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Spectral and Chromatic Analysis in Art Work Authentication

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Spectral and Chromatic Analysis in Art Work Authentication

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The authorship assessment of art works represents one of the most complex and delicate problems, particularly for the art works created during the second half of the XIXth century and the begining of the XXth century, when the falsification industry had unprecedented proportions. In this context, the determination of the authorship of art works should start with the technical and stylistical analysis and has to be completed by physico-chemical analysis in order to answer on a scientific basis to various aspects related to the technique used by the artist, composition of pigments, or the impact caused by environmental and incidental factors on the degradation state of art issues. This article aims at demonstrating the authorship of two paintings attributed to Victor Brauner, considered at present one of the greatest artists of the XXth century. In order to assure a scientific approach of these art works and for a better understanding of the correlation between the chromatics of paintings and the composition of pictorial materials, a data base has been created, consisting in a number of 29 pigments covering the main groups of monochromatic colors, which individual or in a mixture can lead to the wide palette of nuances used in paintings. This collection has been completed by other 4 pigments dated in 1920 period when these drawings have been created. The techniques used for physico-chemical analysis of standard pigments and of the samples taken from the works were: UV-VIS-NIR spectroscopy in diffuse reflectance mode, FT-IR spectroscopy, elemental analysis and chromatic analysis in CIE – $L^*a^*b^*$ system. By corroborating spectral and chromatic analysis of samples with elemental analysis of metals in the signature, the authorship of two of Victor Brauner paintings has been certified.

Keywords: artwork authentication; chromatic analysis; drawing pigments; technical and stylistical analysis

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INTRODUCTION

The determination of authorship of art works represents one of the most complex and delicate research problems in the field of cultural heritage. Even high-class specialists with well-established expertise in research of art works can arrive on various ways to the interpretation of a pictorial image, and as a result, can contribute to a confused atmosphere around the authorship of an art work [1]. A high degree of difficulty related to hystoriography and authentication exhibit mainly the art works created during the second half of the *XIX*th century and the first decades of the *XX*th century, when the falsification industry had unprecedented proportions. Many faked drawings or very accurate painting copies provided by diverse private or estate collections represent a valuable documentary material particularly useful for detection of misleading ways practised by falsifiers. This is the main reason for which a detailed analysis is needed in supporting the authenticity certification. In this respect, the authorship determination should start with the technical and stylistic analysis by means of archive documents, iconography, in tight connection with life and creation of artist within the family environment and his further evolution in national and international context. Moreover, there is a need to know and document the changes produced on the work by natural accidents, or those due to the change in esthetic disposition of the author or the restorer interventions.

On the other hand, in order to take a reasonable decision the art specialist should take also advantage of the facilities and complementary data offered by physico-chemical analyses, thus being able to answer on a scientific basis to many aspects related to the techniques used by the artists, materials used, composition of the pigments, or the impact of various environmental and incidental factors on the degradation state of art issues [2].

The Art Museum of Tulcea town, Romania hosts a collection of works, among them being a number of 9 paintings attributed to Victor Brauner, considered at present one of the greatest artists of the *XX*th century. These drawings belong to the beginning creative period of the artist, before 1930, when Brauner left Romania and was established in Paris [3–5].

All these works have been donated by members of his family during the period 1981–1989, but not all of them are clearly dated, officially registered or signed by the artist.

By corroborating the conclusions obtained by stylistic and hystoriographic methods with the experimental results of instrumental analyses, this article aims to demonstrate the authorship of two of Brauner

paintings, "The Tower of Antim Church" and "Balcic," works over which there are uncertainties on their authenticity.

Such rigorous data referring to the knowledge of the initial period of his artistic activity are of utmost importance for a deeper understanding of further evolutions in the life and creation of Victor Brauner.

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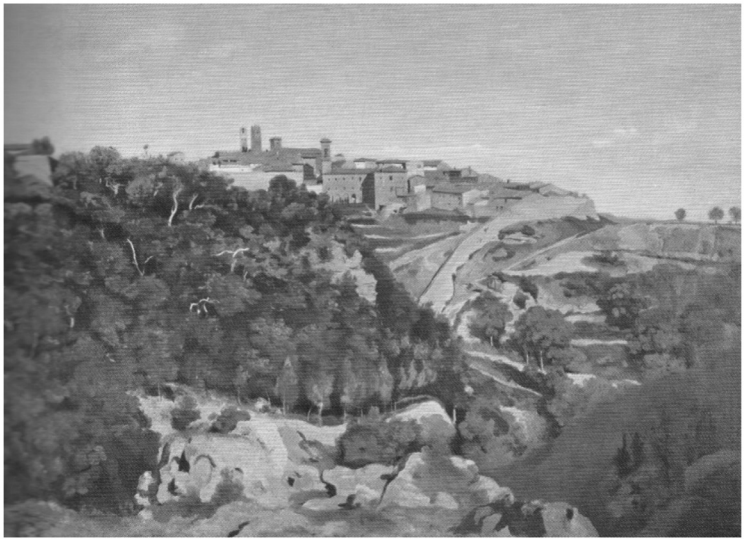
(a)



(b)

FIGURE 1 Comparison of art works: a) Victor Brauner, *Balcic*, 1919–1920, b) Camille Corot, *Volterra*, 1834.

Referring to the work entitled "Balcic" (Fig. 1a), dated at 1919–1920, its name is derived from a little town located near Black Sea in South of Romania, now belonging to Bulgaria. This town has a special significance, since what represented Barbizon for French painters, Balcic represented for Romanian artists. Overwhelmed by those beautiful sites and their special light, many colonies of artists used to come there, to paint "in plain-air".

At that time, Brauner was 16 year old and he was already under the influence of French school reprezented by Cézanne and Corot (Fig. 1b).

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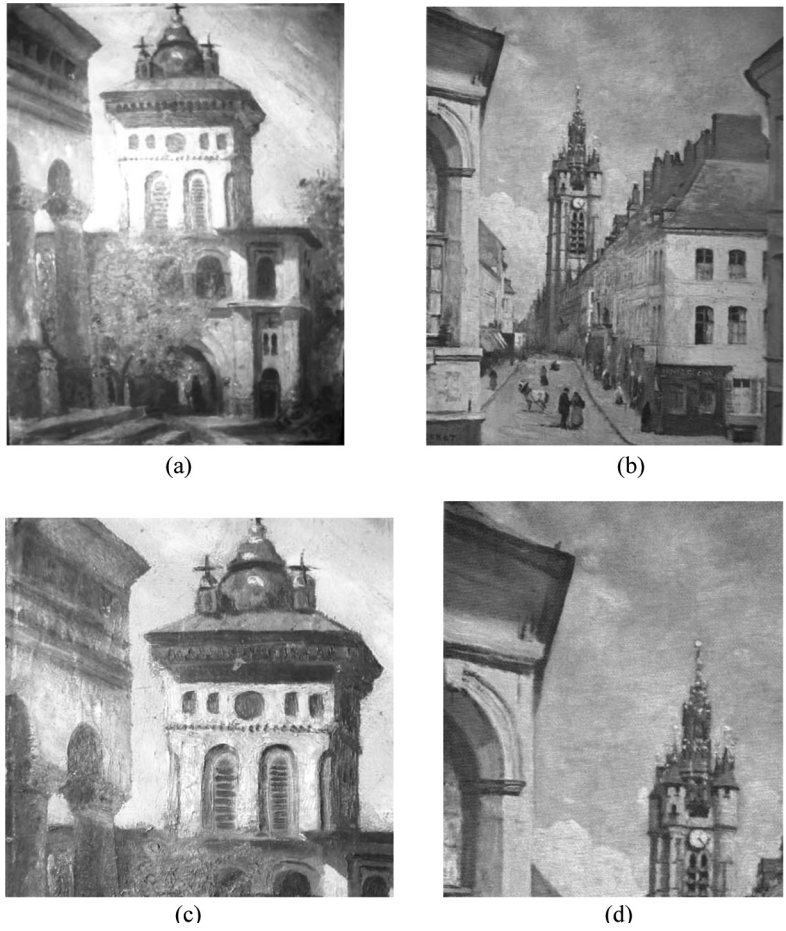

