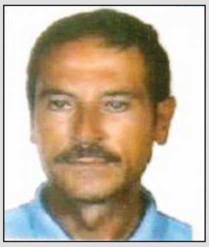
SERGIO RUIZ-MORENO and ALEJANDRO LÓPEZ-GIL SERRA

# Contributions Towards the Palette of Liubov Popova



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In 2009 and 2010, the Galería Manuel Barbié in Barcelona (Spain) commissioned the laboratories of "ACTIO, Arte y Ciencia" (Art and Science) in the Polytechnic University of Catalonia (Universitat Politècnica de Catalunya, Barcelona) to analyse several paintings by Russian Avant-Garde artists. These included works by Ivan Puni, Alexandra Exter, Nina Kogan, Vladimir Lebedev, and Liubov Popova. The purpose of this commission was to determine the pigments used by these artists in view to being able to set up a database of characteristic pigments used by Russian Avant-Garde painters, among other things. Having established that the paintings were evenly aged and would be at least sixty years old, their pigments were analysed using the non-destructive technology of Raman spectroscopy in the Raman Laboratory at the Polytechnic University of Catalonia.

In discovering the pigments employed in the seven paintings by these artists, the results of our findings also established that all these pigments were in common use around 1900, not only in Russia but also in Europe and the United States.

By way of example, we have chosen to present a detailed description of our findings about the Cubist painting by Liubov Sergeievna Popova (1889-1924), *Bottle and Glass* [No. 86] (see page 40), of 1915 (oil on canvas, measuring 63 cm x 42 cm.).

Not only is it most unusual to be able to have access to a work as important as *Bottle and Glass* [No. 86] and to be able to carry out an analytical study of it, we were also able to compare our findings with those of an oil on canvas by Popova of the previous year, 1914, *Articles From a Dyeworks* (see page 44), in the collection of the Museum of Modern Art, New York (there titled, *Objects in a Dyer's Shop*).

The Conservation Department of the Museum of Modern Art found the same pigments in *Articles From a Dyeworks* as we found in *Bottle and Glass*, although the New York painting has a wider range of pigments due to its greater variety of colours.

The presence of the same pigments in both paintings indicates that these pigments relate to Popova's basic palette in those years. This has enabled us to come to the conclusion that the work we present in this article must have been executed during the active period of the artist.

Our method of analysis of pigments is extremely important, for it is the non-destructive Raman technology.

The analysis made by using Raman spectroscopy requires no sort of extraction or any preparation of samples. This photonic technique is described in detail below, in II. "The Scientific Study of Artworks Using Laser Technology".

The pigments identified in Popova's *Bottle and Glass* are zinc white, chrome yellow, vermilion, ultramarine blue, and Prussian blue, plus charcoal black.

# The Scientific Study of Artworks Using Laser Technology

## Introduction

More than two decades have passed since the European Union came to the realisation that the study, conservation and protection of artistic heritage had to be tackled in an interdisciplinary way. That is to say, there should be a joint collaboration of all the public and private professional sectors of the arts and sciences, whose combined knowledge provides the greatest amount of objective information on the problems and issues that customarily appear in the art world.

Since 1994 the Optical Communications Group of the Polytechnic University of Catalonia (UPC) has investigated and worked with different museums on the services that the new photonic technologies can render to the non-invasive, or non-destructive, analysis of the pigments used in an art object. The two basic lines of research, both of them intimately related to the laser, are the non-destructive analysis of pigments with Raman spectroscopy and, secondly, the advantages provided by radiation with pulsed ultraviolet laser (UV) in the local micro-elimination of varnishes and spurious surface materials, especially in relation to easel painting. Other activities that are complementary to the above are infrared reflectography (IR) for the study of underlying preliminary drawings and photomicrography for visualising brushstrokes, craquelures and other details.

