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NON-DESTRUCTIVE ANALYSES FOR MODERN PAINTINGS: THE RUSSIAN AVANT-GARDE CASE

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ABSTRACT

It is now common practice to analyze works of art using non-destructive, non-invasive techniques like classical radiography, macro-photography, infra-red reflectography (IRR) and ultraviolet (UV). This image analysis, unfortunately, does not sufficiently establish with a high level of accuracy the techniques and materials used in painting. Chemical analysis is used instead, for example, to identify the nature of the pigments. In the past, chemical analyses were conducted using destructive techniques such as cross-section or micro sample to SEM analyses. Relatively new non-destructive analyses like X-Ray Fluorescence and Raman Spectroscopy are currently used in order to analyze works of art and give chemical results. The results of these tests on works of art are very important for conservators, art-historians and keepers of private or public museum collections. These investigations reveal information which is of historical interest: the materials that were used and which can be compared with the ones that were available at a certain period in a particular region.

During a study of many of the Russian Avant-guard paintings (1910-1930) a productive collaboration with art historians gave us the possibility to make important discoveries using our non destructive analysis. Three case studies are presented here. The first one shows how non destructive techniques help us to discover how the painter K. Malevitch (1879-1935) used pigments in different ways to obtain specific visual results corresponding to his aesthetic research. The second one shows how advanced image analysis helped us to discover a M. Larionov painting (1881-1964) that we were later able to associate with other known works. The last example concerns A. Exter's (1882-1947) series.

Advanced image techniques and chemical analysis may help us to discover how the painting technique changes in different canvases and which pigments are used during the different states of creating the painting. These case-studies aim at showing how accurate can be the results obtained using the above-mentioned non destructive techniques and how important it is to have an intelligent collaboration between scientists and art historians.

INTRODUCTION

Nowadays art experts, curators, art historians or simply keepers, in order to establish the authenticity of an artwork, can be supported by scientific methods (normally employed in different areas) to take their decisions. The handling of these scientific technologies is the activity of labs similar to ours. To help the experts we must provide a series of results that include an analysis of the status of the artwork's support, many images acquired with different techniques, like infrared, ultraviolet, raking light, macro photography, and finally chemical analysis. Different methods are deployed for different supports. Finally a report about the chemical nature of the pigments used, the status of the support preparation, the nature of the canvas and the type of varnish used, in the case of paintings, is delivered to the expert that, on the bases of this information and his experience, will give a final opinion.

This article describes the systematic methodology used to investigate an interesting number of Russian “Avant-Guarde” painters. The final result consists in a rich database containing much useful information that helps us to rebuild the tumultuous history of Russian “Avant-Guarde” paintings. The structure of this paper follows the steps of the artwork analysis: first the High Resolution imaging in natural light, in infrared and ultraviolet wavelengths and macrophotography, then, once the "corpus" as been studied and validated for further analysis, elemental analyses such as RAMAN, X-ray fluorescence and SEM imaging are used.

FIRST CYCLE ANALYSIS: SCIENTIFIC IMAGES

The first step is to take photos in natural light in order to better identify nuances, contrast and the color palette of the artwork. The power of the light source must be chosen carefully in order not to heat the artwork and not to produce any flashing on the surface. Images are taken with a digital reflex high resolution professional camera. The camera resolution (Nikon DX3) is an important parameter to obtain a detailed image to be able to study the network of cracks, the adherence between the canvas and the paint film and of course, the details of the painting itself [1]. Additional information about the artwork history (signature, museums stamp, wood or canvas provenance, etc) can also appear on the back of the painting.

Raking Light Photography

Raking light photography is very important in painting examination and is obtained by illuminating the painting's surface from one side, with the light source placed almost parallel to the picture plane. This technique of illumination is used in the topographical study of a painting. We can highlight features such as undulations, brushwork, and other surface qualities that otherwise remain invisible.

Macro Photography

A good technique to observe the artwork in detail is macrophotography. This is not a real new method of analysis but the improvement is in the technology used. When an area looks interesting for some details we investigate more deeply. To do this we use a small macro digital camera that using as light source a LED matrix, allowing us to "walk on" the Region Of Interest magnifying the surface up to 24x using optical zoom. As the acquired image is in good spatial quality, we can then apply a digital zoom. To have magnification bigger that this we must use the binocular microscope with all the limitations that its use imposes.

