

Misapplication of the parametric statistics to calculate the uncertainties when calibrating commercial spectrophotometers

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Nowadays, when calibrating spectrophotometers, the uncertainties are calculated based on the premise that the obtained measurements have a Gaussian distribution, but there is no certainty that the latter is completely true. The aim of this work is to show that, when measuring reference materials with different spectrophotometers, most of the results do not have, for all the points in the visible spectrum of the spectral curve, a Gaussian distribution. Also, this distribution is not present in measurements of the chromatic coordinates of these materials. These measurements were performed with two integrating sphere spectrophotometers; a Minolta 2600d [®] (portable) and a Gretag Macbeth 7000 [®] (bench) equipment, under the same measurement parameters and conditions of repeatability, as well as controlled environmental conditions, *i.e.*, $20 \pm 1^\circ\text{C}$. Since a Gaussian distribution is needed to use parametric statistics to calculate the combined uncertainties and consequently, the expanded ones, the statistical method currently used is erroneous. Thus, parametric statistics should not be used to calculate the spectrophotometers' uncertainties.

Keywords: Spectrophotometer; metrology; chromatic coordinates; colorimetry.

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1. Introduction

In general, in the field of metrology, tools of parametric statistics are used to calibrate spectrophotometers of fixed resolution (spectrophotometers) [1, 2]. This statistic treatment is applied without any proof that is the most adequate to quantify the combined uncertainty of the measurements [3, 4].

In the area of statistics, a sample is considered representative to determine the shape of the distribution of a population if it contains more than 100 data. If the distribution of the population is Gaussian, so will be any sample that we take from it [1, 2].

The measurements obtained from the spectrophotometer, *i.e.*, the chromatic coordinates, are correlated variables, and the way to obtain them is purely mathematical [5]. The chromatic coordinates $L^*a^*b^*$ are obtained from the tristimulus values, which are related to the measured object as well as the illuminant used to perform the measurements [6, 7]. Equations (1), (2), and (3) show the relationship that exists between the tristimulus values and these coordinates.

$$L^* = 116 \left(\frac{Y}{Y_n} \right)^{1/3} - 16, \quad (1)$$

$$a^* = 500 \left(\left(\frac{X}{X_n} \right)^{1/3} - \left(\frac{Y}{Y_n} \right)^{1/3} \right), \quad (2)$$

$$b^* = 200 \left(\left(\frac{Y}{Y_n} \right)^{1/3} - \left(\frac{Z}{Z_n} \right)^{1/3} \right), \quad (3)$$

where X, Y, Z are the tristimulus values of the measured object, and X_n, Y_n, Z_n are the tristimulus values of the employed illuminant, which, in this case, is D65.

The tristimulus values of the objects are calculated from: the tristimulus values of the standard observer $\bar{x}_\lambda, \bar{y}_\lambda, \bar{z}_\lambda$, from the spectral reflectance factor of the object ρ_λ , and from a parameter S_λ that represents the illuminant [4].

$$X = \sum_{\lambda=400}^{\lambda=700} S_\lambda \rho_\lambda \bar{x}_\lambda, \quad (4)$$

$$Y = \sum_{\lambda=400}^{\lambda=700} S_\lambda \rho_\lambda \bar{y}_\lambda, \quad (5)$$

$$Z = \sum_{\lambda=400}^{\lambda=700} S_\lambda \rho_\lambda \bar{z}_\lambda. \quad (6)$$

As already mentioned, Eqs. (1), (2), and (3) show the correlation that exists between the chromatic coordinates, which makes these results mutually intertwined. On the contrary, by making a direct measurement of the reflectance from which the tristimulus values are obtained, such correlation is avoided. Due to the latter, it is proposed to analyze the distributions in the reflectance curves instead of doing it in the chromatic coordinates. This in order to see if a Gaussian behavior is obtained for different wavelengths by avoiding the correlation between the coordinates $L^*a^*b^*$.

This paper presents the measurements obtained with two commercial spectrophotometers from different companies,

showing that the distributions given by the equipment when measuring these materials are not all Gaussian and, as a consequence, the use of parametric statistics is not the most appropriate to quantify these uncertainties, especially in the chromatic coordinates.

2. Methodology

Two spectrophotometers were used: a portable Minolta 2600d [®] and a bench Gretag Macbeth 7000A [®]. The white ceramic of each of the spectrophotometers was measured 35 times in its own equipment by three technicians. A total of 105 measurements were obtained for each spectrophotometer, which are sufficient to be considered as a statistically representative sample to determine the shape of the population distribution. Each ceramic had its chromatic coordinates $L^*a^*b^*$ and the spectral reflectance curves (from 400 nm to 700 nm) measured. The reflectance curves were obtained at 100% and 0%.

The chromatic coordinates at intervals of 10 nm between data points of three diffuse reference materials with different hue were measured 15 times under the following conditions: specular included component, excluded ultraviolet component, medium aperture, and lighting conditions / diffuse detection / 8°. The entire experimental process was carried out under repeatability conditions [3], controlled environmental conditions, and using certified reference materials.