FIGURE 2 Comparison of art works: a) Victor Brauner *Tower of Antim Church* 1919, b) Jean-Baptiste Camille Corot *Le Beffroi de Douai,* c) 1871 Tower of Antim Church 1919 (detail), d) *Le Beffroi de Douai* 1871 (detail).

[6,7] This affinity is also revealed in the "Tower of Antim Church" (Figs. 2a, c) which remind us of Corot works (Figs. 2b, d). Both of these works have been painted during the same period and provide evident proofs on his outstanding intelligence and strong cultural background since that early age, but also the huge talent and artistical intuition with which Brauner was endowed [8,9].

EXPERIMENTAL

Materials

In order to assure a scientific approach of these art works and also for a better understanding of the correlation between the chromatics of paintings and the composition of pictorial materials, firstly it was necessary to study the main types of pigments used at the beginning of the *XX*th century, in comparison with those existent at present.

In this respect, a data base consisting in a number of cca 30 pigments has been created, by covering the main groups of monochromatic colors, which individual or in a mixture can lead to the wide palette of nuances used in drawings. In the Table 1 the list of pigments used as standards is presented, together with their probable chemical composition, the main characteristics of their electronic spectra and the chromophors responsible for the color.

This collection has been completed by a few number of pigments used during 1920 period (Table 2). Particularly useful was the paper of Louisa Gomez [10] which provided valuable information on the composition and chemical structure of various classes of pigments, these data being completed by adequate investigation techniques as it will be illustrated later.

As for most of pigments the composition assigned is of dominant mineral constitution, the elemental analysis for some of these pigments is presented in the Table 3, these data being very useful in supporting or confirming their chemical formula.

Sampling

The sampling has been performed according to the regulation procedures stipulated in the field of art work investigation [11]. This assumed to take samples from the parts of the paintings (usually on the margins) without causing significant damages on the original work. Thus, a number of four samples have been taken from the "Tower of Antim Church" and two samples from "Balcic" (Figs. 3a, b) all of them being various tones of green or violet colors. The procedure of sampling is illustrated in the Figure 4.

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TABLE 1 Characteristics of UV-VIS-NIR Spectra and Chromophor Assessment for Standard Pigments

	Pigments				
No.	Color	Probable formula	λ, nm	Chromophor	Assignment
1	Zinc white	ZnO	270–300, 1450, 1920	Diluter	Charge transfer (CT) harmonics vSO_4
2	Burnt sienna	$Fe_2O_3 + MnO_2 +$ natural earth	340–520	Mn^{4+}, Fe^{3+}	Defects, CT d-d
3	Natural sienna	$Fe_2O_3 \cdot H_2O +$ natural earth	320–500	Fe^{3+}	Defects, CT d-d
4	Terra Pozzuoli	$Fe_2O_3 \cdot H_2O +$ natural earth	440, 652	Fe^{3+}	Defects, CT d-d
5	Van Dyck brown	Hidroxisilicat de Fe, Mg, Al, K	380–800	Fe^{3+}	Defects, CT d-d
6	Massicot (yellow)	PbO	350–420, 510 u	Pb^{2+}	CT Me-O
7	Zinc yellow	$4ZnO \cdot CrO_3$	350–450	Cr^{6+}	CT
8	Permanent yellow	$BaCrO_4 +$ natural earth	250, 340–400–510	Cr^{6+}	CT Me-O
9	Chrome yellow	Pb CrO_4	350–420	Cr^{6+}	CT
10	Yellow ochres	$Fe(OH)_3 +$ natural earth $+ CaSO_4$	350–420, 510 u, 658, 750 s, 1440, 1920	Fe^{3+}	Defects, CT d-d vSO_4
11	Cadmium orange	CdS (Se)	350–500	Cd^{2+}	CT
12	Cadmium red	CdS (Se)	324, 440–542	Cd^{2+}	CT
13	Miniu Pb (red)	Pb_3O_4	350–400–494–550	Pb^{2+},/Pb^{3+}	CT Pb^{2+},/Pb^{3+}
14	Red iron oxides (Fe_2O_3)	Fe_2O_3	350–400–550, 870	Fe^{3+}	CT Me-O d-d
15	English red	$Fe_2O_3/BaSO_4$	288, 400–508–550 872, 1446, 1920	Fe^{3+}	CT Me-O d-d

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16	Vermilion	$HgS/BaSO_4$	292,440–525, 1446, 1926	Hg^{2+}	CT Me-S harmonics vSO_4
17	Permanent red	$HgS/BaSO_4$ (different proportion compared to vermillon)	290, 420–560, 1446, 1926	Hg^{2+}	CT Me-S harmonics vSO_4
18	Garancine lac	Alizarin ($C_{20}H_{14}O_{11}$) + Purpurin	290, 450–560	Organic	π-π^*
19	Permanent violet	$(NH_4)_2\ Mn_2\ (P_20_7)_2$ + alizarin	450–550 ,870	Mn^{2+}	CT d-d
20	Ultramarine blue	$Na_{6\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$	350, 50–660–750	Al-Si lattice	Defects
21	Cerulean blue	$CoO \cdot nSnO_2$ + ultramarine	590–640	Co^{2+} Al-Si lattice	Defects CT d-d
22	Prussian blue	$Fe_4[Fe(CN)_6]_3 + Cr_2O_2$	300–820, 850–900	Fe^{2+} Fe^{3+}	Fe-CN Fe^{2+}-Fe^{3+}
23	Cobalt blue	$CoO \cdot Al_2O_3$	260, 550–650, 870–900	Co^{2+}	d-d tetrahedral
24	Emerald green (veronesse)	Sn, Fe, Ca Alumino-silicate	280, 440, 420 metamerism, 640	Al-Si lattice	Defects
25	Green natural	$Cr_2O_3 \cdot SnO_2$	280, 350, 420	Cr^{3+}	CT Cr-Sn d-d
26	Chrome oxide green	Cr_2O_3 anhydrous	380, 480–640	Cr^{3+}	CT d-d
27	Zinc green light	$Cr_2O_3 \cdot nZnO$	360–450, 600–700	Cr^{3+}	CT d-d
28	Zinc green deep	$Cr_2O_3 \cdot nZnO$	380–470, 600–750	Cr^{3+}	CT d-d
29	Ivory black	99% amorf carbon	350–750	Calcined mineral	