Figure 1: Gontcharova, details - digital zoom and macro photography (24X)

But unfortunately visible light (figure 2) doesn't give us all the information we need, the use of multispectral techniques is more and more used in Cultural Heritage. We now describe the scientific image methods that we use [2].

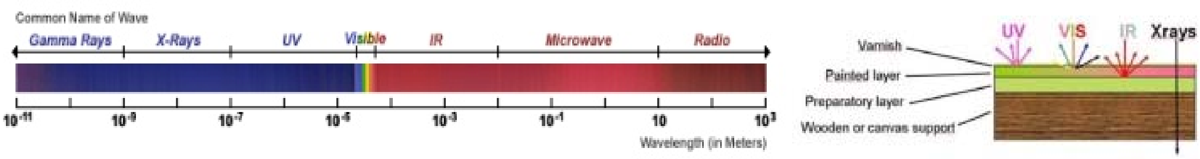

Figure 2: on the left the radiation spectra, on the right,
the information that we can retrieve using different wavelength

Infrared Reflectography (IR)
Infrared reflectography is a widely used non destructive investigation technique mainly applied in the study of ancient paintings. The peculiarity of infra-red reflectography is that it appears to be the best technique allowing underdrawing detection, useful to document deeper paint layers and canvas status. Underdrawing designates the compositional sketches done by the painter usually during the initial phase of the composition. These elements are of great importance to experts and professionals as they can provide crucial information about authorship as “pentimenti” (figure 3), changes in the painter's original intentions, and previous interventions on the painting layer [3]. This technique is the natural evolution of the infrared photography that is limited to the real near infrared (1050 nm). Modern customized digital NIR cameras can obtain images with a wavelength in the near infrared (800nm – 2000nm) with a reasonable resolution [4]. Our camera is able to register 9 filters of which 4 are infrared at 750,850,950,1200 nm.

Often it happens that with infrared we identify not only underdrawing or “pentimenti“, but also signatures, dates, inscriptions or monograms that help in the characterization of the artwork. The difference in absorption between pigments and drawing creates a high contrast in the IR image and this is even more evident if the preparation layer is made with clear colors.

Figure 3: M. Larionov, Promenade en Province, 1909 ca. detail. a) RGB color image b) infrared image, we can clearly see the underdrawing totally invisible to the naked eye.

Moreover, if we compare the calibrated color image with the different spectral images, we can assess the order in which the different painting layers have been applied. Some interesting information obtained from the analysis of more recent paintings will be shown in the case studies.

False Colors
False color infrared photography is used to differentiate pigments having the same color under a certain light but different chemical compositions and reflectance spectra. This is a well known effect named “metamerism” [5,6]. This is achieved by exploiting differences in the pigment reflectance characteristics in the NIR band of the spectrum. To perform this we use the output of the multispectral digital acquisition (multiple images at different spectral wavelengths: red, green, blue and infrared narrow bands are used) that we “combine” with a visible color image. In the resulting color image, or better pseudo color image, we can see the contribution of the infrared information making visible the differentiation of the material because of the existing differences in the reflectance spectrum. In the resulting image we can then identify groups of pigments depending on their composition. We can also recognize some special pigments (like lapis) and clearly evidence restorations done in different moments of the artwork's history.

Ultraviolet Photography (UV)
Opposite to infrared, in terms of human eye perception, there is the ultraviolet light. In our case only near ultraviolet is used (between 320 and 400 nm). It is an electromagnetic radiation with a wavelength shorter than 400 nm but longer than soft X-rays (1-200 nm). Ultraviolet reflectography or photography is based on the measurement of the ultraviolet radiation reflected by the artwork. Typically the sample is illuminated directly with special ultraviolet light and the visible light is filtered using a blocking filters on the camera lens. These filters allow only the ultraviolet light to pass and impress the CCD by stopping the visible and infrared ray. Better results can be obtained using the ultraviolet fluorescence photography. This technique is slightly different than the previous one. The same ultraviolet light sources are used, but instead of filtering the reflected light, we filter directly the light source. In this way we stop the visible light and only the ultraviolet light excites the painting surface. This last method, in artwork studies, allows us to identify different varnishes and over-paintings. Indeed, photons in the UV region of the spectrum are absorbed by the painting varnish and this effect allows us to characterize the materials used, to evaluate the artwork's state of conservation and to localize retouches and previous restorations [7].