In 1973 John Asmus and an interdisciplinary team of professionals demonstrated in Venice that the optical pulses of an IR laser could eliminate the layers of dirt on the stone-based heritage of that city. They achieved more effective and less aggressive results than those obtained with conventional methods of abrasion and solvents. Two decades later, on the island of Crete, Costas Fotakis became a pioneer in the elimination of spurious materials adhering to Greek icons, and this without damaging their polychromy. On that occasion the pulsed laser employed was ultraviolet, which turned out to be ideal for eliminating old varnishes and their polymeric adhesions. Laser cleaning had been born. To sum up, if the pulsed IR laser is suitable for the elimination of stone surfaces, the pulsed UV laser is equally so for polychromed surfaces. These two processes are based on their respective thermal and non-thermal photoablation effects. With either the one or the other, scientists have also managed to clean stained-glass windows, maps, parchments, textile materials, ivory, watercolours and oil paintings. And all this through a controlled, precise procedure.

Our research group, ACTIO, Arte y Ciencia, K2M Project, North Campus, Polytechnic University of Catalonia (UPC), in Barcelona, is developing a new optical system that permits irradiation with pulsed ultraviolet laser and molecular analysis using Raman spectroscopy, thus minimising the acquisition time of pigment spectra. This is one of the fundamental innovatory projects of the new spin off created on the UPC's North Campus. In this way "ACTIO, Arte y Ciencia" will be able to offer complete analytic and artistic studies at a minimum cost to the end user. When it comes to contributing to the objective, non-invasive study of the great art collections, the die is cast.

## The Non-Invasive Molecular Analysis of Pigments: Raman Spectroscopy

As we've already observed, this methodology enables us to molecularly identify the essential materials that went into the making of the work of art (pigments, layers of priming and of preparation). This spectral identification is arrived at thanks to the Raman effect, discovered before the invention of the laser, and for which Chandrasekhara Venkata Raman (Trichinopoly, 1888 – Bangalore, 1970) received the Nobel Prize for Physics in 1930. In short, this effect is due to the property that matter has of emitting a "special" frequency of its own – namely, one characteristic of the molecules that go to form it – when illuminated by monochromatic radiation (laser). It remains something of a surprise that Raman demonstrated the effect that bears his name thirty years before the application of the first experimental laser!

Given that all pigments have a period of utilisation and in many instances a date of appearance to then fall into disuse, one understands the importance in having a global database that provides information not only about the Raman spectra of pigments used throughout history but also the key dates to do with the origin and processes of synthesis of those pigments. In short, if we analyse an artwork with Raman spectroscopy

Figure 1. Pigments.

