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The discovered painting decoration of the Vorontsov` Palace in St. Petersburg: Spectroscopic characterization in support of conservation

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Abstract. The paper reports about the unique discovery of fragments of wall painting of the middle of the XVIII century from the Vorontsov` Palace in St. Petersburg and its study by means of laser and IR spectroscopic techniques. The history of creation and reconstruction of the palace as well as technical and technological features of paintings are described.

1. Introduction

During the repair and restoration works, taken place in 2015-2017 in the complex of buildings of the St. Petersburg’s Suvorov Military School, located at crossing of Moskovsky avenue and the Fontanka River, fragments of wall painting belonged to the R. I. Vorontsov’s palace were found out. The palace was originally built by the member of one of the prominent families in XVIII Century Saint Petersburg. Roman Illarionovich Vorontsov (1717-1783) was the count of the Roman Empire, General-in-Chief, Senator, Governor-General of Vladimir, Penza and Tambov, and one of the first figures of Russian Freemasonry and the most famous personalities of the Vorontsov family. In 1757 R. I. Vorontsov acquired the estate on the banks of the Fontanka River and in 1759–1760 he built a country mansion there. The architect in charge of the project has not been positively identified, but a search on the documents on Vorontsov’s house property suggested contributions from Francesco Bartolomeo Rastrelli and Giacomo Quarenghi[1].





Figure 1. A view of the Vorontsov Palace before 1863 reconstruction

After the death of R. I. Vorontsov, the country mansion was bought by the Czar Pavel I and was used for hosting of one of the established Military Orphan Homes. However, the house required repairs and alterations for the new destination. The adjustment of buildings was carried out according to the project of architect G. Paulson, and already in 1798 the new use was beginning. The exterior of the Vorontsov's former country mansion was almost unchanged but many internal alterations were made.[2]

In view of the constant lack of space for children, in 1806 the military engineer A.E. Shtaubert attached to the former palace some new buildings together with the Orthodox Church dedicated to the Resurrection of Christ, which were located along Tsarskoye Selo Avenue (now Moscow Avenue). The new buildings connected the new front housing with the former Vorontsov's Palace.[2] The house itself was not rebuilt at that time.

The next reconstruction was carried out in 1863, it affected more in both the external appearance of the Vorontsov's Palace (side wings were built up to three floors, and the triangular pediment was replaced by an attic) and the architectural look of the interior. Some halls were divided by partitions, additional staircases were built in, and interior decoration was partially destroyed. Also, the biggest hall of the palace was rebuilt, and its walls were decorated with illusory paintings imitating architecture. During this reconstruction, part of the hall was used to create a corridor and a separation wall erected. The ceiling was lowered both in the corridor and in the hall itself (Figure 2). As a result, many parts of the original decoration were preserved in the interfloor space. Large areas of the picturesque stucco, painted using the Grisaille technique, were found. Double attached columns of the Ionic order with cannelures and pilasters were depicted. In the walls between the pillars there were decorative mirrors framed with plats with rectangular enlarged ears. The alternating wreaths of laurel leaves and flower festoons were depicted in the mirrors. Samples from these paintings were selected to learn about the original building and decoration techniques. The sample used in this work (shown in Figure 3) was taken from that part of the mural where the characteristic color range was determined. The sample was selected from an area without later inclusions and minimum amount of dirt. For the safe extraction, it was collected from a region where the was already partially detached and along the cracks. The fragment was extracted carefully with the help of scalpel. At a preliminary check, painting was carried out on a two-layer lime-sand plaster. A thin layer of a fine-grained lime coating was applied on the first layer with the coarse silica filler. These samples were further investigated by optical and spectroscopic methods, including Raman and infrared Fourier spectroscopy, in order to identify the pigments on the paint layer and verify the possible presence of organic fixative, extraneous to the artwork. These were often placed on the surface some years after the completion of the paintings and were used in restoration until the beginning of the twentieth century.

These samples were also analyzed in order to understand the technical composition of the paintings, to examine the mortar and to identify the possible presence of salts.