Information about the age of the artwork can be retrieved by the interpretation of these images. In an aged painting the original varnish has different fluorescence properties than new layers. On the other hand, in the case of modern pigments we can notice a different fluorescence emission than from traditional pigments, even if they look alike under visible light. That means that the fluorescence of oil paintings under ultraviolet light shows if any restoration or retouch has been done. UV fluorescence can also be applied to other objects like porcelain, ceramics, books and paper.

Radiography (X-Ray)
Radiography analysis is one of the oldest scientific image techniques used in the investigation of artworks. The first radiography on a painting was done in Germany in 1896 in the wave of interest arising from the discovery of X-rays. Different to IR and UV wavelength the X rays cross the media depending on the nature of the chemical elements composing the analyzed object and its thickness. Different media have different X-ray photon absorption. The radiography technique is well known and extensively applied in medicine. The image we get is a photograph of the artwork obtained by using X-rays as a light source, and it can provide information about its structure, its assemblage, the state of the canvas, possible restorations, etc. Parameters such as energy, intensity of radiation, and the time of exposition are chosen according to the object characteristics. In cases where radiography cannot be used directly, for example if the painting has a preparation done using “Lead white” or if the support is on metal or if the thickness of the artwork is preventing X-ray transmission, it is possible to use X emissiography. While X-ray radiography is measuring the intensity transmitted by the artwork, X-ray emissiography is based on the measurements of the secondary electrons emitted by the sample, therefore giving only information on the surface of the object.

SECOND CYCLE ANALYSIS: PHYSICAL CHEMICAL ANALYSIS
Once the problematic of the artwork is well contextualized with the imaging techniques, we continue with the physical/chemical analyses needed to confirm what we discovered about the nature of the materials. The first two analyses are still not invasive but, in order to be sure of our results, we still need to take a micro sample of the pictorial layer and study it using SEM-EDS technology.

Fluorescence X-Ray

X-ray Fluorescence (XRF) is one of the most utilized elemental analysis techniques in the cultural heritage field, since it's a non-destructive and non-invasive method able to identify the chemical elements present in the sample. When an x-ray beam is directed on a sample, the radiation can be either absorbed or scattered. During the absorption processes an electron from an inner shell could be ejected creating a vacancy, so an unstable condition. When the atom returns to its stable condition an x-ray photon is emitted. Each element has a unique set of energy levels, therefore the produced x-ray photons can only be characterized by a unique set of energy values, that is a “fingerprint” for each chemical element. XRF can then identify and quantify the different elements present in the object. Qualitative analyses allow the identification of the chemical element, quantitative analyses allow us to determine the object chemical composition [8]. The XRF technique fluorescence X-ray allows us to identify anachronistic pigments or recognize restorations. XRF analyses on metallic sculpture can also reveal possible later additions. The limitations of X-ray fluorescence examination is its inability to recognize organic elements (the fluorescence of light elements is easily absorbed by air) and traces of elements. Portable X-ray spectrometers, as the one we are using, allow us to analyze artworks *in situ*, without removing and touching the paintings, reassuring curators that their pieces can be examined safely.

Raman

Raman spectroscopy relies on the measurement of the wavelength and intensity of inelastically scattered light from molecules. Typically the sample is illuminated with a laser beam in the visible, near infrared, or near ultraviolet range. Most of the light is elastically scattered by the sample, while a minimal part (normally less than 1%) is scattered at optical frequencies different from the incident photons, modifying its wavelength because of the inelastic interaction with the atoms that constitute the material. A plot of intensity of the scattered light versus the energy difference is a Raman spectrum. The material can be identified by the measurement of the wavelength shift: Raman spectroscopy provides in fact a fingerprint by which the molecules can be identified (figure 4). Raman spectrometers can be combined with a microscope or camera in order to image the sample and simultaneously the Raman spectrum. Portable Raman instruments are also available and quite commonly used allowing analyses directly *in situ*. Raman analyses are non-destructive and non-invasive therefore this technique became one of the most used for pigment identification in paintings, colored sculptures, manuscripts or ceramics.