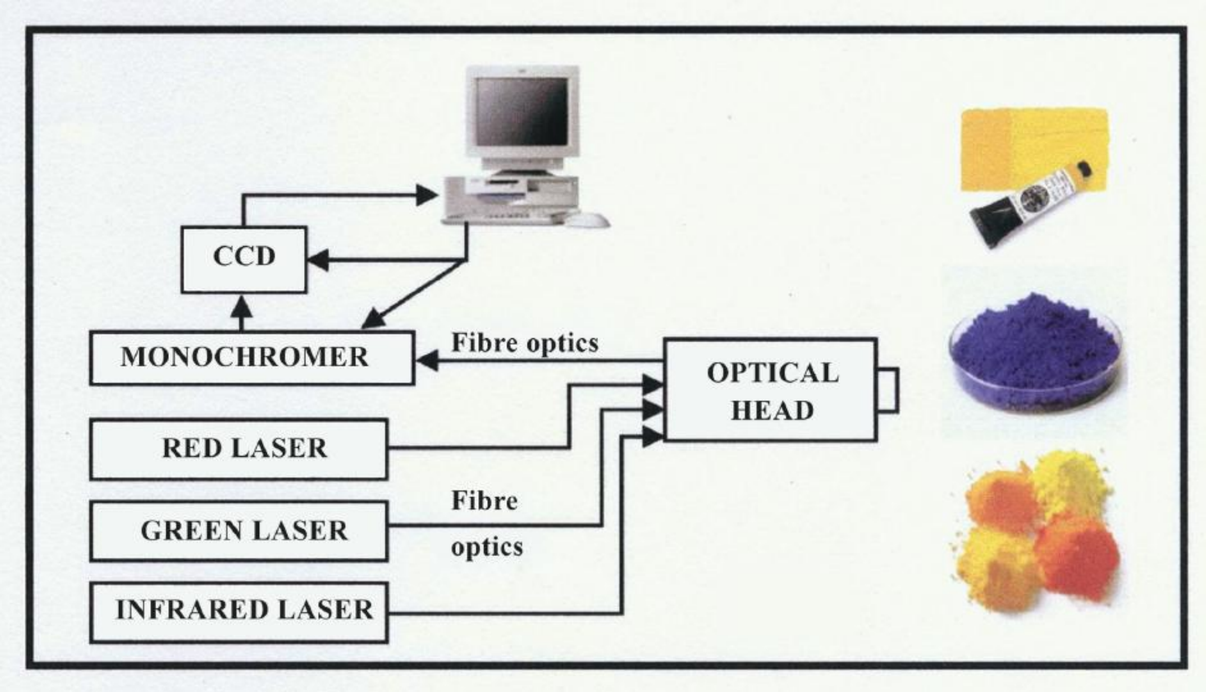


Figure 2. Raman set-up with optical fibre in non-destructive analysis of pigments.



we can ascertain the artist's palette and successfully discover not only his or her period and school, but also have basic qualitative information in order to be able to establish the possible authorship of the work.

## The Laboratory

We have an advanced laboratory at our disposal, in which over a period of fifteen years we have analysed the polychromy of many public and private patrimonial works, be they on a canvas, wood, metal, paper or ceramic support. The laboratory has three continuous lasers (infrared, red and green) for Raman spectroscopy and a pulsed laser (from UV to IR) for the microcleaning of spurious surfaces.

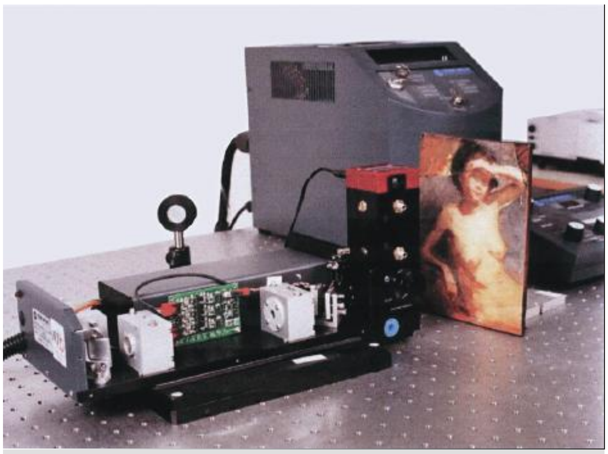

Figure 3. Polaris III.

In Figure 2 the diagram shows the units of the system used in the UPC for the analysis of the work. Broadly speaking, it functions as follows. It consists of three sources of monochromatic light (a HeNe laser at 632.8 nm, an Ar laser at 514.4 nm, and an IR semiconductor laser at 785 nm) whose emission is guided by the fibre-optic excitation system. The aim of the optical head is to focus this light on the area one wishes to analyse and to pick up the dispersed light (the Raman signal) through the fibre collector. This fibre guides the dispersed light to the monochromator, where it is spatially and spectrally separated. The CCD detector realises the conversion of optical intensity into electrical intensity, picks up the spectrum and remits the information to the computer, which also takes charge of controlling the remaining equipment.

The Raman system, movable and with fibre-optic technology, is from the Jobin Yvon (Horiba group, InduRAM model, Figure 2). For the optical cleaning we use a high-performance Polaris III system by New Wave Research that is flexible and extremely compact, Figure 3. As well as the infrared (1064 mn.), this equipment enables us to obtain the second, third and fourth harmonics; namely, wavelengths of 532, 355 and 266 nm, respectively. In this way we have pulsed laser radiation available in three qualitatively distinct registers: infrared, visible and ultraviolet. Thus, optical

Figure 4. The Laboratory.



cleaning, whether it be of stone surfaces with pulsed IR radiation or polychromed surfaces with pulsed UV radiation, can be carried out by this unique system.

