

Use of Molecular Spectroscopy FT-IR and UV-VIS-NIR for Characterization of Pictorial Layers of Artworks

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The determination of authorship of artworks represents one of the most complex research problems in the field of cultural heritage. In this respect, the authorship assessment should start with the technical and stylistic analysis, but this has to be also completed by some objective arguments 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, etc. The present paper aims at using some spectral molecular methods in order to examine the pictorial layers sampled from 7 works belonging to initial creation period of Victor Brauner and to assess the evolution of his pictorial style.

Keywords: artwork technical analysis, spectral methods, chromatic analysis, pictorial layers

The study of art works represents one of the most complex and delicate research problems and 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, etc. 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 [1].

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 XXth century. These drawings belong to the beginning creative period of the artist, before 1930, when Brauner left Romania and was established in Paris [2].

The aim of this paper is the use of spectral methods for examination of pictorial layers sampled from Romanian collection of Victor Brauner works in order to establish the trends in evolution of the pictorial style of the artist in his beginning creative period.

Experimental part

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 XXth 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 colours, which individual or in a mixture can lead to the wide palette of nuances used in drawings. Their probable chemical composition, the main characteristics of the electronic spectra and the chromophors responsible for the colour are presented in detail in a previous paper. [3]

This collection has been completed by a few number of pigments used during 1920 period. Particularly useful was the paper of Louisa Gomez [4] which provided valuable information on the composition and chemical structure of various classes of pigments.

Sampling

The sampling has been performed according to the regulation procedures stipulated in the field of art work investigation [5]. This assumed to take samples from the parts of the paintings (usually on the margins) without causing significant damages on the original work. In the table 1 a number of 7 samples have been selected from different paintings of Victor Brauner, considered as being representative for the evolution of his artistic creation.

Table 1
SAMPLES OF PICTORIALS LAYERS ANALYZED

Nr. crt.	Painting title	Period	Sample	Color
1	Turnul Bisericii Antim	1919-1920	685-ViB	Violet-brown
2	Balcic	1920	686-AVe	Blue-green
3	Adam si Eva	1923	428-AVe	Blue-green
4	Muncitoare	1923	429-ViB	Violet-brown
5	Baiat cu ulcior	1923	430-ViB	Violet-brown
6	Portret de femeie	1925-1928	612-Ver	Green
7	Portretul lui Ilarie Voronca	1929-1930	611-AsB	Blue-brown

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Table 2
CHARACTERISTICS OF UV-VIS-NIR SPECTRA AND CHROMOPHOR ASSESSMENT
FOR SELECTED STANDARD PIGMENTS

No crt.	Pigments		λ , nm	Chromofor	Assignment
	Color	Probable formula			
1	Zinc white	ZnO/ZnSO ₄	270-300, 1450, 1920	diluter	Charge transfer (CT) IR harmonics SO ₄ ²⁻
2	Van Dyck brown	Hidroxisilicate, Fe, Mg, Al, K	380---800	Fe ³⁺	Defects, CT d-d
3	Chrome yellow	Pb CrO ₄	350---420	Cr ⁶⁺	CT
4	Red iron oxide (Fe ₂ O ₃)	Fe ₂ O ₃	350---400---550, 870	Fe ³⁺	CT Me-O d-d
5	Permanent violet	(NH ₄) ₂ Mn ₂ (P ₂ O ₇) ₂ ⁺ alizarin	450---550, 870	Mn ²⁺	CT d-d
6	Ultramarine blue	Na ₆₋₁₀ Al ₆ Si ₆ O ₂₄ S ₂₋₄	590---640	Lattice Al-Si	Defects
7	Ceruleum blue	CoO.nSnO ₂ + ultramarine	350, 500---660--750	Lattice Al - Si Co ²⁺	Defects, CT, d-d
8	Sap green	buckthorn berries extract	400--450, 700--800	Chlorophyll	$\pi - \pi^*$

Equipment

Spectral analyses have been performed by using the following instruments:

- Jasco UV-Vis spectrometer, model V-570 with 200-2500 nm range and a diffuse reflectance system; CIE - L*a*b* JASCO software for trichromatic analysis of colour;

- Jasco FT - IR 620 spectrometer on 4000 - 400 cm⁻¹ range.

Results and Discussion

Spectral and chromatic analysis of standard pigments

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

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 [6].

