# Research on the Chromatic Palette of a Modern Romanian Painter

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*The paper focuses on two works of art, Chrysanthemums and Roses, painted by Stefan Luchian, a representative painter for the modern Romanian art from the beginning of the 20th century. The two paintings were analyzed by several non-invasive techniques (optical microscopy, grazing light and UV examination, IR reflectography, XRF and Raman spectrometry) in order to get information concerning the chromatic and to assess the state of conservation. The study is focused in particular on yellow, red and white pigments, which are different in the two pictorial compositions: in Chrysanthemums the predominant pigments are Madder lake, cadmium yellow and zinc white mixed with lead white, while in Roses cinnabar, strontium yellow and lead white were found, according to the XRF and Raman analysis.*

*Keywords: pigments, optical microscopy (OM), IR reflectography, XRF spectrometry, Raman spectrometry*

This study refers to two plastic works, *Chrysanthemums* and *Roses* painted by Stefan Luchian. Stefan Luchian (1868-1916) is one of the more representative painters for the modern Romanian art from the beginning of the 20th century. The painter is the one who developed the theme of flowers, transforming it into a stand-alone genre within the Romanian painting. The two paintings belong to a second creation phase characterized by the theme of flowers (1907-1910), singularized by an intense brilliance and by the study of chromatic forces [1, 2]. The flower paintings, one of the richest chapters of his works, are those which express the perfection of the artist's mastery, being considered *the genius interpreter of this motif*. Even if the flowers organization is the same in most of his works the chromatic approached in each of them leads to an endless variety. This variety was obtained using a great number of pigments in pure state or in mixtures.

The artistic expertise is made through the corroboration of several modalities of painting analysis(anamnesis, multispectral examination, chemical analysis of materials, etc.) [3-6].

The chromatic palette of the studied paintings was determined based on an analytical protocol using optical microscopy (OM), IR reflectography (IRR), XRF and Raman spectrometry.

This research is part of a broader study *Innovative interactive artistic mediation system designed for the capitalization of the art patrimony of Romanian museums* (SIMAP) and is focused on the characterization of two oil paintings on canvas painted by Stefan Luchian (*Chrysanthemums* and *Roses*), from the collection of the Art Museum – Moldova National Museum Complex of Iasi, Romania.

## Experimental part

The areas analyzed by different analytical techniques were selected observing the requirements for works-of-art analysis and the complex composition of the two paintings. The analysis were carried out in 19 points (labeled C1-C19) for the painting *Chrysanthemums* and in 17 points (labeled R1-R17) for the painting *Roses*, respectively.


Fig.1. Paintings on canvas, 20th century, Stefan Luchian C. Chrysanthemums T. Roses

*Grazing light examination*: the ART LUX4 lamp, CTS Italy, was also used to take photos at grazing light in order to evaluate the general state of conservation of the paintings.

The roughness and the irregularities of paintings surface (folding, bending and other deformations), concerning the state of conservation, were revealed by this examination. The study under grazing light can also reveal some repainting.

*UV examination*: UV fluorescence excited with Black Light lamp, CTS Italy, was used to obtain information concerning the varnish degradation, retouching or other interventions on the painting surfaces.

*Optical Microscopy* (*OM*): the paintings were examined by OM using a SMZ 800 NIKON microscope, at magnification between 50X and 100X. This investigation concerned the color layers, superposition and mixture of pigments, the working technique, the possible fissures, cracks and other types of degradations [3, 4, 7].

*IR reflectography* (*IRR*): the paintings were analyzed using the IR reflectography system MOD MIR 10 new, CTS Italy, using 0.70-2 μm wavelength. IR reflectography is a non-destructive method used in art forgeries detection,

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which highlights the preparatory drawing, changes of the painting composition and retouches [3, 8].

*XRF spectrometry* (*XRF*): the experimental *in-situ* determination of inorganic components of the pigments and preparation layer [7, 9-12] was carried out using a XRF spectrometer type INNOV-X Systems Alpha Series Bruker, non-destructive portable instrument. The apparatus is equipped with an X-ray tube with W anode, working at the maximum parameters of 35kV voltage and 40μA current intensity; the fluorescence radiation is detected and analyzed with a PIN Si detector, thermoelectrically cooled, controlled by a minicomputer. For spectra acquisition and semi-quantitative analysis, for heavy matrix, the analytical mode software has been selected, with 30s excitation duration, and for light matrix (60s excitation), the Soil mode software was used.

