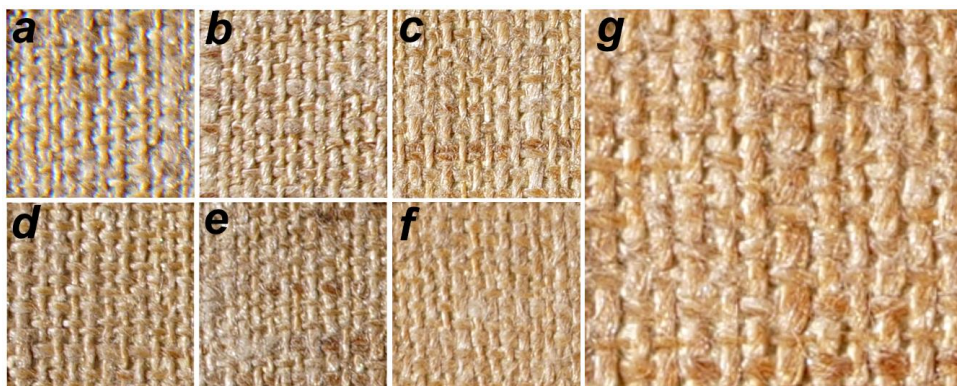


Fig. 2. Photographs of fragments (1 x 1 cm) of canvases of the etudes *Old Olive* (a), *Muslim Town* (b), *Foothills* (c), *Arcades* (d), *Valley* (e), *Landscape with a mountain village* (f), and *The roof of the house* (g).

This led us to assume that there should have been a bigger piece of canvas that the artist cut into fragments and then used for the etudes. This correlates with the suggestion that Pavel Filonov painted the etudes during a rather short period of time during his journey in 1905 – 1907.

In the composition of the grounds of the other two etudes, we identified lead white with either chalk (in *Arab*) or barium sulphate (in *Dam on the river*) as an inert filler.

Whites

Zinc white was identified in all of the investigated works. In six of the paintings (*Old olive, Muslim town, Foothills, Valley, the roof of the house, Dam on the river*), the pigment was in its pure form, and the white paints of the others contained various inert components. In *Arcades*, barium sulphate had been added to the zinc white; in the *Landscape with a mountain village*, calcite had been added; the white paints in *Arab* contained ZnO with calcite and barium sulphate, as well as a mixture of zinc and lead whites in the coloured paints. The presence of such inert fillers is typical of white paints of the first third of the XX century [7].

Reds and oranges

Red and orange ochres or mares were identified in all works except the *Dam on the river*. In all of the works, except *Old Olive, Muslim town*, and *Arcades*, we found vermilion. In two of the works (*Muslim town* and *the roof of the house*) red lead was also found.

Presence of red organic pigments was observed in all of the works by means of PLM. We could not obtain Raman spectra of those components, due to their luminescence excited by the available lasers, and there were no characteristic peaks in the FTIR spectra of the samples containing organic pigments, due to their low concentration in the paint mixtures and presence of inorganic compounds in the samples, thus their composition could not be identified.

Madder lake

Only in the etude *Arab* we identified pure red dye, which emitted intensive UV-induced orange light with maxima of fluorescence at 570 and 605cm⁻¹ and a shoulder at 661cm⁻¹ (Fig. 3, red line). Similar fluorescence properties are observed in the reference samples of madder dyes. Maximum values of their luminescence are presented in Table 2.

Table 2. Maxima of the original luminescent spectra of fluorescent Madder dyes (max) and peaks calculated by the deconvolution of the original spectra ($\lambda_{exc} = 325\text{nm}$).

