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SPECTRAL ANALYSIS OF THE COLOR OF SOME PIGMENTS

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Abstract. Optical spectra of some diffuse-reflecting pigments, have been measured and analyzed to establish their Chromaticity Coordinates in the CIE* Chromaticity Diagram. Color differences between nearly indiscernible colors have also been determined by using specific calculations. The spectra have been recorded in the 380–780 nm domain, using a Varian, Cary Model 118 Spectrophotometer to which an integrating sphere, constructed and adapted by us, has been added. Data acquisition was performed at a 5 nm spectral interval – 81 points – using a PC and a CMA 12-bit UIB A/D converter interface. Calculation of the CIE Chromaticity Coordinates of the colored samples was carried out with a Visual Basic software (also set up in our Lab) in agreement with the International Standards. The experimental set up, acquisition method and the calculation programs are suitable for any diffuse reflecting materials, or, with little changes, for the transmitting ones. Results are meant to be used in paintings restoration, authenticity check, or establishing the origin and type of the natural and the synthetic pigments.

Key words: pigments, color, optical spectroscopy.

1. INTRODUCTION

The main characteristic of a pigment is its color. Usually, pigments baring the same name do have the same, specific, color values. Measured color is a physical and physiological characteristic of the spectral composition of a global radiation, visually indiscernible.

Human color perception is a trichromatic phenomenon. This means that the eye perceives color as a combination of three stimuli which can be described by the corresponding spectral Tristimulus Values, $\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{z}_\lambda$, in the CIE-1931 Standard [1, 2], derived from the natural, measured, $\bar{r}_\lambda$, $\bar{g}_\lambda$ and $\bar{b}_\lambda$ tristimulus values [3] corresponding to the three specific absorbing substances in the eye for the Red, Green and Blue colors.

The perceiving color exhibited by an opaque object in a measuring experiment can be determined, in the CIE-1931 frame, by calculating the corresponding Chromaticity Coordinates, x, y and z ($x + y + z = 1$, always) as follows:

$$
\begin{aligned}
x &= \frac{\sum_{\lambda} \bar{x}_{\lambda} P_{\lambda} \rho_{\lambda}}{\sum_{\lambda} \bar{x}_{\lambda} P_{\lambda} \rho_{\lambda} + \sum_{\lambda} \bar{y}_{\lambda} P_{\lambda} \rho_{\lambda} + \sum_{\lambda} \bar{z}_{\lambda} P_{\lambda} \rho_{\lambda}} \\
y &= \frac{\sum_{\lambda} \bar{y}_{\lambda} P_{\lambda} \rho_{\lambda}}{\sum_{\lambda} \bar{x}_{\lambda} P_{\lambda} \rho_{\lambda} + \sum_{\lambda} \bar{y}_{\lambda} P_{\lambda} \rho_{\lambda} + \sum_{\lambda} \bar{z}_{\lambda} P_{\lambda} \rho_{\lambda}} \\
z &= \frac{\sum_{\lambda} \bar{z}_{\lambda} P_{\lambda} \rho_{\lambda}}{\sum_{\lambda} \bar{x}_{\lambda} P_{\lambda} \rho_{\lambda} + \sum_{\lambda} \bar{y}_{\lambda} P_{\lambda} \rho_{\lambda} + \sum_{\lambda} \bar{z}_{\lambda} P_{\lambda} \rho_{\lambda}}
\end{aligned}
\tag{1}
$$

where P_λ is the spectral power distribution [2] of the source illuminating the object and ρ_λ is its diffuse reflectance. Summation is performed over 81 points (5 nm intervals in the 380–780 domain). The sums in (1) are the integrated Tristimulus Values, X, Y and Z.