TABLE 2 Chromatic Characteristics of Pigments of 1920 Collection

No.	Pigments 1920	λ, nm	L^*	a^*	b^*	C^*	H
1	Burn umber HS	340–850	54.70	−0.12	0.74	0.69	92.32
2	Garancine lac TR	320, 500–560	77.91	9.89	0.82	9.93	4.76
3	Violet lac S	320, 500–630	37.85	6.02	−5.20	7.95	−40.82
4	Sap green (Jugo green) S	400–450, 700–800	48.42	−11.98	17.59	21.28	124.27

TR – *Talens Rembrandt*, Olanda.
HS – *H. Schmincke & CO*, Düsseldorf, Germania.
S – *Schmidt*, Düsseldorf, Kreuzstr. 60, Germania.

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Equipment

- Jasco UV-Vis spectrometer, model V-570 with 200–2500 nm range and a diffuse reflectance system; CIE – $L^*a^*b^*$ JASCO software
- Jasco FT-IR 620 spectrometer with 4000–400 cm^{-1} range;
- AAS 6 (Analytik Jena) instrument with flame ionization. For AAS sample preparation the wet digestion has been used. The samples weighted have been treated with hot nitric acid 65% (Merck) and hydrogen peroxide 30% (Merck). The solution was filtered off and quantitatively decant to a 25 mL flask.

RESULTS AND DISCUSSION

Spectral and Chromatic Analysis of Standard Pigments

The color of mineral pigments appears as a result of selective absorption of some light radiations in visible domain (350–750 nm).

As can be seen from the Table 1, for mineral pigments most of the chromophors are transition ions with incomplete 3d or 4f electronic shells. They exhibit some specific absorption bands in UV-VIS and NIR domains due to their characteristic d-d and/or charge transfer transitions [12].

In this respect, zinc ion, even though it is transitional, having a complete electronic shell configuration ($3d^{10}$) it has no d-d transitions, but only one charge transfer transition located in UV region. This is the reason why ZnO is used as white color or as a diluter for other dyes. Other ions like: Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+} belonging to chromophoric properties, and as a result, they act also like diluters.

The ions in fundamental state of singlet with half-occupied electronic shell ($3d^5$) as in the case of Mn^{2+} and Fe^{3+} species provide

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TABLE 3 Elemental Analysis (%) for Standard Pigments

Pigment	Pb	Zn	Si	Mg	Fe	Cu	Al	P	Sn	Ti	Cr	Mn	Ni	Sb	Na	Ca	Co	K	S	C	Ba	As	Hg
Burnt sienna	0.07	0.04	**zp**	**0.96**	**zp**	0.07	**0.89**	0.53	≅0	0.08	0.01	**5.88**	0.03	0.01	0.22	0.29	0.02	0.13	–	–	0.22	≅0	≅0
Yellow ochre	0.03	0.11	**0.79**	**0.85**	**zp**	0.01	0.28	0.01	≅0	0.02	0.01	0.01	0.01	0.01	0.13	**18.1**	0.01	0.06	–	–	0.01	≅0	≅0
Miniu Pb	zp	0.01	0.03	0.02	0.01	0.01	0.02	0.01	0.01	≅0	0.01	≅0	≅0	0.01	0.14	0.05	0.01	0.02	–	–	0.01	≅0	≅0
Red iron oxides	0.11	0.02	0.15	0.08	**zp**	0.01	0.02	0.01	≅0	1.46	0.03	0.02	0.02	0.02	0.14	0.15	0.01	0.04	–	–	0.04	≅0	≅0
English red	0.03	0.01	0.12	0.01	**zp**	0.01	0.02	0.01	≅0	≅0	0.04	≅0	≅0	≅0	0.35	0.06	0.01	0.03	–	–	**zp**	≅0	≅0
Vermilion	0.50	0.01	0.08	0.03	0.03	0.01	0.04	0.01	≅0	≅0	0.01	≅0	≅0	0.01	0.36	0.27	0.01	0.05	**2.94**	–	**zp**	≅0	**4.37**
Ultramarine	0.08	**1.51**	**1.61**	0.26	0.61	0.66	**3.29**	0.02	0.01	0.06	0.02	0.01	0.01	0.05	**4.34**	0.61	**0.12**	0.51	**6.30**	**9.21**	**zp**	≅0	≅0
Cerulean	**1.38**	**5.65**	0.07	0.04	0.22	0.35	0.01	0.01	0.01	0.01	0.05	0.01	0.02	0.05	0.29	0.59	**0.39**	0.04	**10.8**	**8.16**	**zp**	≅0	≅0
Prussian blue	0.05	0.05	0.03	0.10	**zp**	0.03	0.01	0.10	≅0	0.21	**zp**	0.06	0.01	0.02	**1.47**	0.12	0.02	0.12	–	–	0.25	≅0	≅0
Emerald	0.04	0.05	**zp**	**1.36**	**zp**	0.11	**1.40**	0.15	≅0	0.51	0.18	0.03	0.07	≅0	0.23	**5.01**	0.01	0.14	–	–	0.01	≅0	≅0
Green natural	≅0	0.35	0.14	0.90	0.06	0.02	0.58	≅0	**zp**	0.01	**zp**	≅0	≅0	0.10	0.38	0.16	0.01	0.04	–	–	0.03	≅0	≅0
Chrome green	0.01	0.05	0.17	**15.3**	0.02	0.01	0.03	0.02	0.01	0.01	**zp**	0.01	0.05	0.09	0.25	0.05	≅0	0.02	**4.01**	**5.18**	0.48	≅0	≅0

zp signifies values higher than **10**%.

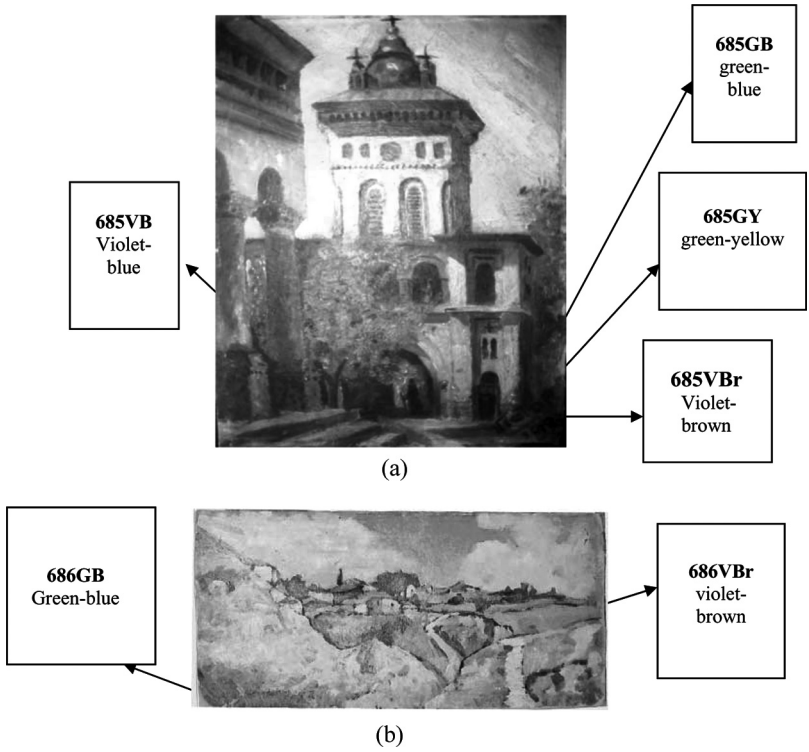

FIGURE 3 Sampling sites: a) "Tower of Antim Church," b) "Balcic".