№	Sample	Maxima of original spectra, nm	Peaks calculated by the deconvolution, nm
1	Paint from <i>Arab</i>	570, 606	570, 606, 661
2	<i>Rose Madder</i> , W&N oil paint chart, 1930s	612	564, 608, 656
3	<i>Rose Madder</i> , W&N Permanent Water Colours paint chart, 1930s	615	602, 642, 698
4	<i>Pink Madder</i> , W&N Permanent Water Colours paint chart, 1930s	606	573, 603, 650
5	<i>Rose-dore</i> , W&N, water colours, before 1960	606	575, 606, 654
6	<i>Rose Madder</i> , W&N, water colours, before 1960	625	620, 662, 709, 788
7	<i>Rose Carthame</i> , W&N, water colours, before 1960	595	571, 597, 652
8	<i>Brun de Madder</i> , Lefranc, water colours, before 1960	613 max	555, 609, 661, 783

The paints with the most similar spectra of fluorescence to that of the paint from *Arab* were *Rose-dore* and *Rose Carthame* of Winsor & Newton (from the archive of the Nevskaya Palitra Paint Factory), and *Pink Madder* of Winsor & Newton Permanent Water Colours paint chart from the 1930s (Fig. 3).

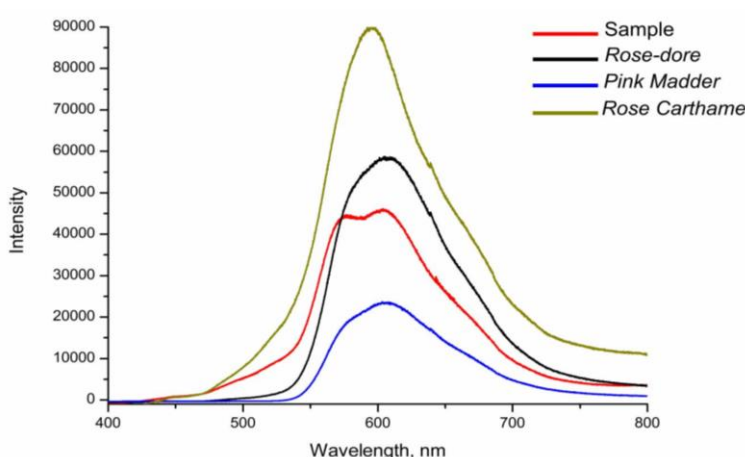


Fig. 3. Spectra of fluorescence of the samples: red line - paint from the painting *Arab* (#1 in Table 2), black line - *Rose-dore* (#5 in Table 2), blue line - *Pink Madder* (#4 in Table 2), olive green line - *Rose Carthame* (#7 in Table 2).

The two resolved maxima of fluorescence (570 and 606cm^{-1}) of the sample from the painting can be attributed to purpurin and pseudopurpurin, and the shoulder at 660cm^{-1} must be present due to the emission of alizarin lake [8]. Those compounds are the main components of the Madder Lake dyes produced from the roots of the plant *Rubia tinctorum*. Similar unresolved peaks can be evident in the reference samples, but as the resulting fluorescence of these samples is affected by the extraction method and ageing of the dye, a shift of the maxima occurs [9]. Nevertheless, the similarity between the reference samples of Madder lakes and the sample from *Arab* is evident. Furthermore, their FTIR spectra were similar as well (Fig. 4), thus, we can surely state that Pavel Filonov used this dye in his work.

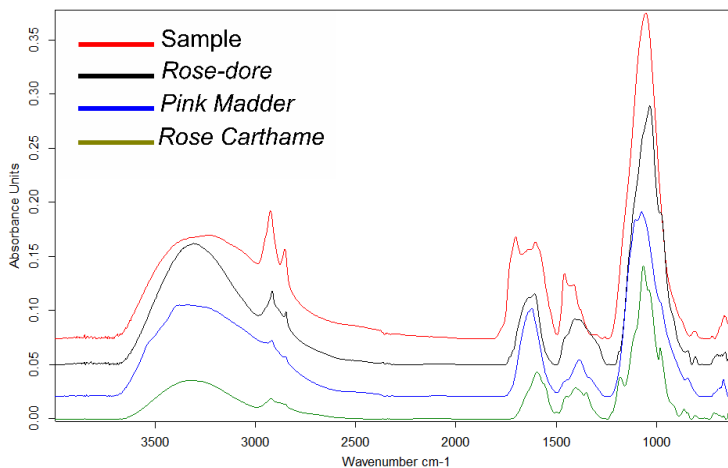


Fig. 4. FTIR spectra of the samples: red line - paint from the painting *Arab* (#1 in Table 2), black line - *Rose-dore* (#5 in Table 2), blue line - *Pink Madder* (#4 in Table 2), olive green line - *Rose Carthame* (#7 in Table 2); in the latter sample absorption of barium sulphate is also present.