The color of an object can be precisely represented by two coordinates, x, y, in the Chromaticity Diagram, Fig. 1. All perceived colors can be indicated by a point on or inside the curve of the pure spectral colors and a straight line unifying the extreme points of the considered spectrum like, for example, 380 and 780 nm, Fig. 1. This Diagram is connected with the sensitivity of the normal (average) human observer, concerning the eye and the nervous system (the optic nerves and

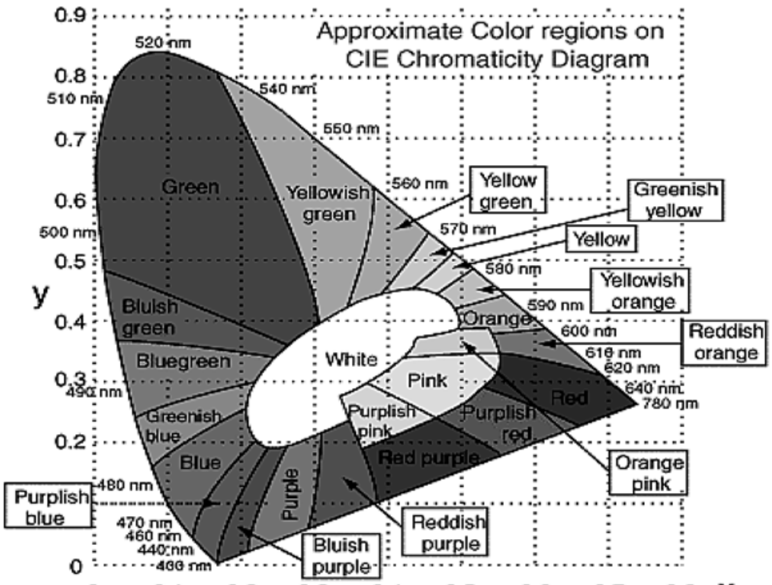

Fig. 1 – Approximate Chromaticity Diagram (The color borders do not exist in reality: they are smoothly interpenetrating).

the brain) and respond additively when it is simultaniously stimulated by two or more monochromatic or composed colors.

CIE-1931 Chromaticity Diagram is good enough in many cases of measuring colors. However, matching or distinguish two colors barely different ones like, for example, in a restoration operation, this Standard is not satisfactory: the CIE-1976, also called CIELAB Standard [4], has been set up for measuring Color Differences. In this frame new parameters have been introduced: L^*, a^*, b^*, standing the Psychometric Lightness, the Red-Green and the Yellow-Blue axes respectively:

$$L^* = 116(Y/Y_n)^{1/3} - 16$$
$$a^* = 500[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}] \quad (2)$$
$$b^* = 200[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]$$

Equations (2) are for X/X_n, Y/Y_n, Z/Z_n greather than about 0.01. If Y/Y_n is less than 0.008856 then $L^* = 903.3(Y/Y_n)$·X_n, Y_n and Z_n are the integrated Tristimulus Values corresponding to a perfectly white (neutrally) reflecting surface, along the entire spectral domain of interest.

Measuring Color Diferences is connected with the eye's ability to detect as litle difference as possible, *i.e.*, on how far from a xy-point one has to go to sense a change in color. Unfortunately this distance depends on the place in the x, y-Diagram and on the moving direction. In other words, the CIE-1931 space is not uniform. This problem has been solved in an acceptable manner by the mentioned CIE-1976, CIELAB space, based on the CIE-1931 space that is transformed by an algebraic operation, leading to relation (2). Since a^* and b^* depend on L^* there is no Chromaticity Diagram in CIELAB-1976.

In these conditions [2] the Color Difference is expressed by,

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (3)$$

Another two parameters are defined in this system: Chroma,

$$C^*_{ab} = (a^{*2} + b^{*2})^{1/2} \quad (4)$$

and Hue Diference,

$$\Delta H^*_{ab} = [(\Delta E^*_{ab})^2 - (\Delta L^*)^2 - (\Delta C^*_{ab})^2]^{1/2} \quad (5)$$

In this paper we present color specification calculated from the diffuse reflectance spectra of some pigments met in painting activities.