Other, complementary equipment consists of a camera sensitive to IR radiation (Lambda Scientifics) which reveals the possible under drawing and even eventual signatures and changes; a Leica MZ-12 stereomicroscope with a photomicrographic resolution of 600 magnifications; and lastly, a Sony (Videoprint) system digitally visualises all the information.

## An Experimental Example and Conclusion

In view of the above, it is obvious that science can and must play an important part in the analysis and conservation of patrimonial works. Historically, the certifying of artworks has been carried out by people with more or less profound knowledge in the field of the history of art. It is undeniable that there is a great number of professionals with sufficient ability and experience to provide an opinion as to whether an artwork is or is not by a particular artist. But what is also necessary, and society is also becoming aware of this, is the objectivity, seriousness, precision and interdisciplinarity with which these studies must be carried out. And this, principally, is what the multidisciplinary group of professionals who make up "ACTIO, Arte y Ciencia" in the Polytechnic University of Catalonia's K2M Project seeks to offer society. There are quite a few cases in which works certified (a curious concept in art) and attributed to a given artist have then been studied scientifically and the pigments have been found to have been patented after the death of the supposed painter.

In Figure 5 we present, by way of example, an experiment done on a Flemish panel, about which we now know, thanks to the new technologies, not only the period in which it was painted, but also its authorship and date. In short, science applied to the analysis and conservation of artistic works is a fact that must not be overlooked. It is paradoxical that the term technology comes from the Greek word *techne*, which means, oddly enough, art.

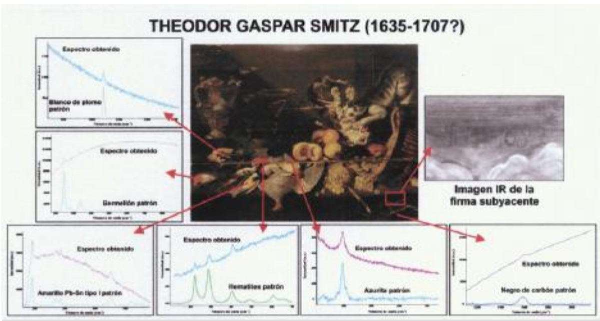


Figure 5.

# Raman Laser Spectroscopy Used for an Analytical Study of Pigments in Liubov Popova, *Bottle and Glass* [No. 86], 1915


## 1. Visible Photograph


## 2. Infrared Photograph

## Characteristics of the painting under analysis

- Medium: Oil on canvas
- Title: *Bottle and Glass* [No. 86]
- Dimensions: 63 cm x 42 cm.
- Signature: unsigned

## Index of the Study:

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2. Infrared photograph
3. Pigments identified with Raman spectroscopy
4. Conclusions
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## 3. Pigments Identified with Raman Spectroscopy

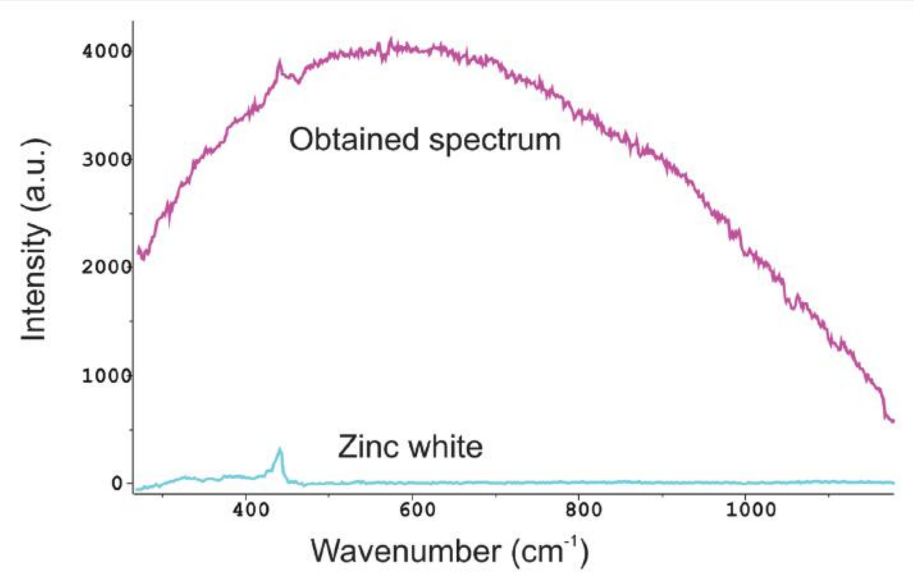
The pigments identified in this oil painting on canvas using Raman laser analysis and the original areas in which they have been identified (see Areas Analysed) are listed below and constitute the basic and original palette of this work.