In this respect, zinc ion, even though it is transitional, having a complete electronic shell configuration (3d¹⁰) 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 colour or as a diluter for other dyes. Other ions like: Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Al³⁺ belonging to the main groups, have no chromophoric properties, and as a result, they act also like diluters.

The ions in fundamental state of singlet with half-occupied electronic shell (3d⁵) as in the case of Mn²⁺ and Fe³⁺ species provide d-d transitions of rather low intensity and displaced towards NIR domain, this conferring a quite slight coloristic power. In order to enhance the colour of such compounds a dominant contribution brings about the charge transfer transitions metal-ligand or metal-metal 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, Cr₂O₃ - green, MnO₂ - brown, MnO₄⁻ - violet, CrO₄⁻ - yellow, etc. Charge transfer transitions involving metals of variable valence are found in Pb₃O₄ (miniu) - red, Fe₃O₄ - red etc. Another way to provide colour 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 representative standard pigments used in this study the chromatic characteristics are revealed by means of their electron spectra recorded in diffuse reflectance mode, and presented in the table 2. It can be noticed that for yellow chrome the absorbance band is centered at 380 nm, for red iron oxide around 450 nm, permanent violet at 500 nm, ultramarine blue around 620, and for Sap green around 750 nm, the entire visible domain being thus scanned. For van Dyck brown most visible domain is covered by a continuous evolution, with dominant absorbance on the left half side of electronic spectrum.

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 cellulosic materials existent in the composition of drawing support or that of the blank used during spectral registration.

The interpretation of pigment colour 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 presented in table 3.

The interpretation of the IR spectra of these selected standard pigments can be made in relation to their dominant composition. Thus, the pigments number 1, 3, 4 have an oxidic composition, their IR spectra are quite simple, the main bands being assessed to Me-O vibrations. Another type of pigments are those based on aluminosilicate minerals (numbers 2, 6 and 7), where dominant bands arise from Si-O-Si vibrations. The pigments 5 and 8 have mainly an organic composition which is further enriched by a high content of mineral oil as basic matrix.

*Analysis of standard pigments in CIE-L*a*b* chromatic space*

The colour 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 [7, 8], where:

Table 3
CHARACTERISTICS OF IR SPECTRA AND THEIR ASSESSMENT FOR SELECTED STANDARD PIGMENTS

1*	2	3	4	5	6	7	8	Assignment
3435	3467 3010	3430		3423 3010	3446	3446	3404 3008	O-H associated C-H in CH ₃
	2925			2923			2923	C-H assim in CH ₂
	2854			2852			2854 2080	C-H sim in CH ₂
	1745			1743			1738	C=O from R-COOH, oil
1634		1632			1652	1624	1620	CH=CH oil
				1575 1540			1576	S-H C=C
	1427	1383		1461 1415			1461 1360	O-H deformation CH ₂ deformation
	1163 1095 1035						1180 1120 1086	Si-O-Si
		1095 1075						CrO ₄
		doublet						
1040								C-O
		858						CrO ₄
	835						977	CH=CH
	715			721	696		669	(CH ₂) _{n>4}
668		627 598 doublet	533	609	665 582	642 525	607	Me-O
480	574 480	467	453	497	486	460	451	Me-O

*The number of pigments is the same as in the table 1

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 - yellow 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,

C*: <30 for white, black, grey, brown, usually for polychromatic colours, with electronic spectra quite continuous, at constant absorbance,

>30 - monochromatic colours are clearly distinct, electronic bands are intensive;

H_{ab}: 0 - 90 for the Ist quadrant red - yellow, 90 - 180 for the IInd quadrant yellow - green, - (90 - 180) for the IIIrd quadrant green - blue, - (0 - 90) for the IVth quadrant blue - red.

For the standard pigments analyzed in this paper 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. For all the other pigments the values L* > 50 are obtained for light colors and L* < 50 are for relatively dark colors. The brown pigment, van Dyck brown, has a dark tone, L* = 27.8, and has also the lowest chroma (C* = 1.51). This value is in accordance with its electronic spectrum that shows a wide plateau on the entire spectral domain (table 2). Being so close to luminosity axis (small chroma) its polychromatic

composition is obvious. Usually the brown pigments are located into the first, positive quadrant (a*, b*), having as major contributions the specific chromophors for yellow (+b*) and red (+a*) colours. The value of H_{ab} ∈ 67 - 70 indicates the dominance of red component.