Blues and Greens

French ultramarine was present in all of the investigated works. In six etudes (*Old olive*, *Muslim town*, *Foothills*, *Arcades*, *Landscape with a mountain village*, and *Arab*) we also detected cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$).

Greens are represented in Filonov's palette with a slightly greater diversity. Most often he used viridian (in 8 of 9 paintings), but also cobalt green and glauconite were found in the works. To create green in *Arab*, he mixed cadmium yellow and French ultramarine, plain green paint in this etude contained mostly emerald, green with an addition of red organic pigment, whites, and soot.

Yellows

As for the yellow pigments, cadmium yellow occurs most commonly in paint mixtures (found in 8 artworks). Ochre, mars and organic pigments were also found in the paint layers.

In some of the works, crystals of cadmium sulphide appeared in the polarizing microscope in unusual shapes. Commonly, cadmium yellow is a finely dispersed pigment whose individual particles are not visible in polarized transmitted light. However, in the painting *Arab* separate extraordinarily large (around $10\mu\text{m}$ in diameter) round particles of cadmium yellow were found (Fig. 5, *a*). In the etudes *Muslim town* and *Old Olive* cadmium yellow particles were smaller than in *Arab* but bigger than usual (several microns). These paints also contained small colourless spherical particles that had a black cross under crossed polaroids (Fig. 5, *b*). In the FTIR spectra of those two paints, characteristic absorption bands of CdCO_3 (1795 , 1397 , 858 and 722 cm^{-1}) were detected.

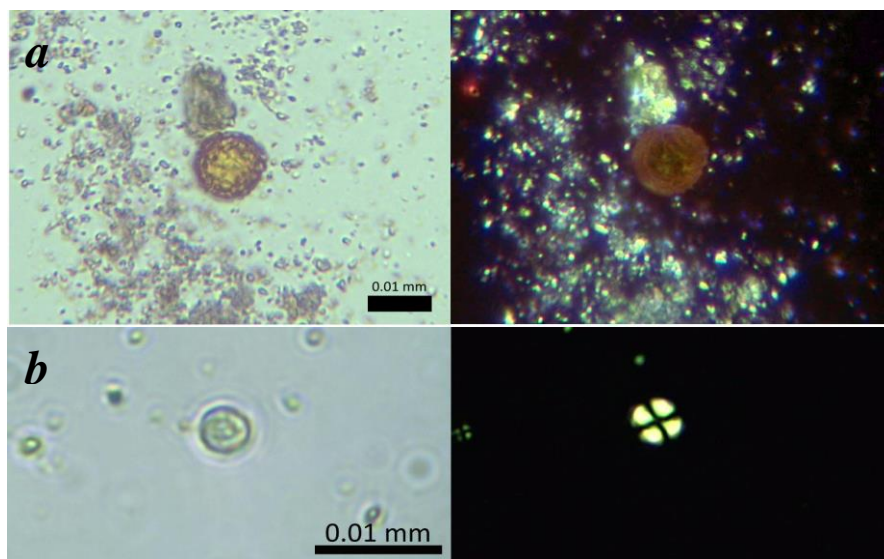


Fig. 5. Optical microphotographs of yellow paints from the painting *Arab* (a) and *Muslim Town* (b) viewed in transmitted polarised light with parallel polaroids (left) and under crossed polaroids (right). Alongside lead-zinc whites in the paint from *Arab* (a), there are yellow spherical particles that are identified as cadmium yellow.

The elemental composition of yellow samples was studied by SEM-EDX and this confirmed that the spherical particles and some of the fused particles consist of cadmium (Cd) and sulphur (S). In *Muslim Town* some of the toroidal particles contained cadmium but no sulphur (Fig. 6). The FTIR spectrum and SEM-EDX mapping of this sample lead us to conclusion that those toroidal particles (Fig. 5, b; Fig. 6) are cadmium carbonate. This substance was probably used as a precursor for CdS synthesis or formed as a result of its degradation [10, 11].