- Zinc white (areas 1, 2, 3)
- Chrome yellow (areas 4, 5)
- Vermilion (areas 5, 6, 7, 8, 9)
- Ultramarine blue (areas 10, 11, 12, 13)
- Prussian blue (areas 13, 14, 15)
- Charcoal (areas 16, 17, 18)

Areas Analysed


## Zinc white (ZnO, zinc oxide)

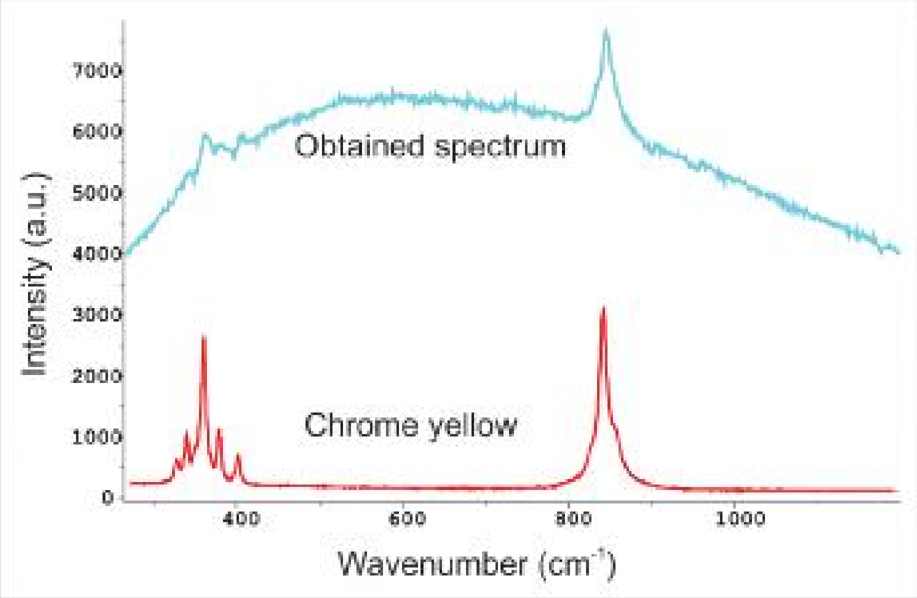
Zinc white was introduced as a watercolour pigment in 1834 but was not commercialised in oil paint form until 1844 by Le Claire (Paris). In 1845 its large-scale production began and five years later its manufacture got underway throughout Europe. It is still in use today, although with the introduction of the titanium whites (before 1920) its use declined greatly or else it was used along with these. Zinc white has certain advantages over lead white due to the fact that it does not darken from the sulphur in the air (or that contained in other pigments). Furthermore, it is not toxic and is less expensive than lead white (Ref. [1, 2]). Zinc white was one of the most commonly used white pigments by Russian Avant-Garde painters.




Intensity a.u. (arbitrary units)
Spectrum obtained
Zinc white model
Wavenumber (cm$^{-1}$)

## Chrome yellow ($PbCrO4$, lead chromate)

A rare mineral called crocoite exists which contains lead chromate, enabling the French scientist, Jean-Louis Vauqulin, to identify the mineral that he would call "chromium" in 1797. It could then be synthesized in the laboratory. In the early 19th century, deposits of the natural mineral, chromite, were discovered and this contributed significantly to the producton of the group of chrome pigments. Chrome yellow pigment was manufactured and commercialised for the first time around 1814, and was progressively introduced into painting (Ref. [1, 3, 6]). At the end of the 19th century artists noticed that chrome yellow tended to darken with age, the Impressionists, for example, turning to other yellow pigments such as cadmium yellow. Chrome yellow is often found in Russian Avant-Garde painting.

