



## Tutorial article

# The chromatic variance matrix in digital image based methods for the potential evaluation as quantitative procedures



Angel Lopez-Molinero <sup>\*</sup>, Javier Jimenez-Lamana

Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Zaragoza, Spain

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## ABSTRACT

The dispersion matrix or chromatic variance of digital images was proposed to characterize the color amplitude and hence the potential sensitivity of Digital Image Colorimetric determinations. The study provided a generalizable model that quantitatively explained the influence of the analyte and instrumental factors in the color measurements. RGB reflected colors of the yellow-orange complex formed by Hydrogen Peroxide with Ti(IV) were captured by a compact digital camera in an experimental dynamic range. In this context, the dispersion Covariance-Variance matrix of the color information provided the amplitude of the chromatic system. Subsequently Analysis of Variance and Multivariate Statistical demonstrated that 87% of the chromatic variance could be justified by the Hydrogen Peroxide concentration influence, while the camera, as an instrumental effect, and the preparation method, accounted for the 10% and 3%, respectively. Also, the behavior of alternative chromatic variables has been compared. Hydrogen Peroxide presented a ready and efficient digital determination in the range 1–40 mg L<sup>-1</sup>. Statistical comparison with standard procedures demonstrated the absence of systematic errors.

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## 1. Introduction

Digital images obtained by commercial off-the-shelf (COTS) devices such as digital cameras, webcams, mobile phones, scanners or tablets are currently implemented in many different scientific and technical fields [1]. They have been proposed in quantitative measurements [2–4] to produce results at affordable cost-efficiency. Two methods could be distinguished according to the wavelength working range: i-Digital Image Colorimetry, DIC, based on RGB colors, with measurements in the spectral visible range [5–6] which has demonstrated a high potential. And ii-Hyperspectral-or Multi-spectral techniques which work at longer wavelengths [7,8].

The principles of the imaging methods for quantitative measurements are based in the singular behavior of detectors formed by Complementary Metal-Oxide Semiconductors (CMOS) or Charge Coupled Detectors (CCD). They produce sensitive signals, at common and causal conditions, even in portable equipment [9,10]. The number of applications has undergone a spectacular increase in recent years and in many different fields. Such as forensic science [11], clinical analysis [12,13], environment [14,15] or food control [16,17,18]. All of them are faced to answer to important challenges of high demand in the number of essays to maintain the levels of quality in their fields.

We discuss in this paper the quantitative potential of DIC based on chromatic variance that the RGB colors of digital images captured. We changed the perspective of the Covariance Matrix, from the Dispersion Matrix to the Amplitude Matrix. Hence this variance provided the sensitivity potential of the method. It was firstly calculated from direct experimental chromatic values. Secondly, and separately, an ANOVA study deals with the influence of three key chromatic sources: the analyte, the instrument and the method. The congruency between both results allowed to develop a chemometric prediction model of the quantitative potential of DIC and interpretation of the influences.

Finally, a new DIC method was implemented for the quantitative determination of Hydrogen Peroxide as a ready method. It was developed with digital images captured by a compact camera and adapted to practical quality control. The method could be compared with other determinations described in the bibliography, such as the applications in qualitative and quantitative determinations of Hydrogen Peroxide (HP) at levels of minor-major component [19,20] or with determinations by sensitive [21] or classical colorimetry [22,23].

## 2. Material and methods

### 2.1. Instruments and software

A Hewlett Packard model 8452A Diode Array molecular absorption spectrometer was used. This has a 2 nm resolution in the spectral range 190–820 nm.

<sup>\*</sup> Corresponding author at: Department of Analytical Chemistry, Faculty of Sciences University of Zaragoza, P.O. Box: S-50009, Zaragoza, Spain.  
E-mail address: [anlopez@unizar.es](mailto:anlopez@unizar.es) (A. Lopez-Molinero).

An Olympus SP-510UZ, digital compact camera, with the characteristics shown in Table 1 was used.

MATLAB R2011b (Mathworks, Natick, MA, USA) was used for reading RGB colorimetric data and to calculate the parameters of the Factor Analysis. Excel (Microsoft Excel, Redmond, WA, USA) was also used.

### 3. Reagents

All the reagents were of analytical grade. Deionized water from a Milli Q water purification system was always used, unless otherwise stated.

A HP 30% (w/w) solution (Panreac PA, Spain) was used. Diluted solutions were prepared by appropriate addition of deionized water in calibrated flasks. The solution content was periodically checked and standardized by titration with  $\text{KMnO}_4$  (Panreac PA) standard solution.

Standard Ti(IV)  $600 \text{ mg L}^{-1}$ , in 2.9 M sulfuric acid solution, was prepared by dissolution of 0.1 g  $\text{TiO}_2$  (Panreac PA) with 6.4 g  $(\text{NH}_4)_2\text{SO}_4$  and 16 ml of concentrated sulfuric acid (Panreac PA). The mixture was heated and stirred in a hot plate until dissolved and finally diluted to 100 ml in a volumetric flask.