We report the measurements of six powder samples used in mural paintings [5]: 1 – ZnO, 2 – CdS:CdSe, 3 – $Na_7Al_6Si_6S_2O_{24}$, 4 – Pb_3O_4 and PbO, 5 – $PbCrO_4$, 6 – Fe_2O_3 and FeO(OH). They have been separated into two groups: a) having rather distinct colors (the first three) using equation (1) for deriving their Chromaticity

Coordinates, x, y, z, and those showing nearly the same color (the last ones) using relation (2) for determination of the Color Differences.

2. EXPERIMENTAL

For spectra recording of the diffuse reflecting samples we used a Varian, Cary Model 118 spectrophotometer to which a self made Integrating Sphere [6], Fig. 2, was adapted.

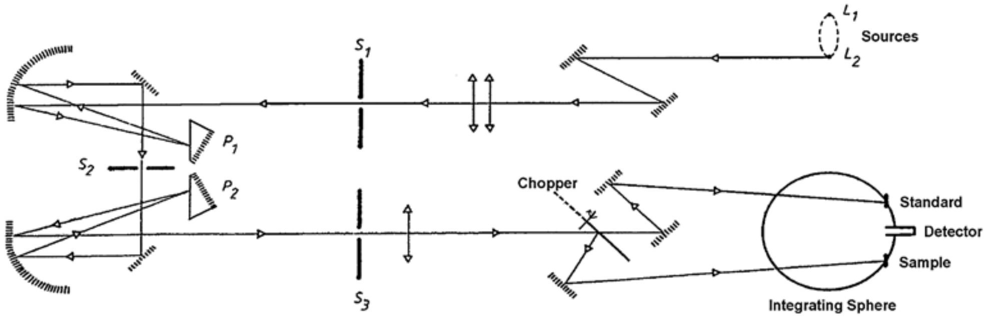

Fig. 2 – Experimental set up. Cary spectrophotometer and the Sphere.

The spectral domain was 380 to 780 nm, in agreement with the CIE 1931 (2° solid angle) standard. The reflecting material inside the sphere was $BaSO_4$ having a reflecting power of 98-99% over the interval of interest. A 2 mm layer of MgO has been used as reference, whose reflectance was over 98% along the same spectral interval. The illuminating source was the standard “A”, a tungsten lamp at a temperature of 2856 K. Acquisition of the experimental data concerning reflectance of the six samples has been performed using a PC and a CMA 12-bit UIB A/D converter interface [7]. Calculation of the Chromaticity Coordinates x, y and z and the Color Differences, DELTA (E^*, C^* and H^*) has been performed using our own software [7, 8].

1 – ZnO. From the diffuse reflectance spectrum of the ZnO, Fig. 3.a.1, one can see that the sample reflects over 90% in the visible domain. So, the color is almost perfectly White. The Reflectance drop under 400 nm has little influence on the naked eye.

2 – CdS:CdSe. The Red of Cadmium is a mixture of synthetic pigments: Naftol Red and Azoic Yellow. It reflects primarily in the 650–780 nm, Fig. 3.a.2 (moderate in the middle and nothing in the blue regions of the spectrum). The color is a vivid red one.

3 – $Na_7Al_6Si_6S_2O_{24}$. This pigment reflects light at both ends of the visible spectrum with a predominance in the blue, Fig. 3.a.3. It has a dark (Ultramarine) Blue