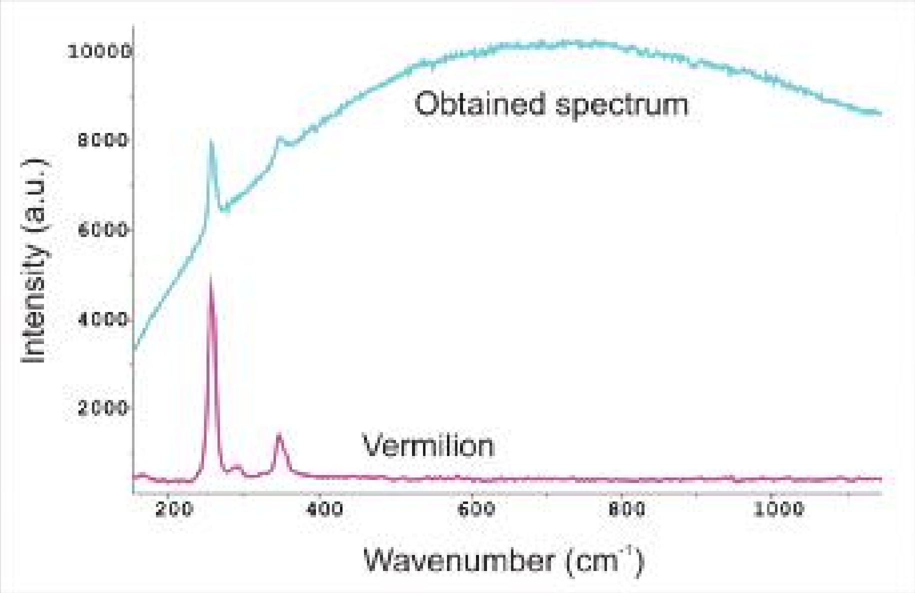



Intensity a.u. (arbitrary units)
Spectrum obtained
Zinc white model
Wavenumber ($cm^{-1}$)



## Vermilion ($HgS$, mercuric sulphide)

Vermilion, or mercuric sulphide, has existed as a mineral (cinnabar) pigment since antiquity. However, the synthetic version (which dates from the 8th century in European references) has been the one normally used in painting for many centuries. This pigment was utilised into the 20th century, when it was gradually replaced by the cadmium reds (commercialised in 1910) (Ref. [1, 2, 4]). Vermilion is a basic icon pigment so has been used for centuries in Russia. It was readily and cheaply available and is the standard red pigment found in Russian Avant-Garde painting.




Intensity a.u. (arbitrary units)
Spectrum obtained
Zinc white model
Wavenumber ($cm^{-1}$)

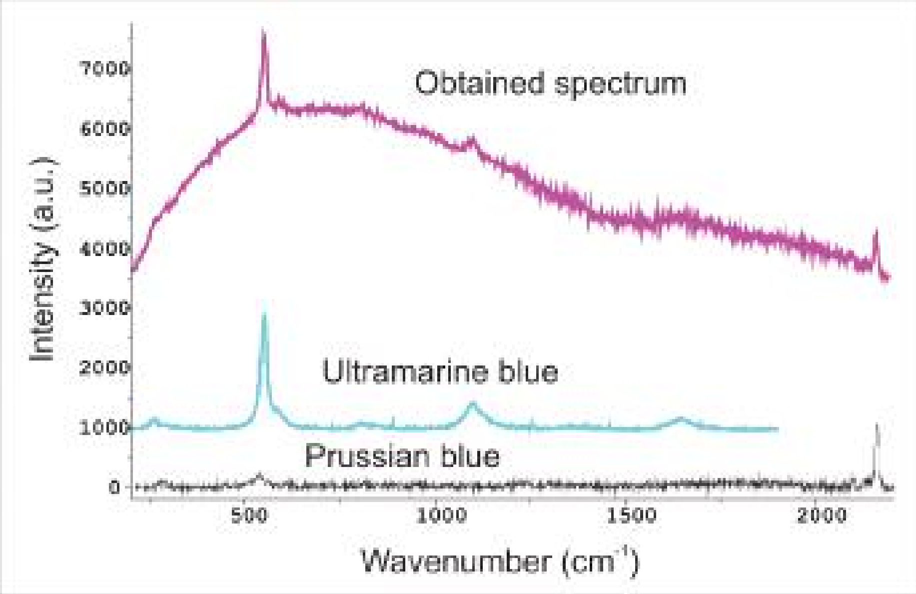
## Ultramarine blue [(Na10Al6Si6O4S2)x]