d-d transitions of rather low intensity and displaced towards NIR domain, this conferring a quite slight coloristic power. In order to enhance the color of such compounds a dominant contribution brings about the charge transfer (CT) transitions metal-ligand or metal-metal

FIGURE 4 Sampling procedure: a) "violet–blue," Tower of Antim Church," b) violet–brown, c) green–blue, "Balcic".

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with variable valence. There are many examples of pigments based on charge transfer transitions: CdS(Se) – red, PbO (massicot) – yellow, HgS (cinnabar) – red, CoO – blue, Cr_2O_3 – green, MnO_2 – brown, MnO_4^- – violet, CrO_4^- – yellow, etc. Charge transfer transitions involving metals of variable valence are found in Pb_3O_4 (minium) – red, Fe_3O_4 – red etc.

Another way to provide color is the creation or existence of some lattice defects, as is the case of most natural alumino-silicates used as pigments: ultramarine, emerald green, Van Dyck brown, etc.

For the production of high quality pigments there are various ways to create a stable crystalline structure by including the chromophor ions into a specific stereochemical configuration assured by a spatial symmetry of the coordination polyhedron. A special effect for intensifying the color based on transition ions as chromophores is produced by the enhancement of crystalline electric field interactions provided by ligands like NH_3, CN^- etc. Well known examples are Prussian blue – $Fe_4[Fe(CN)_6]_3$ or $[Cu(NH_3)_4]Cl_2$, $K_3[Cr(NCS)_6]$ etc.

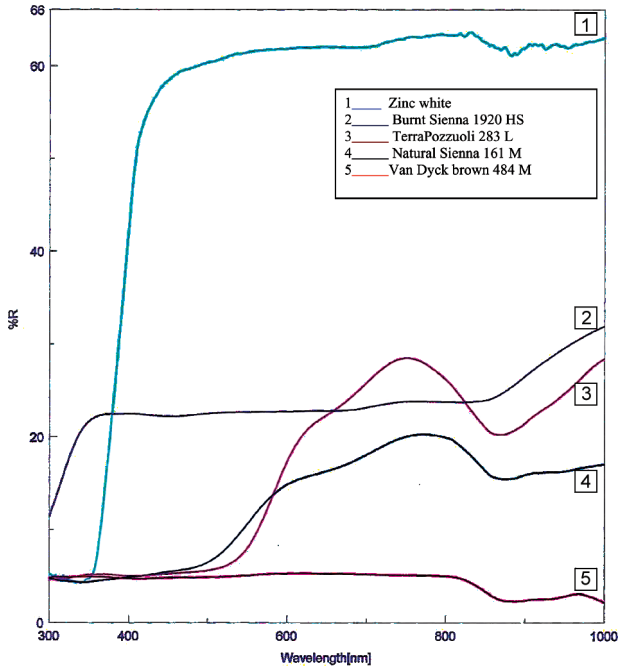

FIGURE 5 Comparison of electronic spectra for brown pigments.

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For the representative pigments used in this study the chromatic characteristics are revealed by means of their electron spectra recorded in diffuse reflectance mode, and grouped on specific colors in the Figures 5–9. Even though relevance for chromatic analysis has only the visible domain (350–750 nm), the registration of spectra also in NIR domain (750–2500 nm) provides complementary information on the nature of some transition ions (d-d transitions) present into the mineral pigments. Moreover, in case of the art work samples this domain can evidence some interferences with harmonic or combination IR bands specific to cellulose materials existent in the composition of drawing support or that of the blank used during spectral registration.

The interpretation of pigment color based on electronic spectra in UV-VIS-NIR domain in relation to the chromophor nature was performed in tight connection with vibrational transitions of functional groups noticed in IR spectra and also with data of elemental analysis from Table 3.

In Figure 5 the spectra of four brown pigments are presented. The brown shade is specific for an intensive and continuous absorption on

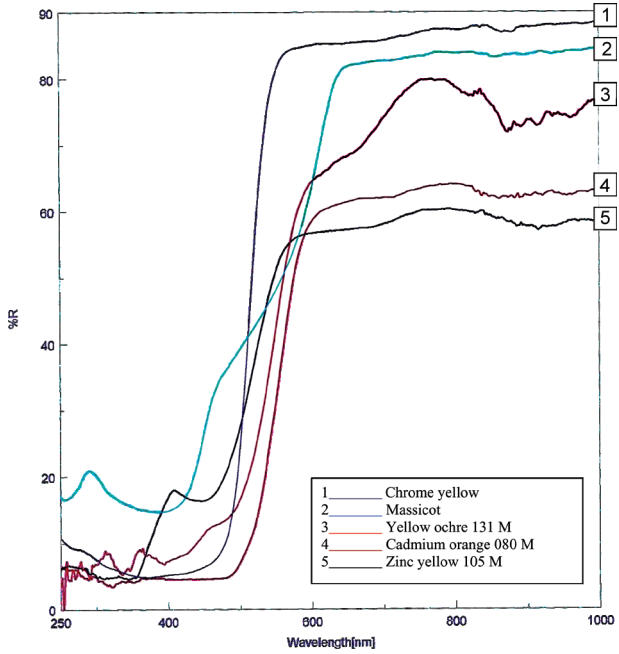

FIGURE 6 Comparison of electronic spectra of yellow pigments.

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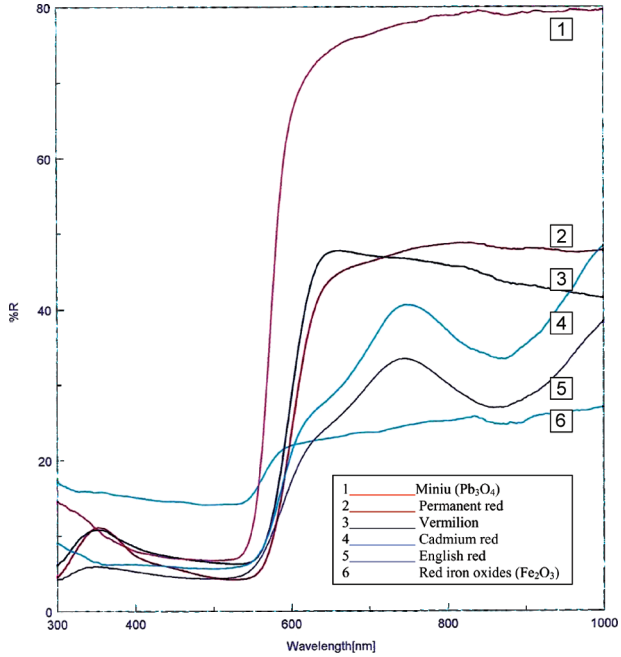

FIGURE 7 Comparison of electronic spectra of red pigments.

the left half of the visible domain (350–600 nm), two of them having continuous absorption extended also in NIR domain. By comparison, the white zinc has only the charge transfer transition band bellow 350 nm, being completely transparent on the entire visible and NIR domains.