Figure 2. The area upon which the pilaster sided entablament was leaned

2. Materials and Methods

Raman spectra were obtained on a Renishaw RM2000 spectrometer equipped with a Leica DMLM microscope and a semiconductor laser with emission wavelength at 785 nm. The objective lens used for all measurements was a 50x/0.80N.A. Fine grains obtained from the original samples have been analyzed directly, without any preliminary treatment.

Attenuated total reflectance-FTIR spectra were recorded by a Perkin Elmer Spectrum 100 spectrometer. The reflection system (the universal attenuated total reflectance) consists of a diamond crystal, a flat focusing lens made of KRS-5, and a movable device applying on the sample a pressure aimed at eliminating air. The detector is FR-DTGS (fast recovery deuterated L-alanine triglycine sulfate) and the spectral range is $4000\text{--}380\text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} .

Polished cross sections were prepared embedding the sample in a bi-component epoxy resin (Epofix, Struers DK). The cross sections were then observed with optical microscope, a ZEISS Axio Scope.A1 polarized microscope equipped with a 5 Mpixel camera and a dedicated Axio Vision image analysis software was used.

3. Results and Discussion

The different spectra obtained from the samples revealed a wealth of information about the decoration process and the building materials. The identification of the different constituents was possible by a simple comparison with spectra of reference materials we have collected over time.

Raman spectroscopy data were mostly useful for identification of the materials used for the wall decoration [3] Figure 3 shows the image of the plaster sample taken from the decoration and Figure 4 shows Raman spectra obtained in the different colored area. The list of materials that we have found on the samples is presented in Table 1.

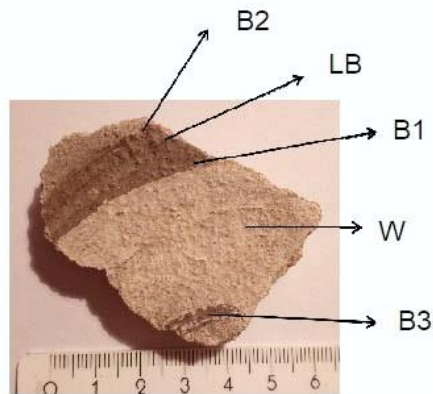


Figure 3. The plaster sample representative of the mural decoration used in this work

Table 1. List of materials identified by Raman spectroscopy

Description	Mineral phases
Brown 1 area	
B1_Y1 (yellow grain)	goethite + amorphous carbon
B1_W1 (white grain)	hematite + calcite + amorphous carbon
B1_R1 (red grain)	hematite
Brown 3 area	
B3_B1 (black grain)	graphite
B3_R1 (red grain)	hematite + goethite + amorphous carbon + manganese oxides
B3_W1 (white agglomerate)	calcite + amorphous carbon
B3_W2 (defined white grain)	calcite
Light brown area	
LB_R1 (red grain)	hematite
White grain	calcite + amorphous carbon
Red grain	hematite + amorphous carbon
White area	
W_B1 (black grain)	calcite + amorphous carbon
W_W1 (white grain)	calcite