For yellow pigment (No 3) the highest luminosity value among coloured pigments is observed (L* > 80) due to its relative lighter tone. In the case of red pigment (No 4) it is reasonable for the red tone to be dominant over yellow component (H_{ab} ∈ 33.53). For permanent violet pigment (No 5) the red tone is dominant over the blue tone (a* = 11.66, b* = - 2.85).

For the two blue pigments (No 6 and 7) it is obvious that blue tone is the dominant component (b* = -32), but this is in a mixture with a small amount of red tone for ultramarine blue (a* = +4.34), while for cerulean blue the dominant blue is in a mixture with a small amount of green color (a* = -3.54). This is confirmed by electronic spectra (table 2) where this pigment has the most intensive absorption of blue band extended further to the green region (700 - 750 nm).

Sap green pigment selected from 1920 collection (No 8) has the hue angle H_{ab} = 124.27 as a result of a mixture of yellow and green colors, in accordance with electronic spectrum that shows characteristic bands in these regions (table 2).

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 (table 5) in tight connection with their electronic and infrared spectra (table 6).

It can be noticed that samples from various works but with similar colour exhibit quite similar chromatic characteristics. The three violet-brown samples (685, 429

Table 4
CHROMATIC CHARACTERISTICS CIE-L*a*b* OF STANDARD PIGMENTS

Nr.cr	Pigments	L*	a*	b*	C*	H _{ab}
1	Zinc white	82.53	-0.70	-4.84	4.89	-98.23
2	Van Dyck brown	27.08	0.59	1.41	1.51	67.31
3	Chrome yellow	81.41	-3.82	88.56	88.60	-87.53
4	Red iron oxide (Fe ₂ O ₃)	39.86	28.55	18.65	34.13	33.53
5	Permanent violet	26.56	11.66	-2.85	12.01	-13.75
6	Ultramarine blue	38.67	4.34	-32.12	32.40	-82.30
8	Cerulean blue	47.92	-3.54	-32.38	32.57	-96.24
9	Sap green	48.42	-11.98	17.59	21.28	124.27

and 430) have a continuous absorbance on the entire visible domain with intensity dominant on the left side of the spectrum. Therefore no specific maxima can be mentioned, but a wide plateau characteristic to brown colour. For the blue-brown (611) the plateau is still wider, until 800 nm. They have also similar values for trichromatic parameters: $L < 50$, $a^* > 0$, $b^* < 0$, and H_{ab} around -70.

On the contrary, the other samples have distinct bands in visible domain, with the main maximum around 600 nm for blue greenish samples (686 and 428 AVe), the green tone being obtained due to the contribution of the shoulder at 720-750 nm. This mixture of blue and green is confirmed by both negative values for a^* (green) and b^* (blue), with clear dominance of the last parameter.

The green sample (612) is the lightest in this series, with the highest value of the luminosity ($L^* = 75$). It has also distinct absorbance bands, but in this case the green colour is metameric as it is obtained by a combination of the band

specific to yellow (385 nm) with that for blue (600 nm), and only a shoulder in the green region of reflected light (720 nm).

Similar features for samples of the same colour are noticed also in infrared domain (table 6), where the assignment was based on the main vibrations of the functional groups previously revealed for standard pigments (table 3). Most of common bands come from the mineral oil of paintings, while the differences in various chromophores appear mainly in the regions specific to Me-O and Si-O-Si groups from oxides or aluminosilicate pigments. The elemental analysis of metal content determined by Atomic Absorption Spectroscopy provided a decisive contribution in differentiating the composition of pigments, but this alternative method used for art works authentication was presented in another paper [9].

By comparing all the samples analyzed in this paper it can be concluded that most of pictorial layers consist in a

Table 5
CHROMATIC CHARACTERISTICS OF PICTURAL LAYERS

Sample	L*	a*	b*	C*	H _{ab}	λ , nm
685-ViB	44.99	+1.87	-7.58	7.80	-76.14	580-600 wide
686-AVe	48.94	-0.53	-4.55	4.58	-96.58	405, 590, 700sh
428-AVe	34.99	-0.39	-9.75	9.80	-97.71	405, 620, 750sh
429-ViB	42.59	+1.11	-3.17	3.36	-70.70	400-600 wide
430-ViB	29.14	+0.96	-1.73	2.00	-60.97	400-600 wide
612-Ver	75.35	-3.17	+5.51	6.35	+108.4	385, 600, 720sh
611-AsB	38.62	+0.39	-1.34	1.40	-73.38	400-800 wide