3. Results

The histograms obtained for the coordinates $L^*a^*b^*$ with the Macbeth 7000A are shown in Fig. 1 and those obtained with the Minolta 2006d equipment are shown in Fig. 2. At first sight, it is observed that only in the case of the Minolta 2006d equipment for the b^* coordinate there is a certain Gaussian tendency -although it is not very well defined-, and in the rest of the coordinates, for both equipment, this tendency is not present. This was expected to happen, since we are plotting correlated variables by plotting the chromatic coordinate we are plotting correlated variables, as can be seen from Eqs. (1), (2), and (3).

It can be seen in Figs. 3 and 4 the spectral reflectance curves that were obtained with both the Macbeth 7000A as well as the Minolta 2006d devices, respectively. These measurements were made to avoid the correlation that exists in the case of the histograms of the chromatic coordinates. Thus, we can check if this direct measurement gives us a Gaussian behavior for each different wavelength of the measured spectrum. Each curve is shown with the corresponding histograms at each wavelength.

Afterwards, a comparison between the histograms is made for the best and worst cases, with the purpose of observing in which wavelengths exists (or not) a Gaussian behavior.

It can be observed that one of the best matches for the measurements made with the Macbeth 7000A equipment is at the wavelengths of 430 nm and 460 nm [Fig. 5a) and 5b)],

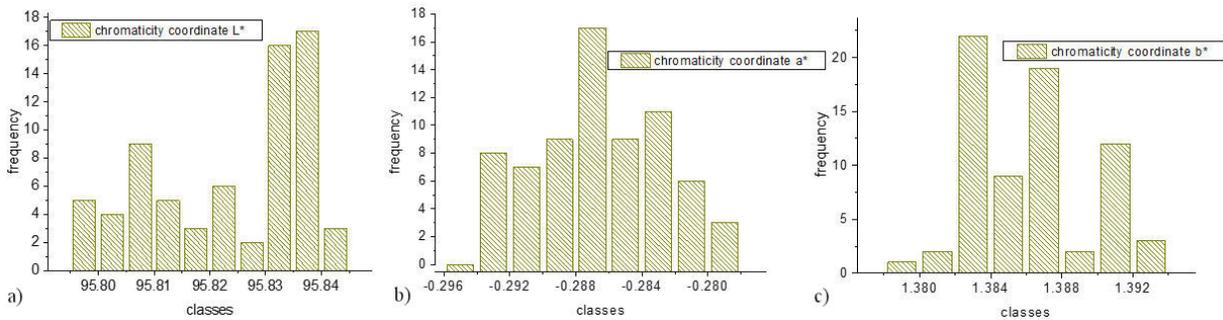


FIGURE 1. Histograms of the chromatic coordinates $L^*a^*b^*$ of the white ceramic measured with the Macbeth 7000A spectrophotometer.

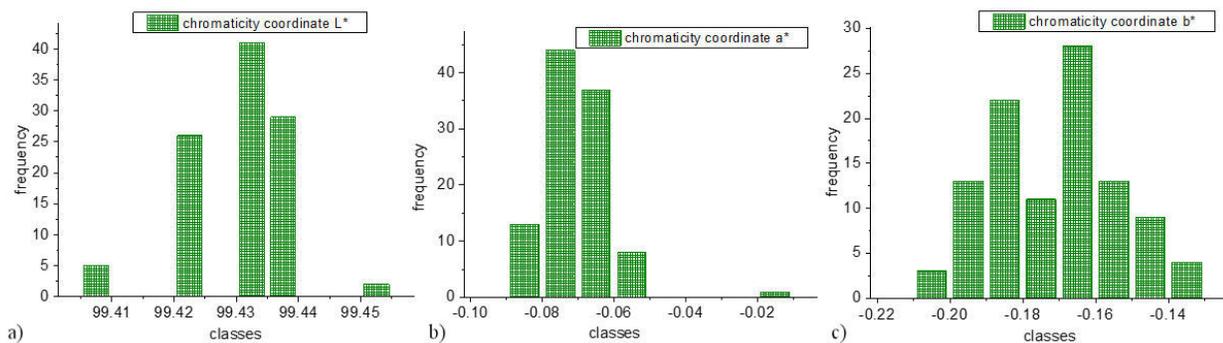


FIGURE 2. Histograms of the chromatic coordinates $L^*a^*b^*$ of the white ceramic measured with the Minolta 2600d spectrophotometer.

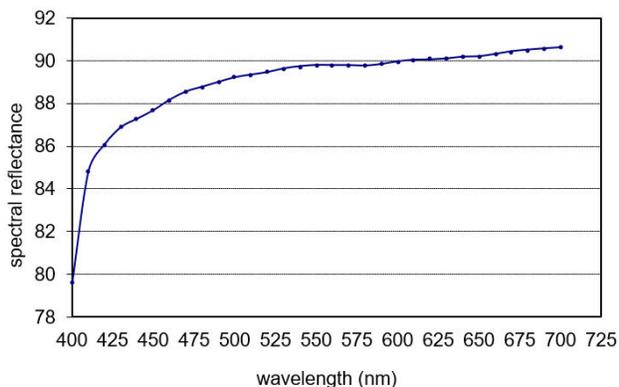


FIGURE 3. Spectral reflectance curve for the white ceramic reference of the Macbeth 7000A spectrophotometer.