Jean Baptiste Guimet was the first to synthesise this pigment in France in 1828, and it became commercially available in 1830. It forms an alternative to the ancient and very costly pigment of lapis lazuli blue (Ref [1, 4]). It was a standard pigment used in Russian icon painting as well as in the palettes of Russian Avant-Garde painters. Ultramarine blue continues to be a widely used pigment.

## Prussian blue (ferric ferrocyanide)

This strong, deep blue pigment was discovered in 1704 by a pigment-maker in Berlin, Diesbach. By 1730 it was being used on an ever-increasing scale and it continues to be widespread still today (Ref. [4, 5]). It is commonly found in Russian Avant-Garde painting.

Intensity a.u. (arbitrary units)
Spectrum obtained
Ultramarine blue model
Prussian blue model
Wavenumber (cm$^{-1}$)

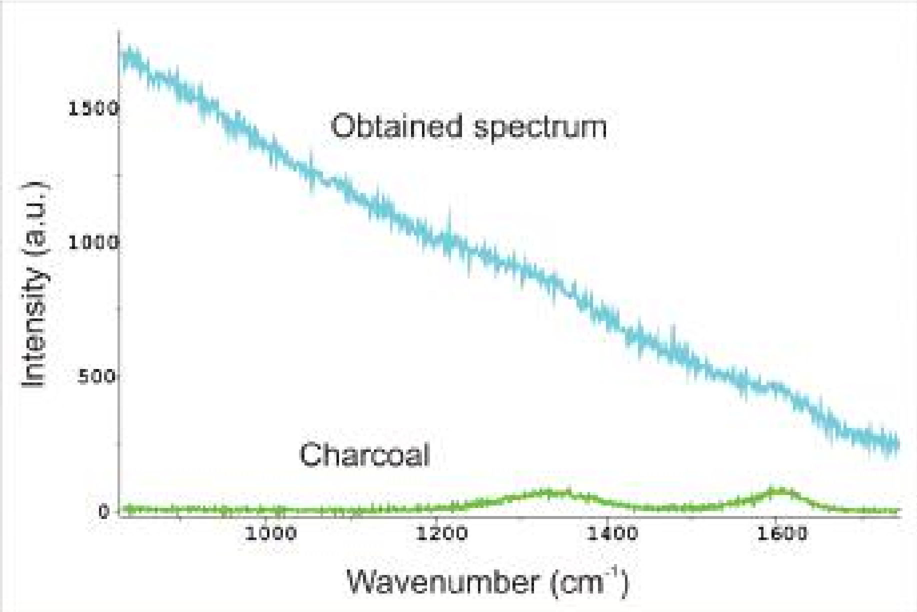





## Charcoal

This type of charcoal is obtained from the carbonisation of wood, mainly willow, beech and linden. It has been used as a pigment from the era of cave painting (Ref. [7]).

Intensity a.u.
Spectrum obtained
Charcoal model
Wavenumber (cm$^{-1}$)



## 4. Conclusions

The painting, *Bottle and Glass* [No. 86], presents schematic brushstrokes made with charcoal (see infrared photograph), typical of this kind of composition. Ultraviolet light captured some dark stains that suggest areas of repainting or retouching. The basic palette employed in the execution of this oil painting on canvas consists of the following pigments:

- Zinc white
- Chrome yellow
- Vermilion
- Ultramarine blue
- Prussian blue
- Charcoal

Both vermilion and charcoal are pigments that have been used in painting since time immemorial, and are still in use today. Vermilion remained the basic red pigment among the Russian Avant-Garde painters, perhaps because it was a standard icon pigment and so it was easily available.