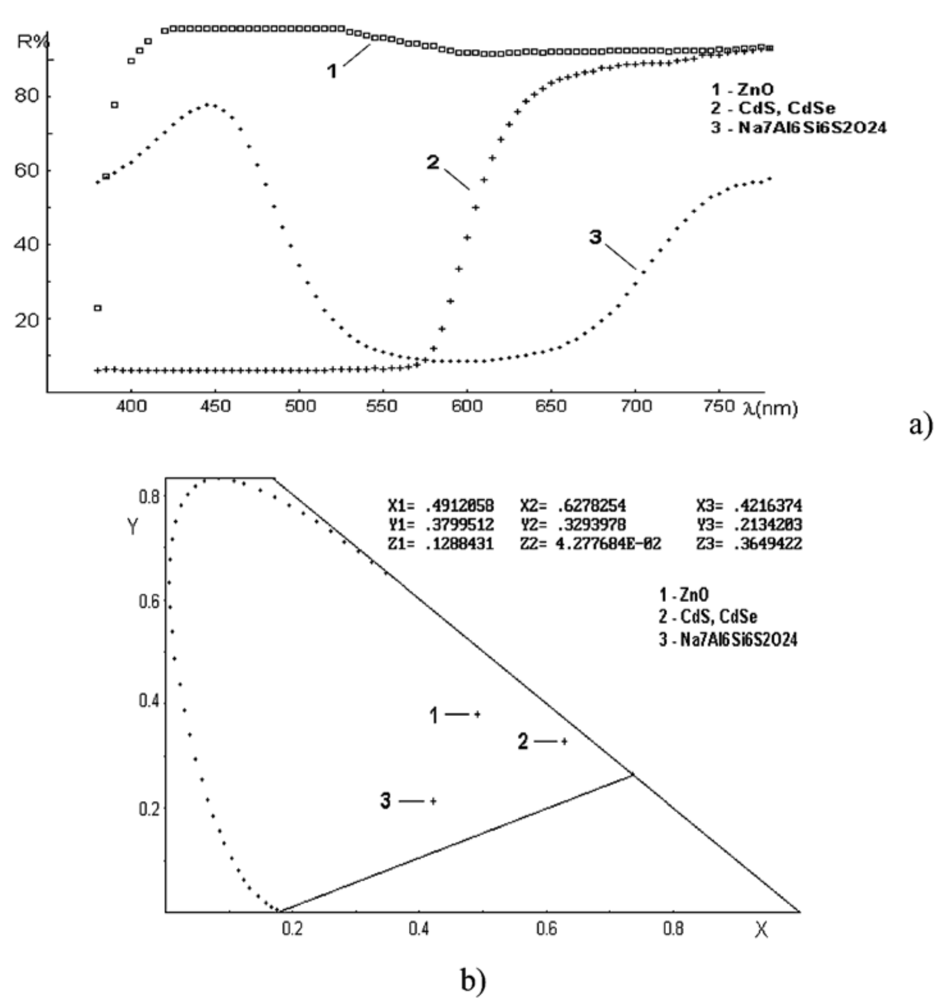

Fig. 3 – Reflectance spectra of the ZnO, CdS:CdSe, and $Na_7Al_6Si_6S_2O_{24}$ samples, a) 1, 2, 3 respectively, and their positions in the Chromaticity Diagram, b).

color. Its darkness could be explained by the low reflectance in the middle of the spectrum.

For the next three samples, 4, 5 and 6, the *xy* Diagram is also given, to have a comparison with the first group of samples, but without their printed x_i and y_i values. The corresponding calculated Delta data are given instead.

The positions of these three colors in the Diagram is given in Fig. 3.b.

4 – PbO and Pb_3O_4. Preparation of this sample is usually performed by the calcination of the white lead at high temperature, for a long time, to obtain both, Pb_3O_4 – minium, as well as the PbO – yellow. By raising the PbO concentration the red color of the minium turns the color of the sample into orange. In our case

one can observe in the spectrum, Fig. 4.a.4, and by sample's yellow-orange color, the predominance of the PbO.