Table 6
CHARACTERISTIC BANDS IN IR, ν , cm⁻¹

685-ViB	686-AVe	428-AVe	429-ViB	430-ViB	612-Ver	611-AsB	Assignment
3429	3450	3450	3427	3427	3422	3427	O-H
2920	2920	2920	2919	2919	2919	2919	CH ₂ in
2855	2855	2855	2854	2855	2859	2854	R-COOH oil
1670	1670	1670	1719	1719	1724	1738	C=O in
			1625	1625	1654	1590	R-COOH oil
					1629	1540	
1470	1520	1460	1430	1430	1460	1455	CH ₂ def.
1460	1460						CO ₃
1388	1388						
1153	1153	1153	1150	1150		1167	Si-O-Si
1135		1135	1130	1130	1112	1096	
1035	1035	1050	1056	1056	1057		
	721	695			873	723	(CH ₂) _{n>4}
682		682	673	670			SO ₄
660		660	600	600	608		Me-O
580	580	565					Me-O
565	510	545			-		
	440	520	464	464		470	

mixture of many pigments resulting into metameric colours, dominant for the coloristic pallet of the artist being brown tones. These could be obtained by applying directly the brown pigment, such as van Dyck brown, but also by mixing three or four pigments with bands in the first half of visible domain: yellow, red, violet. This can be assigned based on the specific bands appeared in infrared domain and completed with elemental analysis of metal content by Atomic Absorption Spectroscopy.

Another aspect revealed after analysis of a larger number of samples of Victor Brauner works was that in the beginning creation period he used metametric mixing of yellow-ochre with blue pigments to obtain green tones while for the last period (after 1925) he also used single pigments like Sap green. By complementing these observations resulted from physico-chemical analysis with those of technical and stilistic analysis of paintings, some interesting conclusions could be drawn on the evolution of the pictorial style of the artist.

Conclusions

Chromatic analysis of some pictorial layers sampled from Victor Brauner artworks has been performed by comparison with similar data obtained for a series of standard pigments. This approach allows assessing the chromophores, most of them being of mineral nature, oxides, or pigments impregnated on aluminosilicate matrix, which explain their high stability in time.

The coloristic pallet used by the artist was objectively interpreted by using trichromatic analysis of pigments, in

tight connection with their electronic and infrared spectra. Spectral and chromatic analysis provides valuable information needed to complete technical and stylistic analysis of paintings, such a complementary approach being very useful in supporting the authorship and authenticity certification of artworks.

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UV-Vis-NIR is ideal for characterizing the optical and electronic properties of various materials such as films, powders, liquids, and monolithic solids. UV-Vis-NIR. Optical design of 150 mm integrating sphere. Photo credit: Perkin Elmer. Ultraviolet-Visible-near-IR Spectroscopy (UV-Vis-NIR). Measurements in the ultraviolet/visible region (UV-VIS) cover wavelengths from about 200 nm to 800 nm. The absorption of ultraviolet or visible radiation by a molecule leads to transitions among the electronic energy levels of the molecule. It is ideal for characterizing the optical and electronic properties of various materials such as: films, powders, monolithic solids, and liquids. The near-IR region (NIR) of the electromagnetic spectrum utilizes wavelengths from about 800-2500 nm. [73]. Use of fluorescence spectroscopy is a recent development and is especially advantageous as a non-invasive tool to detect dyes with relatively good emission quantum yield [74]. Anthraquinone colorants with fluorescence properties are widespread in nature, absorbing around 500 nm and emitting over a spectral region of 550-650 nm relating to the number and position of hydroxyl groups as well as surrounding environment [20]. The optical characterization was used to address and interpret the nonlinear results obtained by MPEF, and the comparison of MPEF with OCT measurements allowed the potential of NLOM in the 3D survey of highly scattering painting media to be highlighted. ... The second is: how to stabilise the pictorial layers? UV Vis spectroscopy is a powerful technique for characterizing pharmaceuticals, chemicals, biotech products, foods & beverages, etc. Learn about terms, fundamentals, applications and more. The spectroscopic techniques commonly used for chemical analysis are atomic spectroscopy, ultraviolet and visible spectroscopy (UV Vis spectroscopy), infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance. Type of Spectroscopy. Type of Radiation. Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible regions of the electromagnetic spectrum. This means it uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the spectrum, atoms and molecules undergo electronic...