Talanta 146 (2016) 303–309

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A general method for the quantitative assessment of mineral pigments

M.C. Zurita Ares [a], J.M. Fernández [a,b,*]

[a] Department of Inorganic Chemistry and Chemical Engineering, E.P.S. of Belmez, University of Córdoba, E14240, Spain
[b] Department of Inorganic Chemistry and Chemical Engineering, Faculty of Sciences, University of Córdoba, E14071, Spain

ARTICLE INFO

Article history:
Received 14 June 2015
Received in revised form
21 August 2015
Accepted 27 August 2015
Available online 29 August 2015

Keywords:
Diffuse reflectance spectroscopy
Kubelka–Munk function
Second derivative
Mineral pigments
Colored mortars

ABSTRACT

A general method for the estimation of mineral pigment contents in different bases has been proposed using a sole set of calibration curves, (one for each pigment), calculated for a white standard base, thus elaborating patterns for each utilized base is not necessary. The method can be used in different bases and its validity had ev en been proved in strongly tinted bases. The method consists of a novel procedure that combines diffuse reflectance spectroscopy, second derivatives and the Kubelka–Munk function. This technique has proved to be at least one order of magnitude more sensitive than X-Ray diffraction for colored compounds, since it allowed the determination of the pigment amount in colored samples containing 0.5 wt% of pigment that was not detected by X-Ray Diffraction.

The method can be used to estimate the concentration of mineral pigments in a wide variety of either natural or artificial materials, since it does not requiere the calculation of each pigment pattern in every base. This fact could have important industrial consequences, as the proposed method would be more convenient, faster and cheaper.

1. Introduction

The production of colored materials has a highly industrial importance. Because of that, there are two related issues of great importance when working with pigments: the saturation level and the determination of the minimum amount of pigment necessary to obtain the desired color. For this latter one, there are rudimentary procedures based on printed color charts (with a more or less comprehensive set of concentrations) as well as on spectroscopic studies (that include the entire range of concentrations, from 0 wt% to the saturation level) [1]. Methods based on spectroscopic studies minimize production and business costs, since they permit to obtain the desired color using the minimum of pigment content. It is noteworthy that pigments are more expensive than the bases (mortars, ceramics, et cetera).

Colored mortars and concrete have become popular among engineers and architects for theirs applications. For instance, colored asphalt [2,3] makes traffic safer (guides traffic, shows the way, designates zones and decorates squares), colored mortar [4] and colored concrete [5] are used to accentuate an architectural effect and to increase aesthetic and the visual appeal of buildings, colored paving stones [6,7] are used for bicycle paths, crosswalks, speed bumps, parking lots and approach ramps, colored in-situ concrete [8] is a trend adopted by numerous architects in search of awards for their buildings, et cetera. One main aspect is to get permanent colors without producing adverse effects on mortars and concrete: it is imperative that the coloring agents can be used in a confident and safe manner [6,7,9,10].

Any tinting material can be of great use in many fields thus detecting and estimating the presence and quantity of these substances is of great importance, whether theirs origin is natural or synthetic, organic or inorganic [11–15]. It is highly interesting to notice that not all pigments have the same capacity of tinting [14,15]. The quantity of pigment is inversely proportional to its tinting strength.

The diffuse reflectance spectrum of each sample depends on the different components present in the sample. In fact, by inspecting the spectral shape, the specific component contributing to a particular color mixture can be identified [1,16,17]. Each color mixture has a characteristic curve that depends on its color [17–21]. This fact allows using a reflectance spectrum to quantify individual pigments present in the sample [1,16,22].

The Kubelka–Munk theory [23] has been found to be useful when working with diffuse reflectance and it has been used successfully to describe the color as well as to carry out quantitative studies in different fields: dyes [24], ceramic tiles [15] and ceramic glace [25–27], soils [14,21,28–30], heterogeneous catalysis [31], odontology [32,33], pharmaceutical [34,35], et cetera.

For an infinitely thick, opaque layer the Kubelka–Munk equation may be written:

* Correspondence to: Dpto. Química Inorgánica e Ingeniería Química, Campus de Rabanales, Universidad de Córdoba, E14071 Córdoba, Spain. Fax: +34 957218621.
E-mail address: um1feroj@uco.es (J.M. Fernández).

http://dx.doi.org/10.1016/j.talanta.2015.08.061
0039-9140/

$$\frac{K}{S} = \frac{(1 - R')^2}{2R'} \quad (1)$$

where R' is the absolute reflectance of the layer and K and S are the absorption and scattering coefficients, respectively. The absorption and scattering coefficients for a mixture of pigments can be expressed as linear combinations of those for the individual components (K_i and S_i) and their concentrations (c_i) [14,15,20,22]:

$$K = c_1K_1 + c_2K_2 + \ldots + c_nK_n$$
$$S = c_1S_1 + c_2S_2 + \ldots + c_nS_n \quad (2)$$

The relative reflectance R, which is measured against the reference standard $BaSO_4$, has been used instead of the absolute reflectance R'. Then, the former equation becomes:

$$f_{KM}(R) = \frac{(1 - R)^2}{2R} \quad (3)$$

and a linear relationship should be observed between $f_{KM}(R)$ and the absorption coefficient K if S is constant [36].

The Kubelka–Munk function (Eq. (3)) for a mixture M consisting of n components C_1, C_2, …, C_n will then take the form [1,16,17,36]:

$$f_{KM}(R_M) = a_1 \cdot f_{KM}(R_{C1}) + a_2 \cdot f_{KM}(R_{C2}) + \ldots + a_n \cdot f_{KM}(R_{Cn}) \quad (4)$$

where coefficients a_1, a_2, … a_n represent the intensity of color of each pigment and they will be used for calculating the concentration percentages of the pigments in the mixture.