*Raman spectroscopy*: the vibration spectra were acquired with a VERTEX 70 (Bruker) IR spectrophotometer, equipped with Raman accessory, RAM II and the probes MIR and Raman for nondestructive analysis; the excitation source was NIR laser, 1064 nm (Nd:YAG), 1 ÷ 500 mW power and 1mW resolution, and the detector - ultra pure Ge solid state detector, cooled with liquid nitrogen. The FT-Raman spectra were acquired by direct reflection on the sample, in the spectral domain 50 - 3500 $cm^{-1}$, at 4 $cm^{-1}$ spectral resolution, 1 - 500 mW power of laser source (1064 nm), 500 scans. The spectra processing was done using OPUS_65.software.

## Results and discussions

The purpose of our research was the identification of pigments used in the creation of the two paintings, to assess the deterioration or to identify previous paintings or modifications of the original pictorial composition.

The state of conservation of the pictorial layer was provided by visual examination. At the painting *Chrysanthemums* (fig. 1C) some tears, fine cracks, matting, pigment grains and slight deformations were observed; *Roses* (fig.1R) painting showed deeper fissures, small lacuna and erosions of the pictorial layer on the whole length of borders, branched cracks, some whitish spots, slight matting on small non-uniform surfaces. In some areas of the pictorial layer deep extended craquelures were observed. The development of these cracks varies function of color and is more pronounced in light color areas, which contain less binder and, consequently, are less elastic.

OM was useful for the assessment of the chromatic and compositional characteristics of the pictorial layers [7, 12, 13]. The analytical points on the two paintings (tables 1 and 2) were selected under OM in order to choose the representative areas for pigment analysis, namely single color layers, without color superposition or mixtures.

The OM study of the signature relived its uniformity with the rest of the painting: the color layer is uniform, the signature areas are more prominent, but the color did not penetrate in the fissures, as it would happen if the signature was false.

Studied under grazing light *Chrysanthemums* painting shows an uneven superficial structure, with medium height brushstrokes relief. The canvas texture can be observed in the areas where the color layer is thin. The greenish-blue fluorescence of the varnish observed under UV illumination is specific to natural resins from its composition. The fluorescence image shows that the varnish was unevenly

**Table 1**
*CHRYSANTHEMUMS* PIGMENT LAYER CHARACTERIZATION

| Point | Color | Optical microscopy observations |
|---|---|---|
| C1 | Background | Mixture of pigments- blue, white, red particles on brown-yellow- ochre background |
| C 2 | Background | Red, blue, brown pigment on ochre - green- brown background |
| C 3 | Background | Mixture of particles of blue and brown pigment on brown background |
| C 4 | Background | Particles of blue and brown pigment spread on reddish background |
| C 5 | Yellow chrysanthemum | Yellow color |
| C 6 | Yellow – orange chrysanthemum | Streaks of yellow and red color |
| C 7 | Orange chrysanthemum | Particles of blue, red pigment on yellow and red background |
| C 8 | White chrysanthemum | Particles of red and brown pigment on white background |
| C 9 | Red chrysanthemum | Mixture of white and brown particles on red background |
| C 10 | Leaf | Particles of blue, ochre – yellow pigment on green background |
| C 11 | White – pink chrysanthemum | Mixed colors- red, pink, white and green-brown color spots |
| C 12 | White – pink chrysanthemum | Mixture of pigments- white, pink, green spotting |
| C 14 | Background | Non-uniform color, particles of blue, red and brown pigment on brown - green background |
| C 15 | Vase, yellow | Particles of blue, red, ochre and brown pigment on ochre background |
| C 16 | Vase, yellowish-white | Particles of blue, red, brown pigment on white background |
| C 17 | Leaf | Particles of blue pigment on light green background |
| C 18 | Red chrysanthemum | Mixture of particles of brown pigment on red background |
| C 19 | Signature | Particles of dark brown - black pigment on reddish brown background |