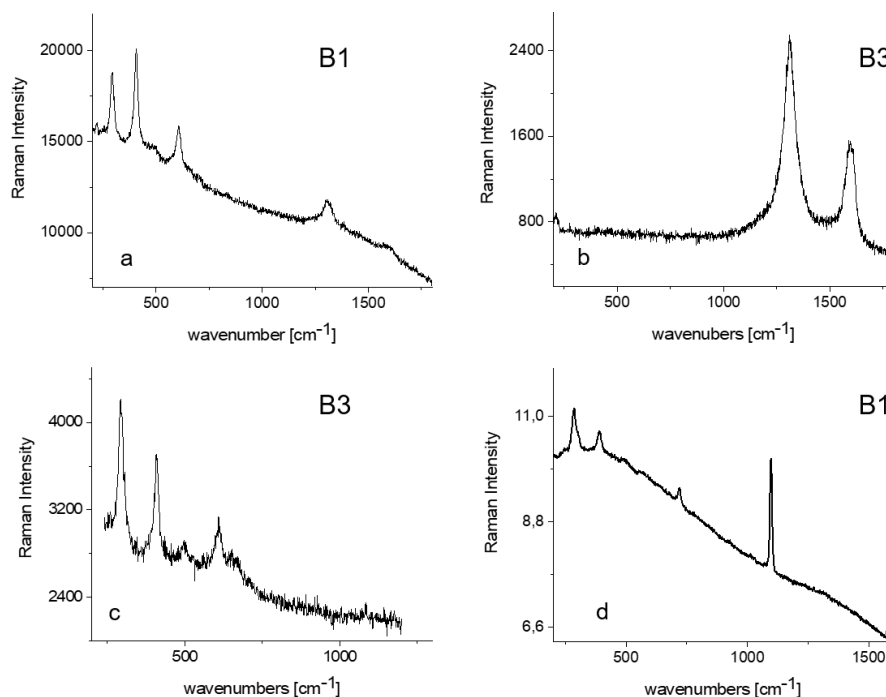


Figure 4. Some representative Raman spectra obtained from different points in the sample: (a) hematite, (b) amorphous carbon, (c) hematite and manganese oxides and (d) calcite

All brown paints revealed the presence of hematite ($\alpha\text{-Fe}_2\text{O}_3$), which gives a well-recognizable Raman signal and the yellowish hydrated form goethite, $\alpha\text{-FeOOH}$. [4] Some representative spectra are shown in Figure 4.

Sporadic black grains were observed in some brown drawings and were identified by micro-Raman as amorphous carbon. However, they were also observed on light brown and white areas. Thus, they appeared more likely to be impurities, rather than a component intentionally mixed to red and yellow ochre to give it a deeper shade.

Instead, in the spectra obtained in the brown bent strip decoration a broad band was observed in a spectral range which is typical of Mn-O and Mn-OH stretching vibration frequencies ($450\text{--}750\text{cm}^{-1}$). [5] The presence of manganese oxides-hydroxides were thus assumed. The identification of such manganese compounds by means of Raman microscopy is known to be quite problematic. No clear Raman signature is often obtained probably because of the low Raman activity of the manganese-based pigments, low crystallinity and high degree of chemical heterogeneity (different manganese compounds can be present simultaneously at the microscopic level). Firstly, manganese oxides/hydroxides tend to undergo thermal transformations under high laser power values, in a manner similar to analogous iron compounds, but in a stronger way. Secondly, manganese exists in several oxidation states and exhibits a lot of hydro-oxides modifications, many of them being non-stoichiometric and disordered compounds. Consequently, only a tentative assignment can be done. The stronger band at $585\text{--}610\text{cm}^{-1}$ was assigned to bixbyite (Mn_2O_3), while the presence of the Raman signal at $643\text{--}652\text{cm}^{-1}$ was attributed to a variable contribute coming from a spinel structure (Mn_3O_4 , haussmanite). The spectrum in Figure 4c shows an additional band at 553cm^{-1} , which may be ascribed to groutite sites (MnOOH). Moreover, black drawings appeared as homogeneous phases in which no distinctive grains could be observed, so that a fine mixture of different Mn(II), Mn(III) and Mn(IV) oxides and hydroxides has to be assumed.

Instead, infrared spectroscopy was used mostly to characterize the mortar which was used to create the plaster layer of mural paintings. The analysis performed on this preparatory layer of the painting has positively identified calcite in the binder structure (calcite is the result of reaction while drying, calcium hydroxide is what supposed to be actually used as binder), and the absence of harmful crystalline salts, such as nitrates and sulfates (see Figure 5).

The optical microscopy analysis of the sample stratigraphy was very helpful to gain insights on the preparation method of the plaster and its decoration. A simple analysis of these images reveal that the painting was made in layers (see Figure 6). These layers are partially mixed, which suggests that the top paint layer was applied on the incompletely dried out background color.

Thanks to the combination of optical images and spectroscopic analysis it was possible to understand the technical execution of the paintings: lime binding material was found in the pigment part, and the paint layer was applied directly on the lime plaster without additional layers of soil, we can conclude that the murals were created using the “*secco*” or “*semi-secco*” mural technique.