The other groups of pigments exhibit maximum absorption bands centered at 350–400 nm for yellow–orange (Fig. 6), 450–500 nm for red tones (Fig. 7), 550–600 nm for violet, 600–650 nm for blue (Fig. 8) and finally 650–750 nm for green color (Fig. 9). Referring to these last pigments, all of them contain as major chromophore component the chromium oxide, and the commercial name of two pigments as zinc green light and, respectively, dark is improper as zinc oxide was only diluter in various extent.

In Figures 10–13 the pigments from collections 1920 period are compared with corresponding contemporary pigments. The spectrum for the brown pigment 1920 (Fig. 10) is similar to that of Van Dyck brown, with a constant absorption between 300–850 nm, but it is situated at a lower intensity, this corresponding to a relative lighter nuance.

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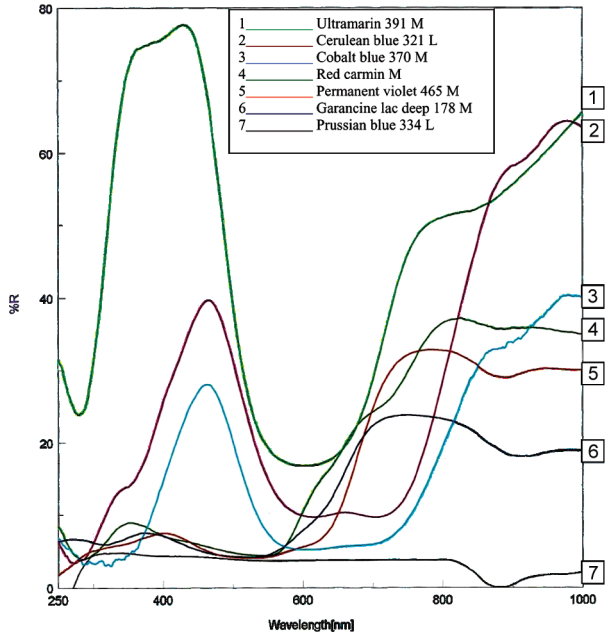

FIGURE 8 Comparison of electronic spectra of red-violet, violet and blue pigments.

The spectrum of garancine lac 1920 shows similar absorption bands to nowadays pigments, Maimeri 178 and Talens (Fig. 11), but once again the pigment 1920 is much lower in intensity, this feature being probably the effect of degradation in time. The same effect but in a lower extent can be also observed for violet 1920 (Fig. 12).

A different behavior was observed in the case of green pigments (Fig. 13). While the two contemporary pigments, zinc light green (Lukas 375) and zinc dark green (Lukas 379) reveal a dominant band centered at 400 nm (yellow region) and another band centered at 600 nm (blue), with a shoulder at 700 nm, the pigment Sap green 1920 has a dominant absorption band in the green region, at 650–800 nm. This means that while nowadays are commonly used green pigments whose color is a methameric effect of a mixture of yellow and blue tones, at the beginning of the *XX*th century the green pigment has a direct color obtained from the mineral extract of buckthorn berries, containing chlorophyll as well.

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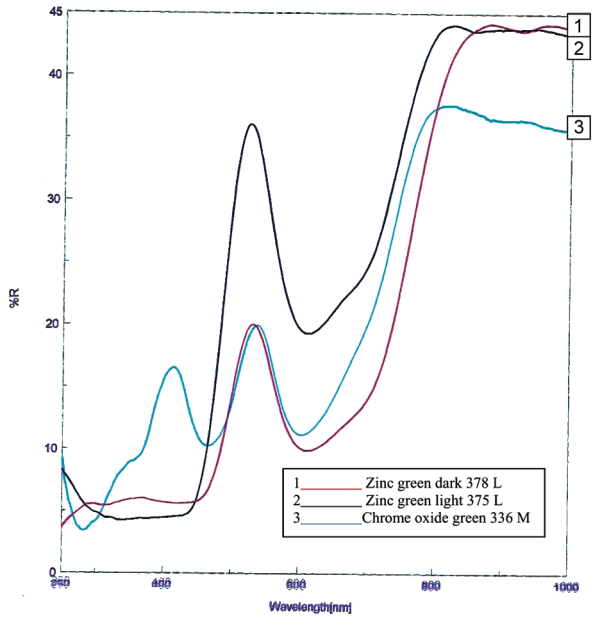

FIGURE 9 Comparison of electronic spectra of green pigments.

Analysis of Standard Pigments in CIE-L* a* b* chromatic space

The color of a sample can be objectively characterized for an observer and a definite source of light by means of one point uniquely located within trichromatic CIE–L*a*b*space [11], where:

L* – luminosity on vertical axis defines position on the light-dark axis,
a* – *x* coordinate in plan defines position on green–red axis,
b* – *y* coordinate in plan defines position on blue–yelow axis,
C* – chroma is the distance from chromatic point to L* axis,
H_{ab} – hue angle between a*and b* axes in horizontal plan.

Significant values for these chromatic parameters are:

L*: 0 – black, 100 – white, 50 – grey,
a*: positive values for red tones, negative values for green,
b*: positive values for yellow, negative values for blue,

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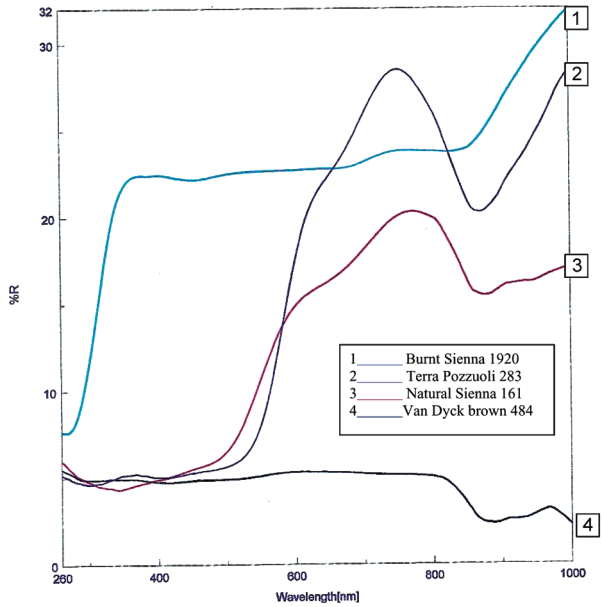

FIGURE 10 UV-VIS-NIR spectra for standard pigments, comparison 1920 and 2005 collections: 1 – Burnt sienna *H. Schmincke & CO* 1920, 2 – Terra Pozzuoli *Lukas 283,* 3 – Natural Sienna *Maimeri 161* 4 – Van Dyck brown *Maimeri 484.*

C^*: < 30 for white, black, grey, brown, usually for polychromatic colors, with electronic spectra quite continuous, at constant absorbance, > 30 – monochromatic colors are clearly distinct, electronic bands are intensive;

H_{ab}: 0–90 for the I^{st} quadrant red–yellow, 90–180 for the II^{nd} quadrant yellow–green, $-(90–180)$ for the III^{rd} quadrant green–blue, $-(0–90)$ for the IV^{th} quadrant blue–red.