The more independent the diffuse reflectance bands of the compounds are, the more valid Eqs. (2) and (4) are [1,17].

The Kubelka–Munk function together with spectral derivation [30,37–39] has been used in order to accurately characterize colors in colored mortars [1,16]. Several authors [16,30,39] have demonstrated that the best results in the determination of the amount of the tinting species in several supports are achieved when the second derivative of the Kubelka–Munk is used.

A mathematical function for each color relating the amount of compound to the intensity of color [1,16] would enable the identification of the amount of the different pigments that are present in the mixture.

A relationship between the amounts of the pigments in the mixtures, and the height of the peak in the second derivative of the Kubelka–Munk function obtained from the diffuse reflectance spectrum has been established.

In order to enhance the sensitivity of the diffuse reflectance spectra by means of their second derivatives, the second derivative of a sample has been expressed as a linear combination of the second derivatives of the pigments in the sample [1]:

$$f''_{KM}(R_M) = b_1 \cdot f''_{KM}(R_{C1}) + b_2 \cdot f''_{KM}(R_{C2}) + \ldots + b_n \cdot f''_{KM}(R_{Cn}) \quad (5)$$

The aim of this study is to propose a general method to quantify the amount of a pigment present in a mixture without having to develop specific patterns for each base.

The standard EN 12878:2014 [40] establishes that 10 wt% of pigment in the mixture should not be exceeded. Since it also recommends a maximum of 5 wt% of pigment in surveys, this will be the highest pigment concentration considered for the calibration curves in the present study. Moreover, the industrial content of pigments in mortars is usually lower than 3 wt%, which is far below the former 5 wt%.

With the aim of reaching the objectives of the present study, patterns from a white reference base were made. Several whitish-mortar base samples were prepared. In addition to this, in order to study the influence of the base color in the quantification of the mixture components, mortars colored with a tinting amount similar to those used in the mixtures were prepared for validating the proposed method even when the bases happened to be strongly tinted.

2. Materials and methods

2.1. Materials

In the present survey, three mineral pigments and two different mortars as well as a white standard have been used for the study. The mineral pigments were namely: Bayferrox Ochre 920C (Ochre), Bayferrox Red 130C (Red) and Green Chromium Oxide GN (Green), all from Lanxess Energizing Chemistry and supplied by Grupo Puma, Cemkosa (Córdoba, Spain). The studied mortars were a single-layer type mortar commercially available under the name Morcendur-R (MR) and a coating type mortar commercially available under the name Morcen Sec thin coat (MS), both from Grupo Puma. The standard white, $BaSO_4$ (DIN 5033) was supplied by Merck.

As it can be observed in the XRD patterns (Fig. 1), the starting pigments consisted of a single species; thus, Ochre was goethite (α-FeOOH, 29-0713 [41]), Red hematite (α-Fe_2O_3, 33-0664 [41]) and Green Cr_2O_3 (38-1479 [41]).

The two mortars MR and MS are a mixture of calcite ($CaCO_3$, 05-0586 [41]), dolomite ($CaMg(CO_3)_2$, 36-0426 [41]) and Portland cement (mainly calcium silicate, Ca_2SiO_4, 23-1043 [41] and Ca_3SiO_5, 42-0551 [41]). The mortars have hydraulic nature. The dolomite is the main phase in both mortars. The amount of dolomite is higher in MR mortar than in MS mortar. The amount of calcite in MS mortar is higher than in MR mortar (Figs. 2 and 3).

Eighteen different bases have been used as bases for the mixtures, being three of them the former White and mortars MR and MS. The other fifteen bases are colored ones made by adding one sole pigment to White, mortar MR or mortar MS (see Table 1).

The coloring process is a mixture (in a dry way) of a mortar with grinding mineral pigments in a mill.

Eighteen two-color mixtures in a whitish base (Table 2) and 15 two-color mixtures in colored bases (Table 3) have been prepared.

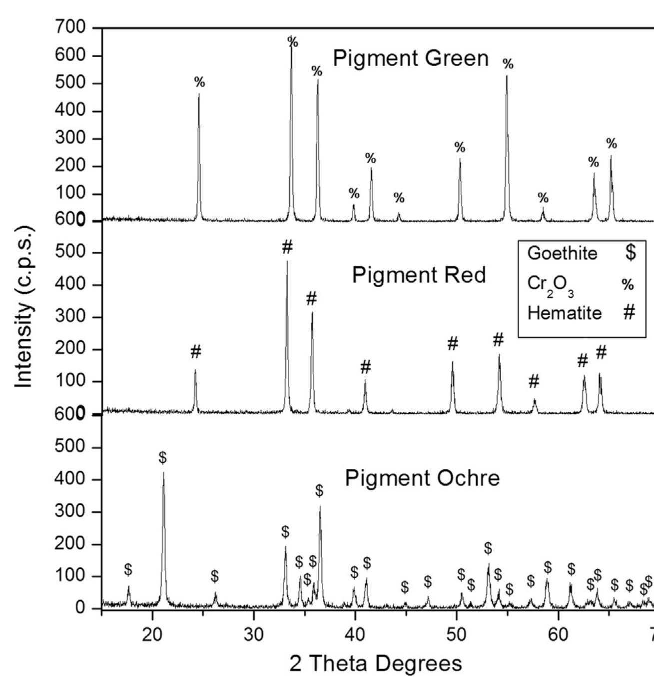

Fig. 1. XRD patterns for pigments Ocher, Red and Green.