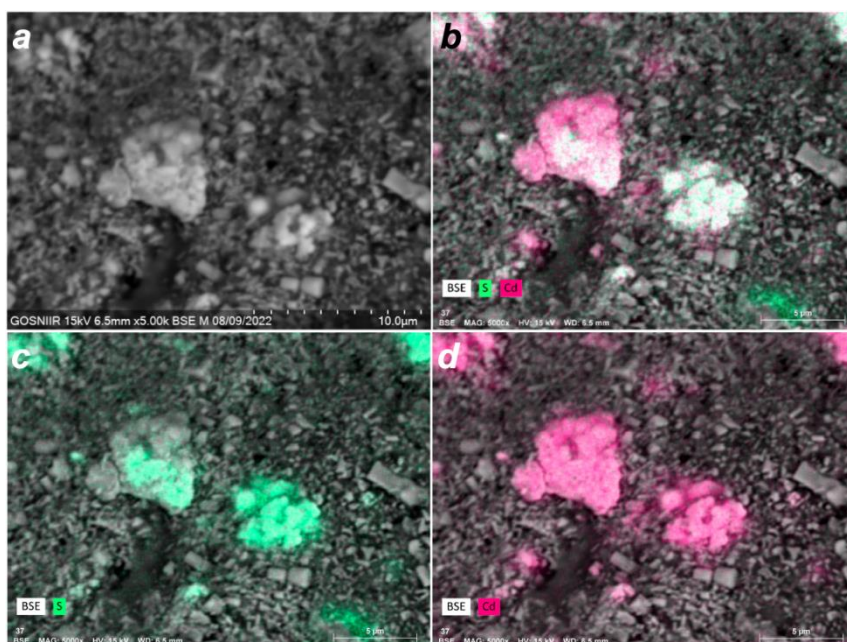


Fig. 6. SEM (BSE) image (a) and SEM-EDX mapping of S (c), Cd (d) on the surface of a sample of yellow paint from the etude *Muslim town*. The overlay of pink and green (b) in CdS particles appears as white, while the spherical particle, that is considered CdCO_3 , is coloured pink.

Browns, Blacks and Fillers

As a black pigment the artist used soot or carbon black. In six of the artwork's mars brown was also identified. In the *Dam on the River* no black or brown pigments were found.

In Filonov's chromatic paints barium sulphate, calcite and gypsum were identified as fillers.

Conclusions

Based on the results of the investigation of the nine etudes, we can conclude that Pavel Filonov used commercially prepared canvases for the creation of his early works, and preferred zinc white, lead white, ochres and mases of various colours, vermilion, red lead, red organic pigments (including Madder Lake), cadmium yellow, yellow organic pigments, viridian, glauconite, emerald, green, cobalts green and blue, French ultramarine, soot, and carbon black. Unusual shapes of cadmium yellow particles were also noted and investigated in the current study. The similarities in the composition of the grounds and pigments of the seven of the investigated etudes indicates their similar origin and the artist's consistency in choosing paints. All of those pigments, as well as fillers (barium sulphate, calcite, chalk, gypsum, kaolinite), are typical for the easel paintings of the beginning of the 20th century [7].

According to the 1910s catalogue of the art materials (*Datsiario* store, Saint Petersburg), paints based on some of the identified pigments, such as cadmium yellow, cobalt green, cobalt blue, and Madder Lake, were relatively expensive [12]. It is interesting that such a poor artist as Pavel Filonov at that time did not begrudge the cost, variety, and quality of the paint materials he used for his studies.

The results of the research will be useful for establishing Filonov's palette and understanding his journey as a painter. More information about the materials of his later works is

needed to track his full artistic path. Nevertheless, the obtained data supplement the statistics of the use of the identified pigments at this time by artists who worked at the beginning of the XX century and reveals Pavel Filonov's rich early palette.

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