For the standard pigments analyzed these chromatic characteristics are summarized in the Table 4. It can be seen that the maximum luminosity, $L^* = 82.53$ has been registered for zinc white as expected, while the minimum value is for ivory black. For all the other pigments the values $L^* > 50$ are obtained for light colors and $L^* < 50$ are for relatively dark colors. All the brown pigments (Table 4, No 2–5) are dark tones ($L^* < 50$) among them the darkest being van Dyck brown ($L^* = 27.8$) which has also the lowest chroma ($C^* = 1.51$). This value is in accordance with its electronic spectrum (Fig. 5) that shows a wide

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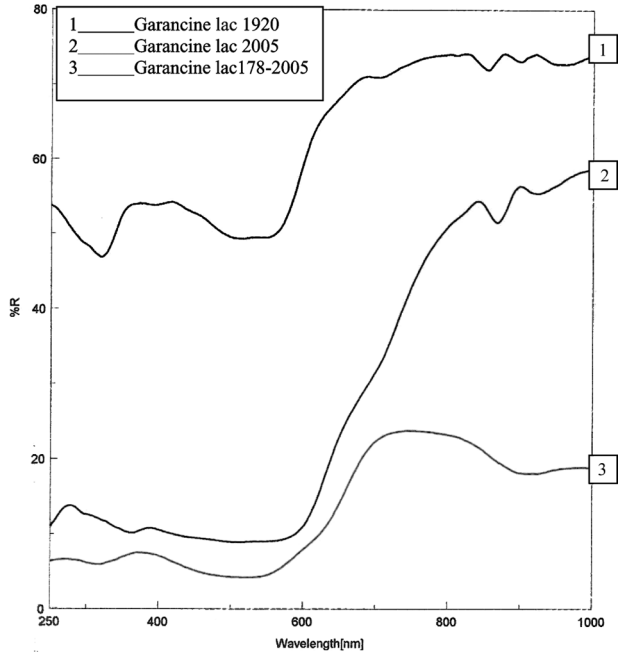

FIGURE 11 UV-VIS-NIR spectra for standard pigments, comparison 1920 and 2005 collections: 1 – Garancine lac *Talens Rembrandt 1920*, 2 – Garancine lac *Talens Rembrandt 2005*, 3 – Garancine lac *deep Maimeri 178–2005*.

plateau on the entire spectral domain. Being so close to luminosity axis (small chroma) its polychromatic composition is obvious. All these brown pigments are located into the first, positive quadrant (a^*, b^*), having as major contribution the specific chromophors for yellow ($+b^*$) and red ($+a^*$) colors. The proportion of these shades is expressed by the value of the hue angle, which is near 45° for Terra Pozzuoli, this meaning an equal contribution of yellow and red colors. For the other three brown pigments $H_{ab} \in 67–70$, this value indicating the dominance of red component. The pigment brown from 1920 collection, burn umbert HS (Table 2, No 1) is similar to van Dyck brown (Fig. 10), this being also polychromatic with a small chroma (0.69) but a higher luminosity (54.70), thus having a lighter nuance, while the high value of hue angle ($H_{ab} = 92.32$) also indicates the dominance of red color.

For yellow pigments (Table 1, No 6–11) the highest luminosity values among colored pigments are observed ($L^* \in 66–87$) due to their relative lighter tones. For all of them the yellow tone is dominant over

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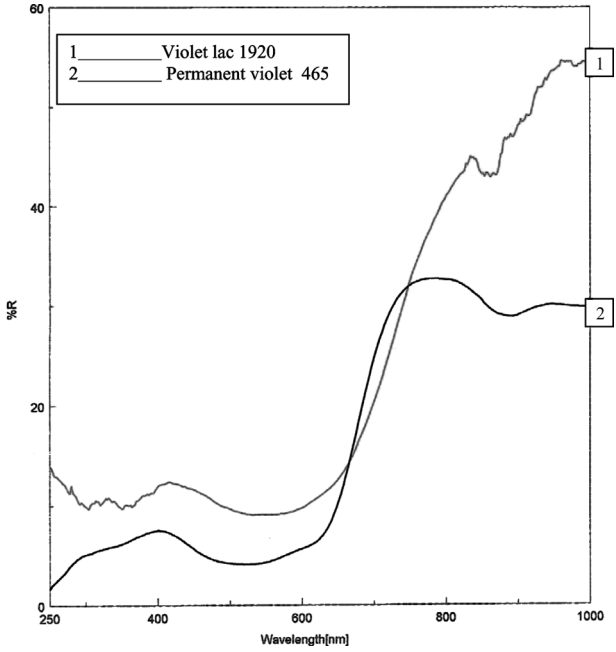

FIGURE 12 UV-VIS-NIR spectra for standard pigments, comparison 1920 and 2005 collections: 1 – Violet lac *Schmidt*, 1920, 2 – Permanent violet *Maimeri* 465, 2005.

the red component ($H_{ab} \in 64–89$), except for yellow ochre when the dominant yellow color is in a mixture with green: $a^* = -3.82$ and $H_{ab} = -87.53$.

In the case of red pigments (Table 1, No 12–18) it is reasonable for the red tone to be dominant over yellow component ($H_{ab} \in 10–35$) except for minium Pb that has almost equal proportions of red and yellow ($H_{ab} = 45.23$).

By comparing garancine lac (Table 1, No 18) with a similar pigment from 1920 collection (Table 2, No 2, Fig. 11) we can see that for the later all the chromatic parameters are lower than for the former pigment, except for luminosity which is much higher, $L^* = 77.91$, by comparing with $L^* = 28.99$. These data are in agreement to previous observation (section 2.1) on pigments belonging to 1920 collection, which have lighter tones comparatively to the pigments used at present.