**Table 2**
*ROSES* PIGMENT LAYER CHARACTERIZATION

| Point | Color | Optical microscopy observations |
|---|---|---|
| R 1 | Background | Mixture of pigments- particles of blue, white, black pigment on reddish brown background |
| R 2 | Leaf | Mixture of pigments- particles of red, blue, white, green pigment on green background |
| R 3 | Table - greenish yellow | Blue, green, greenish - yellow color spots and particles of red, blue pigment |
| R 4 | Table - greenish ochre | Particles of blue and red pigment on ochre background |
| R 5 | Pink rose | Mixture of pigments -particles of blue, red, white pigment on ochre - yellow - pink background |
| R 6 | Pink rose - orange | Particles of red pigment on white - pink - red - yellow background |
| R 7 | White rose - ochre | Particles of blue, red, white pigment on white – ochre - pink background |
| R 8 | White rose - ochre | Non-uniform color, white, green, ochre- brown color spots |
| R 9 | Vase | Mixture of colors- particles of blue and red pigment on white – ochre background |
| R 10 | Vase | Particles of blue, white pigment on white - ochre - pink background |
| R 11 | Leaf | Particles of red and blue pigment spread on light green background |
| R 12 | Pink rose | Particles of red and white pigment on light red background |
| R 13 | White rose - ochre | Mixture of pigments-particles of blue, red, white pigment on white – ochre background |
| R 14 | Red rose | Microscopic red color spots |
| R 15 | Dark green leaf | Non-uniform color, green and brown color spots |
| R 16 | Leaf | Green - brown color spots and particles of blue and black pigment |
| R 17 | Signature | Signature is applied over several layers of color |

applied on the painting surface and some varnish erosions are visible. In the right side of the painting an area of chromatic integration from a previous restoration intervention can be seen.

*Roses* painting examined under grazing light (fig.2a) shows heavy planar distortion of the canvas support due to weak stretching on chassis, and fissures in the pictorial layer. In the areas where the pictorial layer is thin the canvas texture is visible.

The study under UV light (fig. 2b) reveals areas of chromatic integration of a previous restoration intervention

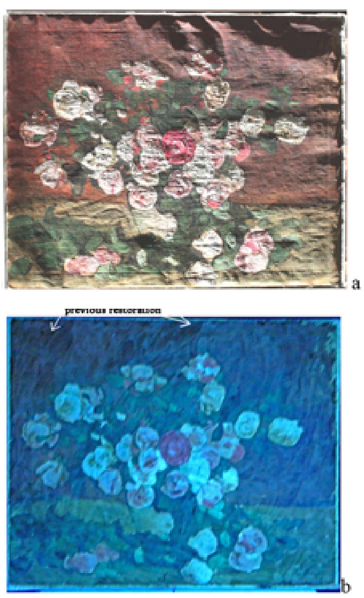


Fig.2. Roses painting - study under grazing light (a) and UV (b)

and varnish wearing. The bluish green fluorescence of the varnish is an indication of natural resins presence in varnish composition.

The IR reflectograms of the two paintings did not show any underdrawings or compositional changes, but clearly highlights the ratio of black and white tones used in the plastic composition, as well as the artist brushstrokes, helping in characterizing the working technique of the painter. No modifications of the composition by the author or by previous restorations interventions were identified.

XRF was used in order to analyze the inorganic chemical elements present. Thus, the basic pigments used in the creation of the two paintings were identified [7, 9, 10, 12-16].

The inorganic pigments present in the two paintings were determined by XRF analysis and the results are presented in tables 3 and 4.

XRF spectra of yellow-orange, orange, white and green pigments in *Chrysanthemums*, are presented in figure 3.

XRF spectra of greenish ochre, red and green pigments of *Roses* are presented in figure 4.

The presence of strontium in two of the analyzed points required an additional investigation.

The results obtained through XRF were completed by Raman spectroscopy data, helping in identifying some inorganic or organic pigments [13, 17]. The Raman spectrometry was used to identify the red pigments, assumed to be of organic nature, and to confirm the lemon yellow.