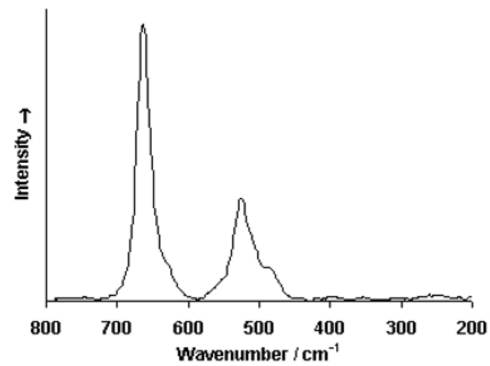

Fig. 4: Raman spectrum of “Cerulean blue” pigment

A limitation occurring when analyzing artwork pigments with Raman spectroscopy is that the presence of varnish and binders usually distort the asset.

Scanning Electron Microscope

SEM analysis is an invasive technique of investigation. It requires sampling the artwork. This sample is normally very small, less than a milligram in weight and it is taken from well chosen region of interest. Metal specimens require no special preparation, while non conductive solid specimens should be coated with a layer of conductive material (graphite, gold...). A high energy electron beam is directed on the sample and from the interaction electrons-sample different signals are generated. Secondary electrons produce a 3D image with the morphological structure; the back scattering electrons give the distribution of elements with different atomic numbers; the X rays emitted by the sample allow qualitative and quantitative identification of chemical elements offering the possibility of acquiring elemental mapping distribution. This technique is widely used since it make it possible to observe morphological characteristics of the sample and elemental information, when combined with Energy Dispersive Spectroscopy (EDS), providing high spatial resolution (nm) and high magnification (some SEM models can reach 100 000x enlargements). The main limitations of this technique are the sample preparation, the sample environment (in vacuum) and low detection limits for organic elements.

CASE STUDIES

The Pigments in Malevich's Volumes

By means of infrared reflectography and X-ray fluorescence, interesting discoveries have been made by art historian Patricia Railing on technical aspects in the painting of Kasimir Malevich (1879-1935). We worked on a series of Malevich's paintings with geometric composition on a white background. Infrared images showed that the background is not done using a simple white color, but it has been obtained mixing the white with different pigments. The macro photographic images reveal the technique used by the painter consisting of small touches with the paintbrush, mixing white pigment with all the colors composing the white spectrum in order to give a sense of animation.

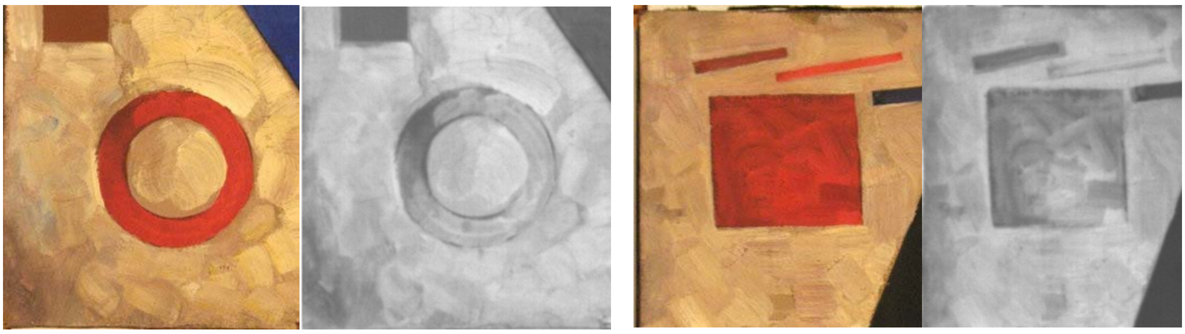

Figure 5,6: Malevich, details, Infrared photographies show the use of different pigments

The use of different pigments to represent movement and 3D volume has been discovered also in another painting by using XRF, infrared techniques (figures 5, 6) and macro photography (figure 7). In this case the 3D volume is represented by a circle done with a superimposition of layers of different red pigments (“Iron Oxide red”, “Vermilion” and “Chrome red”).