For permanent violet pigment (Tabel 1, No 19) the red tone is dominant over the blue tone ($a^* = 11.66$, $b^* = -2.85$), which is quite different from violet lac 1920 (Table 2, No 3), where the two tones are almost

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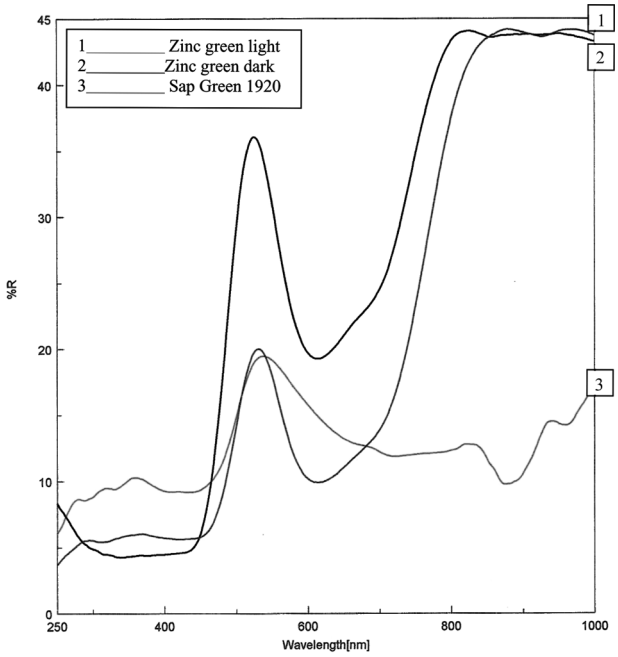

FIGURE 13 UV-VIS-NIR spectra for standard pigments, comparison 1920 and 2005 collections: 1 – Zinc green light *Lukas 375*, 2005, 2 – Zinc green dark *Lukas 375*, 2005, 3 – Sap Green, *Schmidt*, 1920.

in the same proportion ($H_{ab} = -40.82$), and once again the luminosity is higher (35.85 comparing to 13.75). These aspects are also confirmed by their electronic spectra presented in Figure 12.

The blue pigments (Table 1, Nos 20, 22, 23) have blue as dominant component ($b^* = -32$) with a small amount of red tone, except cerulean blue (Table 1, No 21) where the dominant blue is in a mixture with a small amount of green color ($a^* = -3.54$). This is confirmed by electronic spectra (Fig. 8, No 2) where this pigment has the most intensive absorption of blue band extended further to the green region (700–750 nm).

All the green pigments are located into the IInd quadrant ($-a^*$ – green, $+b^*$ – yellow) with the highest positive hue angles $H_{ab} \in (119–147)$, with yellow dominant component ($H_{ab} > 135$) like in the case of Cr_2O_3 green, or green dominant component ($H_{ab} < 135$) for the rest. The latest case is also observed for Sap green pigment from 1920 collection (Table 2, No 4) with the hue angle $H_{ab} = 124.27$. Moreover, in Figure 13 a higher absorption intensity in green region

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TABLE 4 Chromatic Characteristics CIE-L*a*b* of Standard Pigments

No.	Pigments	L*	a*	b*	C*	H
1	Zinc white	82.53	−0.70	−4.84	4.89	−98.23
2	Burnt sienna	38.83	7.29	19.78	21.08	69.77
3	Natural sienna	39.85	8.21	19.73	21.37	67.40
4	Terra Pozzuoli	39.10	19.94	19.74	28.06	44.71
5	Van Dyck brown	27.08	0.59	1.41	1.51	67.31
6	Massicot (yellow)	77.09	9.79	29.81	31.37	71.82
7	Zinc yellow	74.62	0.83	42.54	42.55	88.88
8	Permanent yellow	78.42	24.16	49.61	55.18	64.04
9	Chrome yellow	87.41	−3.82	88.56	88.60	−87.53
10	Yellow ochres	73.52	8.14	46.80	47.50	80.13
11	Cadmium orange	65.77	24.42	67.18	71.48	70.03
12	Cadmium red	48.84	9.63	6.84	11.77	35.38
13	Miniu Pb (red)	60.40	48.70	49.10	69.16	45.23
14	Red iron oxides (Fe_2O_3)	39.86	28.55	18.65	34.13	33.53
15	English red	36.67	27.42	19.37	33.57	35.24
16	Vermilion	44.39	41.05	21.34	46.27	27.46
17	Permanent red	40.08	43.54	20.43	48.09	25.14
18	Garanţa lake	28.99	16.09	3.12	16.39	10.99
19	Permanent violet	26.56	11.66	−2.85	12.01	−13.75
20	Ultramarine blue	38.67	4.34	−32.12	32.40	−82.30
21	Cerulean blue	47.92	−3.54	−32.38	32.57	−96.24
22	Prussian blue	22.81	1.03	−2.65	2.85	−68.69
23	Cobalt blue	36.77	2.02	−35.37	35.43	−86.73
24	Emerald green	68.56	−13.37	23.21	26.56	119.95
25	Green natural	46.79	−1.86	2.63	3.22	125.24
26	Chrome oxide green	46.20	−13.15	8.35	15.58	147.58
27	Zinc green light	58.97	−30.72	36.52	47.72	130.08
28	Zinc green deep	45.29	−23.43	22.99	32.83	135.54
29	Ivory black	36.88	1.02	1.77	2.04	60.14

L* = light (%); a* = red/green; b* = yellow/blue; C* = chroma; H = hue.
L – *Lukas Studio*, dr. Fr. Schoenfeld GMBH & CO, Düsseldorf, Germani.
M – *Maimeri Classico*, Itali.
TR – *Talens Rembrandt*, Holland.

(700–800 nm) for Sap green 1920 is registered by comparing with spectra of zinc green pigments.

Spectral and Chromatic Analysis of Victor Brauner Art Works

A similar study has been performed for samples taken from Victor Brauner paintings by analyzing the chromatic characteristics in tight connection with their electronic spectra.

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A comparison of chromophors used in the work "Tower of Antim Church" is illustrated in Figure 14, where two green samples of different tones, yelow and blue are registered on 250–2300 nm domain in comparison with the paper used as support. It can be noted the very reduced intensity absorbance for the paper, with a small maximum at 593 nm, corresponding to indigo blue nuance, which confers to human eye a shiny white sensation. It follows that in case of sample spectra, the band located at 600 nm is slightly amplified by the paper support that might be provided by the cellulosed material as support of registration and/or as the drawing support of art work. This supposition is confirmed by the bands appeared in NIR domain, at 1494, 1946, and 2100 nm, specific to hydrogen bonds and also to harmonic and combination of vibrational bands of OH groups. The two green colors are obtained by a methameric effect on mixing yellow and blue tones appeared in the spectra at 385 and 600 nm, respectively, to which a relative intensive absorption is added in the green region at 650–800 nm. The difference in tones between these two green samples is derived from the different intensities in these two bands. Therefore, in case of green–yellow sample the band at 385 nm is dominant (referring to its base line), while for green–blue the band

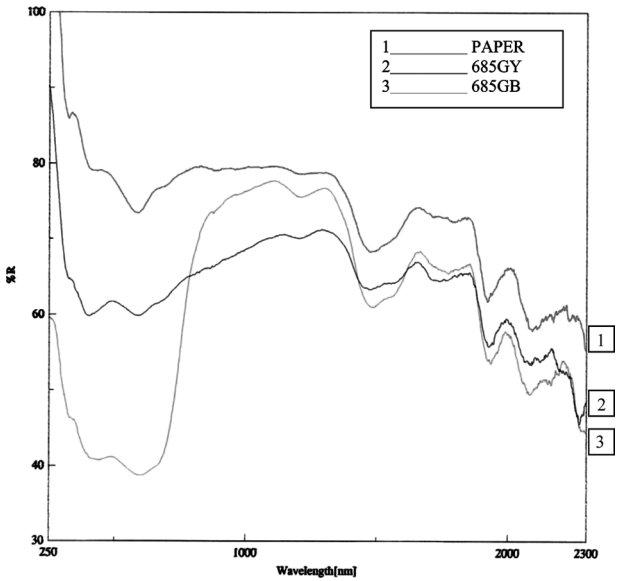

FIGURE 14 UV-VIS-NIR spectra for samples taken from Victor Brauner *Tower of Antim Church*: 1 – PAPER, 2 – 685GY-green–yellow, 3 – 685GB-green–blue.