As for chrome yellow, it began to be employed in a generalised way after 1814. Its use began to decline at the end of the 19th century in Europe due to its tendency to darken and because it is somewhat toxic, although it continued to be used in Russia well into the 20th century.

For its part, artificial ultramarine blue was synthesized for the first time in 1828, becoming available on the market two years later. Its use is still very widespread today.

As for Prussian blue, it was employed in painting after 1730, and is still extensively utilised at the present time.

Lastly, it is worth pointing out that pigments introduced in the early 20th century such as, for example, cadmium red (1910), the compounds of titanium white (c. 1920 or earlier) or the phthalocyanines (1936), were not found in this painting by Liubov Popova.

Taking into consideration the dates of use of the pigments identified in original areas of the painting, as well as the non-utilisation of other compounds from later periods, we can state that this is a palette typical of, and usual for, the period between 1844 and 1926 both in Russia and in Europe.

Moreover, it is worth highlighting the analyses of pigments carried out by the Conservation Department of the Museum of Modern Art in New York on works by the Russian artist, Liubov Popova (1889 – 1924), according to Ref. [8]. Set out below are the pigments identified in three oil paintings by this painter (with the pigments identified in the work we are dealing with underlined).

In the light of the table below, the coincidence is obvious between the palette utilised in the work under analysis and those analysed in the paintings by the Conservation Department in the New York museum.

L. Popova, *Objects from a Dyer's Shop*, 1914.

| Title of the works | *Objects From a Dyer's Shop* | *Painterly Architectonics* | *Painterly Architectonics* |
|---|---|---|---|
| Date | 1914 | 1917 | 1918 |
| White pigments | Lead white, zinc white, calcite & baryte | Zinc white, gypsum & baryte | Zinc white & calcite |
| Yellow pigments | Chrome yellow, zinc yellow & cadmium yellow | Chrome yellow & zinc yellow | |
| Red pigments | Vermilion, red lead, cadmium Red & iron oxides | Vermilion & red lead | Lead oxides |
| Blue pigments | Ultramarine blue | Ultramarine blue | Prussian blue |
| Green pigments | Chrome green | | Emerald green |
| Black pigments | Ivory black | Ivory black | Charcoal |

## 5. References

[1] **Max Doerner,** *Los materiales de pintura y su empleo en el arte*, Barcelona: Editorial Reverté, 1998. [*The Materials of the Artist and Their Use in Painting*. (E. Neuhaus, Trans.). London: Hart-Davis, 1969.]

[2] **Ashok Roy**, Editor, *Artists' Pigments: A Handbook of Their History and Characteristics*, Vol. 2. Washington, D.C.: National Gallery of Art, 1993, 1997.

[3] **Ralph Mayer**, *Materiales y técnicas del arte*, Madrid: Tursen Hermann Blume Ediciones, 1993. [*The Artist's Handbook of Materials & Techniques*. London: Faber and Faber, 1951, 1991.]

[4] **Nicholas Eastaugh** *et al.*, *Pigment Compendium: A Dictionary of Historical Pigments*, Oxford: Elsevier, 2004.

[5] **Ray Smith,** *El manual del artista*, Madrid: H. Blume Ediciones, 2003.

[6] **François Perego**, *Dictionnaire des matériaux du peintre*, Paris: Éd. Belin, 2005.

[7] **S. Pagès-Camara** *et al.*, "Study of Gustave Moreau's Black Drawings: Identification of the graphite materials by Raman microspectrometry and PIXE", *Journal of Raman Spectroscopy*, 35, 2004.

[8] **Magdalena Dabrowski** et al., *Liubov Popova*, Ministerio de Cultura, Museo Nacional Centro de Arte Reina Sofía, Madrid, 1991 & Prestel Verlag, Munich, 1991. [The Museum of Modern Art, New York, 1991.]

This article was translated from the Spanish by Paul Hammond.

Dr. Ruiz-Moreno and Dr. López-Gil Serra have published their studies in the following journals:

- Journal of Raman Spectroscopy
- Studies in Conservation
- Journal of Cultural Heritage
- Applied Spectroscopy