In the Raman spectrum of C18 point (fig.5a) the following pigments were identified: the characteristic

**Table 3**
PIGMENTS IDENTIFICATION BY XRF *CHRYSANTHEMUMS*

| Point | Elements | Pigments |
|---|---|---|
| C1 | Cr, Cd, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 2 | Cr, Cd, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 3 | Cr, Cd, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 4 | Cr, Cd, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 5 | Cd, Fe, Cr, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Yellow ochre |
| C 6 | Cd, Cr, Co, Pb, Zn, Ba,Ca | Cadmium yellow |
| C 7 | Cd, Fe, Cr, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Red lead, Red ochre |
| C 8 | Pb, Cd, Cr, Co, Zn, Ba, Ca | Lead white, Zinc white, Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 9 | Cd, Cr, Co, Pb, Zn, Ba, Ca | Madder lake (Raman spectrometry), Red lead |
| C 10 | Cr, Cd, Co, Pb, Zn, Ba, Ca | Viridian |
| C 11 | Cd, Cr, Co, Pb, Zn, Ba, Ca | Madder lake (Raman spectrometry) Lead white / Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 12 | Cd, Cr, Co, Pb, Zn, Ba, Ca | Madder lake (by Raman spectrometry) Lead white / Cadmium yellow, Viridian, Cobalt blue , Red lead, Lithopone |
| C 14 | Fe, Cd, Cr, Co, Pb, Zn, Ba, Ca | Brown ochre |
| C 15 | Cd, Cr, Co, Pb, Zn, Ba, Ca | Cadmium yellow, Lead white, Zinc white |
| C 16 | Pb, Zn, Cd, Cr, Co, Ba, Ca | Lead white, Zinc white |
| C 17 | Cr, Cd, Co, Pb, Zn, Ba, Ca | Viridian Lead white / Cadmium yellow, Viridian, Cobalt blue, Red lead, Lithopone |
| C 18 | Cd, Cr, Co, Pb, Zn, Ba, Ca | Madder lake (Raman spectrometry), Red lead |
| C 19 | Cd, Cr, Co, Pb, Zn, Ba, Ca | Organic black |

**Table 4**
PIGMENTS IDENTIFICATION BY XRF- *ROSES*

| Point | Elements | Pigments |
|---|---|---|
| R1 | Hg, Fe, Sr, Mn, Zn, Ba, Cr, Co, Ca | Vermilion + Red ochre + Lemon yellow + Lithopone + Viridian + Cobalt blue |
| R2 | Cr | Viridian |
| R3 | Sr, Cr, Co | Lemon yellow + Viridian + Cobalt blue |
| R4 | Cr, Fe | Viridian + Brown ochre |
| R5 | Hg, Pb | Vermilion + Lead white |
| R6 | Hg, Fe, Pb | Vermilion + Brown ochre + Lead white |
| R7 | Pb, Fe | Lead white + Brown ochre |
| R8 | Sr, Cr, Pb, Fe, Hg | Lemon yellow + Lead white + Brown Ochre+ Vermilion |
| R9 | Sr, Cr, Co | Lemon yellow + Viridian + Cobalt blue |
| R 10 | Sr, Cr, Co | Lemon yellow + Viridian + Cobalt blue |
| R 11 | Cr,Pb, Sr | Viridian + Lead white + Lemon yellow |
| R 12 | Sr, Cr, Hg | Lemon yellow + Vermilion |
| R 13 | Hg, Fe, Pb | Vermilion + Brown ochre + Lead white |
| R 14 | Hg, Sr, Cr | Vermilion + Lemon yellow |
| R 15 | Cr, Fe | Viridian + Brown ochre |
| R 16 | Cr, Fe, Co | Viridian + Brown ochre + Cobalt blue |
| R 17 | Fe, Sr, Cr, Co | Organic black / Brown ochre + Lemon yellow + Viridian + Cobalt blue |