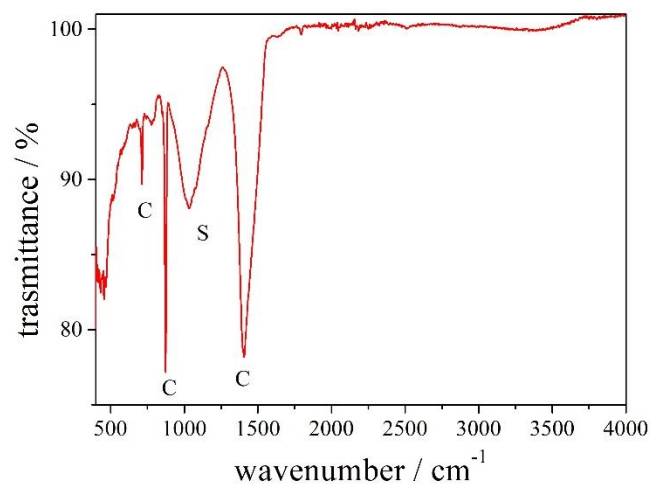


Figure 5. ATR-FTIR spectrum of mortar; the symbols C and S correspond to the principal bands of calcite and silicate, respectively

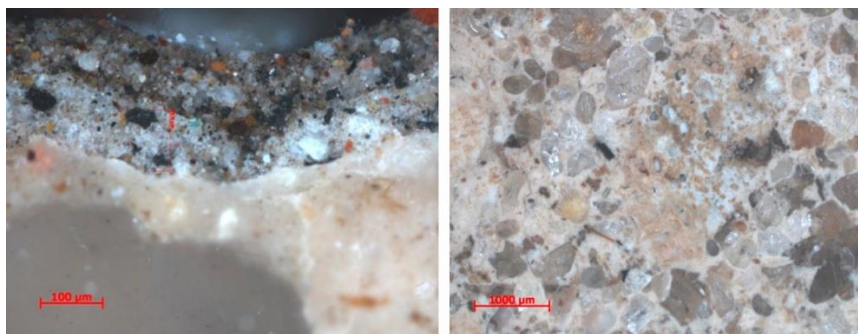


Figure 6. Optical microscope images of a samples's cross section at different magnification



Figure 7. A detail of the wall decoration before (left) and after (right) the cleaning and conservation

The results of the research were helpful to select the necessary materials for the conservation and the following cleaning of the painting surface from the persistent dust pollution. According to the investigations, the consolidation of the plaster structure was carried out with the materials found in the original lime binder. Given the mineral nature of the constituents of the decoration, vulcanized latex sponges Akapad (hard and soft) were used for the dry cleaning of the mural from the contamination of dust and soot. Spots and smudges of later color layers were taken away mechanically, with scalpel. The mortar based on hydrate of white lime KalkInjektionsmörtel was used for the grouting of detached plaster layer. The solution was injected in the hollows of the stucco lags and that parts were then pressed to the basement. The edging repair of the exposed plaster along the lacunae was made with the lime mortar prepared with Kalk-Kontor lime filler and quartz sand 1:2. In Figure 7 we show a portion of the wall decoration before and after the cleaning and conservation process.

4. Conclusions

The spectroscopic characterization of the sample revealed the use of materials typically found in “*secco*” or “*semi-secco*” mural technique. We have found no evidence for possible presence of organic fixative, extraneous to the artwork.

These results were useful for the restorers of the Stiglitz Academy in order to carry out successfully their conservation works of fresco paintings, because most appropriate ways of cleaning and preservation were chosen. Some of such methods were already used earlier used for restoration of wall paintings in St. Petersburg, for instance, in the interiors of the General staff, the State Hermitage and the State Russian Museum. But a comprehensive work on the preservation of fresco painting the restorers of the Academy of Stieglitz conducted for the first time.

It should be noted that the definition of painting technique helped to attract public attention to the wall paintings of the Vorontsov Palace. It made possible to introduce them into scientific circulation as unique, as in the palaces of St. Petersburg fresco painting was rarely used. Moreover, due to multiple repairs and reconstructions most of wall paintings were lost and nowadays there are only few ones of XVIII century.

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