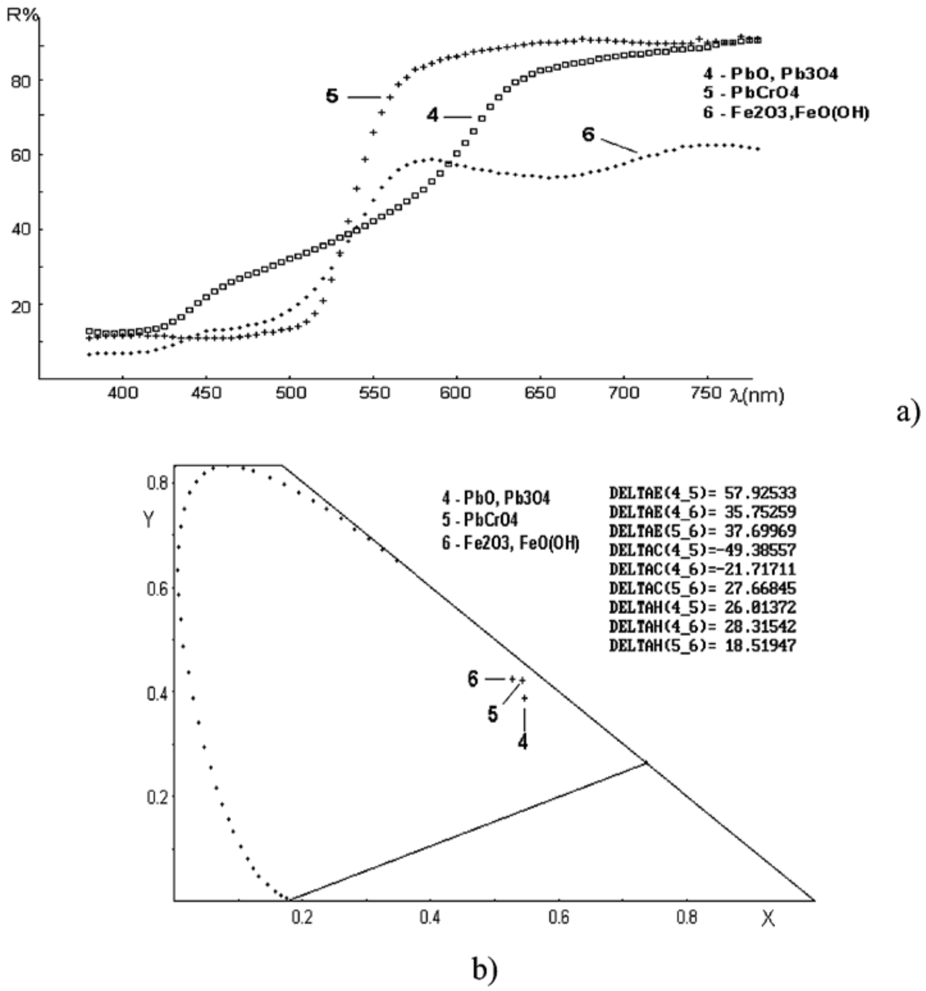

Fig. 4 – Reflectance spectra of the PbO-Pb_3O_4, $PbCrO_4$ and Fe_2O_3-FeO(OH) samples, a) 4, 5, 6, respectively, and their positions in the Chromaticity Diagram, b).

5 – $PbCrO_4$. The spectrum shows that the color of the sample is, roughly, a composition of the 520–780 nm domain, excluding the blue part of it, Fig. 4.a.5. In the Diagram, Fig. 4.b, one can observe the small difference between the Yellow (PbO) lead oxide, and the $PbCrO_4$ (yellow-dark orange), which is rather hard to observe with the naked eye.

6 – Fe_2O_3 and FeO(OH). In the case of the Iron Oxide, two forms are coexisting: Fe_2O_3 (hematite) -dark Red and FeO(OH) (goetit) brownish-Yellow. In

our case one can observe the predominance of the FeO(OH), since the resulting color is a rusty-Yellow. Fig. 4.a.6 shows the corresponding spectrum.

The spectrophotometric measurements are leading to precise positions of the characteristic points of the measured colors in the Chromaticity Diagrams, as shown in Fig. 3.b and Fig. 4.b. Calculated Delta data are also given in these figures.

3. DISCUSSIONS

Determination of the Chromaticity Coordinates and of the Color Differences between various points of a painting, is currently used in restoration of old paintings, in establishing their place of elaboration or their authenticity, and helps finding the original source of minerals for the pigments production, as well as the nature of the synthetic pigments.

While determination of the Trichromatic Coordinates is good enough in many usual cases to solve the above mentioned problems, Color Difference measurements can do a much better job in cases where the analyzed colors are nearly indiscernible, especially if painting restoration is concerned.

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