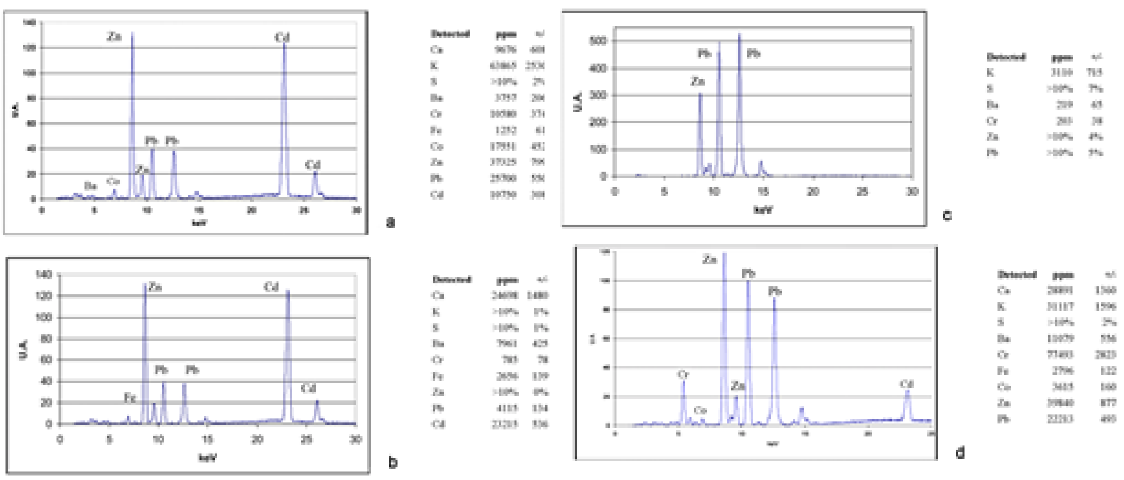

Fig.3. XRF spectra of *Chrysanthemums*: (a) yellow-orange chrysanthemum C6; (b) orange chrysanthemum C7; (c) white chrysanthemum C8; (d) leaf C10

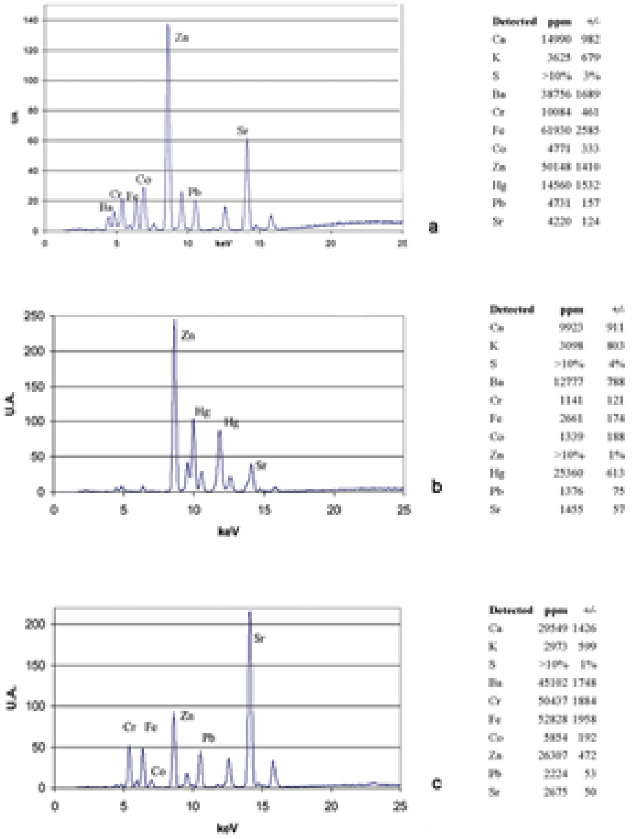

Fig.4 XRF spectra for *Roses*: (a) greenish ochre table R3; (b) red *rose* R14; (c) leaf R16

bands at 1087(s), 712(w), 282(m), 153 (w) were assigned to calcium carbonate, 989 (s) – to barium white and 1639(w), 1517(w), 1482(m), 1359 (w), 1332(w), 1295(m), 1191(w), 240(w) are the characteristic bands of Madder lake.