Figure 7: Malevich, detail, macro photography showing superimposed red layers.

The Hidden Original Composition in a Mikhail Larionov Painting

Although infrared reflectography is a preliminary stage of analysis only based on image, sometimes it may lead to the discovery of elements that immediately help us to identify the painting. Interesting results were found on a painting signed by Mikhail Larionov (1881-1964), another painter from the Russian Avant-Guarde. The artwork represents a subject that Larionov ofter painted at the beginning of the XX century.

With the infrared investigation we discovered a few underdrawings (figure 8, 9). The subjects represented in the hidden images gave us the possibility to compare this painting with another one exhibited (so authenticated) in a public collection. An accurate XRF analysis of the artwork also showed that the first original composition had been modified a few years later.

Figure 8 : left) detail of the Larionov painting right) IR image, we can see the underdrawing done with paintbrush where the man was in a different position.

Figure 9: left) detail of the Larionov painting right) IR image.

Pigments Used by Alexandra Exter

The collaboration with M Jean Chauvelin, a specialist of Alexandra Exter, gave us the possibility to create a heterogeneous corpus of information about this painter representative of the Russian Avant-Guarde. This database contains information on about forty artworks by this painter, all dated between 1911 and 1940 and done on different supports, like paper, cardboard, and canvas and with different techniques, watercolour, gouache and oil. Very interesting results have been observed on the X-rays fluorescence results: we compared the pigments used over all the years by the painter and we could trace a timeline of a possible evolution. For example we have been able to see that at the beginning A. Exter, as yellow, she preferred “Chrome yellow”, stable with oil binder, and she moved, around 1920, to “Cadmium yellow”, a pigment stable in all conditions and resistant to the aging process. A similar change has been noted in her red colors. She started using “Chrome red” which she replaced totally in 1910 with “Cadmium red”. When she went for the first time to Italy in 1912, she started using “Vermilion”.

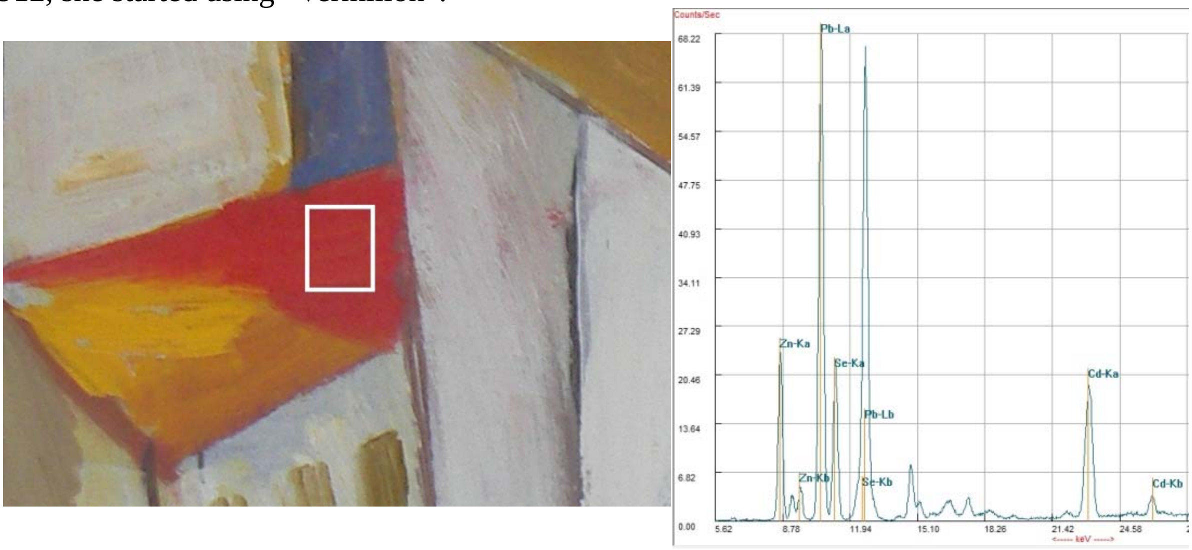

Figure 10: A. Exter, Village (1911), detail. In evidence the area analyzed using XRF and its resulting “Cadmium red” spectrum.