#### 3.1. Colorimetric procedure

Standard calibration HP solutions were directly prepared in 4.5 ml spectrophotometric cuvettes ( $1 \times 1 \times 4.5 \text{ cm}$ ; 1 cm optical path) using the following procedure: i) a constant volume of 1.5 ml standard Ti(IV) solution was added in all cases; ii) 1.5 ml of standard HP solutions, of variable concentrations, were added. The total volume was maintained at 3.0 ml. The solutions were gently stirred manually and then measured. The volume was measured by micropipette in all cases.

Chemical and disinfectant sample solutions were similarly prepared but with the addition of a diluted sample volume, instead of the standard HP solution.

#### 3.2. Imaging measurements

Images of the calibration and sample solutions, in standardized spectrophotometric cuvettes, placed together in an open laboratory-made box, were taken under indirect constant artificial lighting produced by a white cool fluorescent lamp of 36 W. The camera was set to automatic focus mode and all samples were placed to the same equidistant 30 cm length. The size of the pictures was the smallest that could be taken with the camera. The pictures were transferred to a computer using Microsoft Photo Editor (Microsoft XP). The intensity of the RGB reflected colors was obtained from representative regions of 100 pixels, located in each spectrophotometric cell. Individual RGB intensities were measured, in each pixel, with a program

**Table 1**  
Characteristic and optimum conditions for the image capture.

Camera olympus SP-510UZ: resolution	7.1 M pixels
'CCD' Sensor	1/2.5"
Conditions to take pictures	
Function 'mode'	Automatic
Lighting	Indirect, Fluorescent white lamp, 36 W
Focus	30 cm, without zoom.
Exposure	White laboratory-made box Spectrophotometric cuvettes at 30 cm focus length
Record pictures	'jpg' format, 1600 × 1200 pixels
Image processing	
Transfer images to the computer	Microsoft Photo Editor for Windows 7
Color Measurement	Matlab R2011b,

developed by us in Matlab. Finally, the mean and standard deviation were computed.

## 4. Results and discussion

### 4.1. Chromogenic basis

Hydrogen Peroxide reacts with Ti(IV) to give a yellow-orange complex. Conditions described in the literature for the Ti(IV) determination [23] were adapted to our procedure. Thus, typical experiments were prepared in standard spectrophotometric cuvettes where solutions contained constant: 0.1 M sulfuric acid and  $1.3 \times 10^{-3} \text{ M Ti(IV)}$ . The content of HP concentration was ranged in the dynamic interval from 0.1 to  $40.0 \text{ mg L}^{-1}$ .

The colorimetric results showed, in Fig. 1, an apparent enhancement of the yellow-orange luminosity of the solutions as the HP concentration increased. This tendency is characterized by a decrease in the reflected basic Blue color. And the Molecular Absorption Spectrophotometric spectra of these solutions displayed the absorbance increase at 406 nm.

### 4.2. Imaging conditions

Image captures were carried out in an open simplified set-up consisting of a white laboratory-made box, with homogeneous illumination of a cool white fluorescent, and a commercial digital camera. The automatic function of the camera was selected in all cases. The highest reproducibility was obtained with cuvettes located at the lowest focal length: 30 cm. Other conditions were studied and characterized in a similar manner to those described in previous publications [5,6].

RGB color intensities, mean and standard deviation, were measured and computed by Matlab in regions of interest, ROI, with different sizes of: 21–100–1500–3000–15,000 pixels. They did not show significant influence in the results.

For the rest of conditions, the most convenient and reproducible values were selected. These conditions are described in the experimental section as a standard protocol.

### 4.3. Chromatic variance in the digital image and comparison of chromatic variables

The dynamic range of HP concentrations vs. the intensity of RGB and T defined as  $T = R + B + G$  (1) colors can be depicted in Fig. 1. The chromatic information of the experiment formed the initial chromatic matrix  $\mathbf{X}$ . It is composed by  $n$  rows, or points of the dynamic experiment, and 3 columns, or the number of chromatic variables, RGB color bands:

$$\mathbf{X} = \begin{bmatrix} x_{1,1} & x_{1,2} & x_{1,3} \\ \dots & \dots & \dots \\ x_{n,1} & x_{n,2} & x_{n,3} \end{bmatrix} \quad (1)$$

After centring each column of  $\mathbf{X}$  matrix, the  $\mathbf{U}$  matrix was obtained and hence the dispersion matrix or Covariance-Variance ( $\mathbf{X}$ ) was computed:

$$\text{Cov}(\mathbf{X}) = \left( \mathbf{U}^T \mathbf{U} \right) \frac{1}{(n-1)} \quad (2)$$

Its diagonal elements represented the variance of the RGB chromatic variables. The sum deals with the total color variation in the chromatic experiment. It was interpreted as the Color Amplitude in the experiment and consequently as its potential of sensitivity.

The results, in Table 2, describe the total variance of the chromatic experiment and its distribution. It could be seen that B accounted for 86.5%, and R and G accounted for 7.3 and 6.2% of the chromatic variance, respectively.

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