Figure 5b shows the Raman spectrum of the red pigment C12. The lead white was identified by the characteristic bands at 1051 (s) cm-1 and Madder lake by the bands at 1635(w), 1577(w), 1518 (w), 1442(m), 1367 (w), 1326(w), 1298(m), 1188(w), 843(m), 487(m), 238(w) $cm^{-1}$. The Madder lake (natural) or alizarins (synthetic) are two varieties of the same chemical compound: 1, 2-dihydroxyanthraquinone.

The strontium yellow pigment (fig. 5c) was identified in R3 - greenish yellow table, by the characteristic bands at 929(w), 916(m), 893(s), 867(s), 379(w) 344(w) $cm^{-1}$. The cinnabar presence was confirmed by the characteristic bands at 344(m), 287(w), 254(s) $cm^{-1}$, barium white by 990(s), 1088(w) $cm^{-1}$ bands and lead white by the band at 1051(s) $cm^{-1}$.

## Conclusions

The state of conservation of the painting was assessed under the grazing light examination: fissures, deformation of the canvas, etc.

The UV light examination revealed areas of chromatic retouching on both paintings, due to previous restoration interventions. The bluish green fluorescence indicated the presence of natural resins in the varnish composition. The varnish has been unevenly applied on the surface and its wearing is visible.

The IR reflectography did not revealed any underdrawings or previous designs, but showed the ratio of black and white tones used in the plastic composition, as well as the artist brushstrokes, helping in characterizing the painter's working technique.

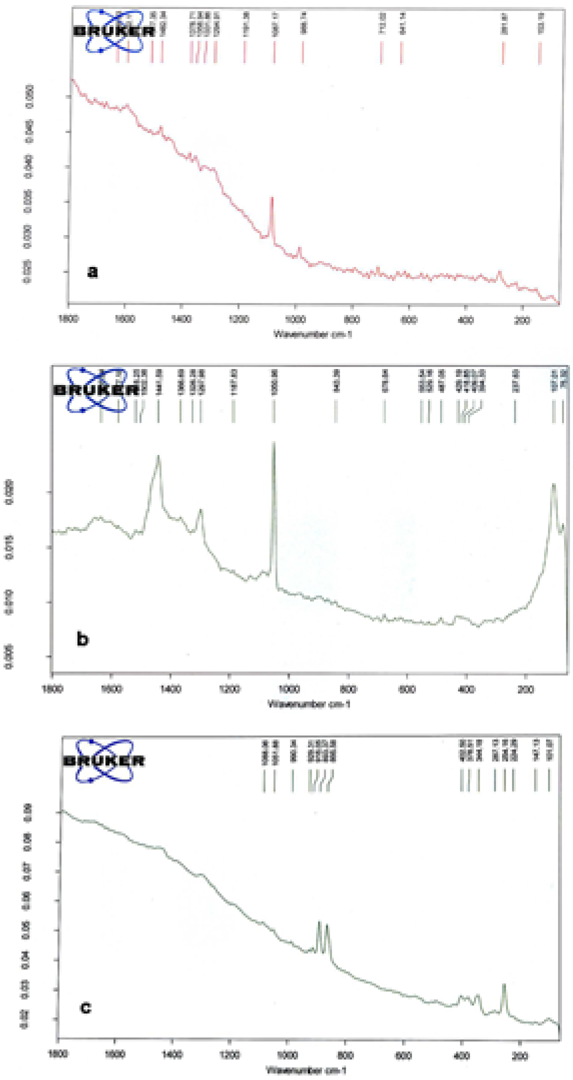

Fig.5. Raman spectrum a. red pigment C18; b. red pigment C12; c. greenish ochre table

Differences in the color palette of the two paintings were found by X-ray fluorescence and Raman spectroscopy. While in *Chrysanthemums* Madder lake, cadmium yellow and zinc white mixed with lead white were used, in *Roses* the red pigment is predominantly cinnabar, the yellow was identified as strontium yellow and the zinc white is no longer employed. The rest of the pigments are the same in both paintings. In both cases the materials used by the artist are concordant with the period in which the two works of art have been painted and no anachronism has been revealed.

The results obtained by non-invasive techniques made possible the identification of the original materials, making the beginning of a database for the pigments of Romanian modern art.

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