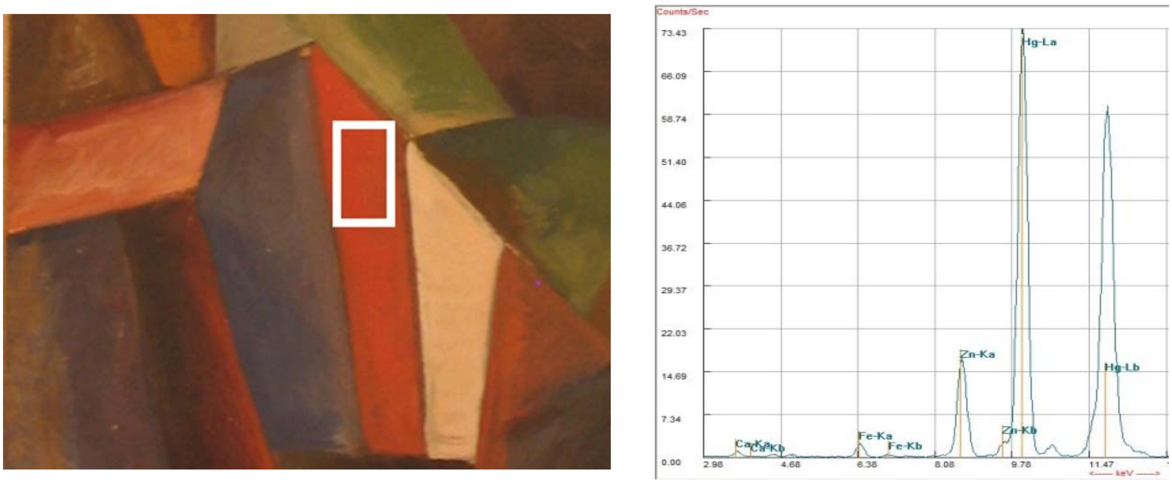

Figure 11: A. Exter, Ville (1912), detail. In evidence the area analyzed using XRF and its resulting “Vermilion” spectrum.

The analyses on Exter's paintings using XRF is a good example since the painter usually used pure colors, particularly that allow us to obtain much more precise results. Among the other pigments we can cite as example the green, where we encounter “Oxide green” pigment that she said was too brilliant and the “Cobalt green” pigment, that she used in big decorative artworks at the end of the 1920s. Exter did a lot of paintings using “Cobalt blue”. Sometimes she combined this blue with “Prussian blue” to obtain special chromatic effects. We start finding “Cerulean blue” in early paintings and in decorative Italian paintings of the 1920s, where the subjects are the characters of the “Commedia dell'Arte” and Venetian buildings.

CONCLUSION

Within the analysis on Russian Avant-Guard paintings we demonstrate that non destructive techniques are useful not only for ancient artwork, but they also show interesting, although different, results when applied on XX century paintings.

A close collaboration between us and scientific laboratories and art historians has allowed us to create an interesting information corpus and scientific database that we can use to compare and to identify common characteristics on Russian “Avant-Guarde” paintings, not well studied until now and not enough documented. Only few scientific publications are available in bibliography [9]. Moreover in this article we have highlighted how, mainly using non-invasive scientific investigations, we put into relationship two Larionov paintings, Malevich's complex pictorial technique, and the timeline in the palette changes of Exter. In addition we discovered that in cases where the canvas has significantly deteriorated the pigments, which usually are of very good quality, are responsible for maintaining the integrity of the pictorial composition.

Again we revealed important elements concerning the technical painting using scientific methods and confirming that these analytical results, the state of the paint layer, the pigments used and the underdrawing, are important not only for the scientific community, but also for art historians and curators.

ACKNOWLEDGEMENT

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