TABLE 5 Chromatic Characteristics $L^*a^*b^*$ of Samples Taken From Victor Brauner Art Works

No.	Works	Samples	L^*	a^*	b^*	c^*	Hab	Color
1	*Tower of Antim Church*, 1920	685GB	81.24	−0.53	−0.19	0.56	−159.79	Green–blue
		685GY	80.87	−0.98	0.90	1.33	−42.35	Green–yellow
		685VB	40.39	2.63	−11.43	11.73	−57.83	Violet–blue
		685VBr	44.99	1.87	−7.58	7.80	−76.14	Violet–brown
2	*Balcic*, 1920	686BG	48.94	−0.53	−4.55	4.58	−96.58	Blue–green
		686VBr	80.61	0.42	−1.22	1.29	−71.0	Violet–brown

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on 600 nm is much more intensive and broadened towards green region, 700–800 nm. The chromatic characteristics in CIE–$L^* a^* b^*$ system of these samples, collected in the Table 5 confirm this mixing of tones. Thus, both of these samples exhibit negative values for a^* parameter (green), while for b^* parameter the negative value corresponds to blue tone and positive value to yellow tone.

For the other two violet samples taken from "Tower of Antim Church" work, their chromatic characteristics are also in agreement with the mixture of tones: dominant blue ($-b^*$) with ($+a^*$) resulting to a violet color. The brown nuance of the last sample is supported by the lower value of chroma ($C^* = 7.80$).

Similar interpretation can be achieved for the samples taken from "Balcic" work (Table 2, No 2), where blue–green color corresponds to both negative values for (a^*, b^*), while violet–brown is obtained for $+a^*$ and $-b^*$.

In Figure 15 the spectra for green samples taken from Victor Brauner works are compared to those of other two predecessor painters, Nicolae Grigorescu and Stefan Luchian. A strong similarity is observed in the coloristic palette used by Brauner with that of Luchian, with specific bands at 420 and 600 nm, but also with significant absorbance in green region at 700 nm, that could be assessed to Sap green 1920 pigment.

Authentication of Signature

For the "Tower of Antim Church" work there where suspicions on its authorship as the signature is not clearly drawn. It is made by using a violet brown color, similar to other works clearly signed such as in "Cavaler" (Chevalier) drawing [16]. The elemental analysis of these samples by comparison with the data of metal content for pigments from 1920 collection (Table 6) brings valuable proofs on the authorship

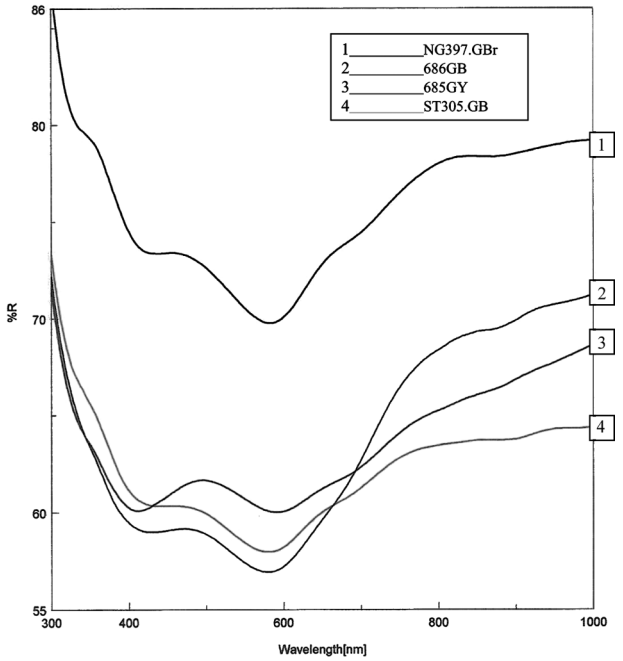

FIGURE 15 UV-VIS-NIR spectra for samples: 1 – Nicolae Grigorescu, NG397GBr-green-brown; 2 – Victor Brauner, *Balcic* 686GB-green–blue; 3 – Victor Brauner, *Tower of Antim Church*, 685GB-green–blue; 4 – Stefan Luchian, ST305GB-green-brown.

TABLE 6 Elemental Analysis of Metal Content

No.	Sample	Work	Metal content					
			Fe	Cu	Co	Cr	Mn	Zn
1	685GB	Tower of Antim Church	1.74	–	–	–	–	0.30
2	685GY	Tower of Antim Church	2.86	–	–	1.74	–	0.94
3	685VBr	Tower of Antim Church	14.3	–	–	1.46	0.15	1.10
4	686BG	Balcic	1.56	0.10	0.11	0.30	–	105.7
5	686VBr	Balcic	1.50	–	0.10	2.03	–	47.1
6	429VBr	Cavaler (Chevalier)	7.35	0.12	–	0.52	0.10	4.78
7	Burnt umber HS	Collection 1920	15.7	–	–	–	0.23	–
8	Garancine lac TR	Collection 1920	0.92	–	–	–	–	–
9	Violet lac S	Collection 1920	0.40	–	–	–	0.28	–
10	Sap green S	Collection 1920	0.93	–	–	0.22	–	–

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assessment. As it was mentioned above referring to the composition of the pigments, for the brown pigments like burnt sienna (Table 1, No 2) or burnt umber (Table 6, no 7) the main chromophore is Fe^{3+} ion, and the violet tone is conferred by Mn^{2+} ion. Quantitavely, the maximum values of iron content are obtained for violet–brown samples from the signatures of "Tower of Antim Church" and "Cavaler" (Chevalier), which is also comparable with the iron content in the Burnt umber from 1920 collection. By corroboration of this argument with the spectral and chromatic analysis, the authorship of this work art can be certainly assessed to Victor Brauner.

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CONCLUSIONS

- The contribution of instrumental methods, particularly of spectral techniques and elemental analysis to complete stylistic – hystoriographic analysis for the authorship certification is demonstrated.
- The relationship between the nature of chromophoric species determined by the chemical composition and the spectral characteristics of pigments is interpreted in connection with trichromatic parameters in CIE–$L^* a^* b^*$ system.
- Based on spectral-chromatic characteristics of standard pigments the chromatics of art works can be objectively analysed.
- The elemental analysis of the metal content of pigments used for the signature provided strong arguments for authorship certification of Victor Brauner art work.

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