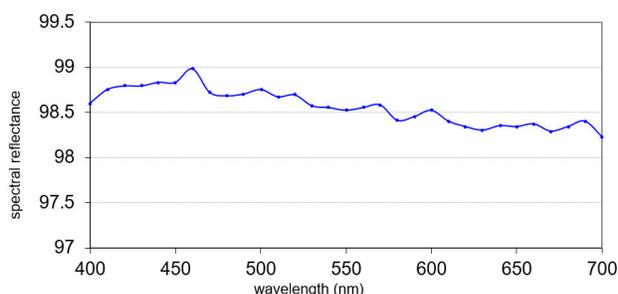


FIGURE 4. Spectral reflectance curve for the white ceramic reference of the Minolta 2006d spectrophotometer.

respectively, and one of the worst is at the wavelength of 700 nm [Fig. 5c)], because the distribution is practically square.

The histograms obtained with the Minolta 2006d equipment show that the best concordances are at the wavelengths of 570 nm and 590 nm. The opposite case happens for the wavelengths in 500 nm and 560 nm, since the distributions are almost square, as shown in the Figs. 6a), 6b), 6c), and 6d), respectively.

The behavior of the distribution in the other wavelengths, both the ones obtained with the Macbeth 7000A equipment and those obtained with the Minolta 2600d, are summarized

TABLE I. Behavior of the different wavelengths obtained with the Macbeth 7000A and Minolta 2600d spectrophotometers.

Wavelength [nm]	Macbeth 7000A	Minolta 2600d	Wavelength [nm]	Macbeth 7000A	Minolta 2600d
400	NoDG	SesDG	560	NoDG	NoDG
410	SesDG	NoDG	570	NoDG	SiDG
420	SesDG	NoDG	580	NoDG	SesDG
430	SiDG	SesDG	590	NoDG	SiDG
440	NoDG	SesDG	600	NoDG	SesDG
450	SesDG	NoDG	610	SesDG	NoDG
460	SiDG	SesDG	620	SesDG	SesDG
470	SesDG	SesDG	630	NoDG	SesDG
480	SesDG	SesDG	640	NoDG	SesDG
490	SesDG	NoDG	650	NoDG	NoDG
500	NoDG	NoDG	660	NoDG	SiDG
510	NoDG	NoDG	670	NoDG	NoDG
520	NoDG	NoDG	680	SesDG	SiDG
530	NoDG	NoDG	690	SesDG	SesDG
540	NoDG	NoDG	700	NoDG	NoDG
550	SesDG	NoDG			

in Table I, where the following nomenclature was used: without Gaussian distribution (NoDG), with Gaussian distribution (SiDG), and with bias in the Gaussian distribution (SesDG). The evaluation of the histograms was made using the criterion of the area under the curve [2].

From the results of Table I, it can be seen that, for the case of the measurements made with the Macbeth 7000A, only 6.5% of the data has a normal variability, while 58.1% do not have it, and the rest (35.4%) has a biased Gaussian distribution, *i.e.*, most of the points do not show a Gaussian behavior. On the other hand, from the data obtained with the Minolta 2600d equipment, it can be observed that only 12.9% of the data have a normal distribution, while 48.4% do not have it, and the rest (38.7%) has a normal biased Gaussian distribution.

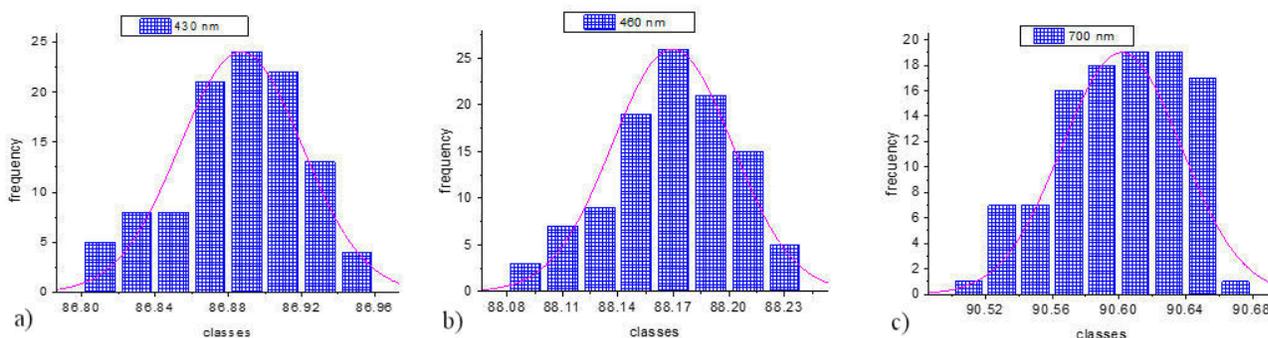


FIGURE 5. Histograms of the Macbeth 7000 spectrophotometer for the following wavelengths: a) 430 nm, b) 460 nm, and c) 700 nm.

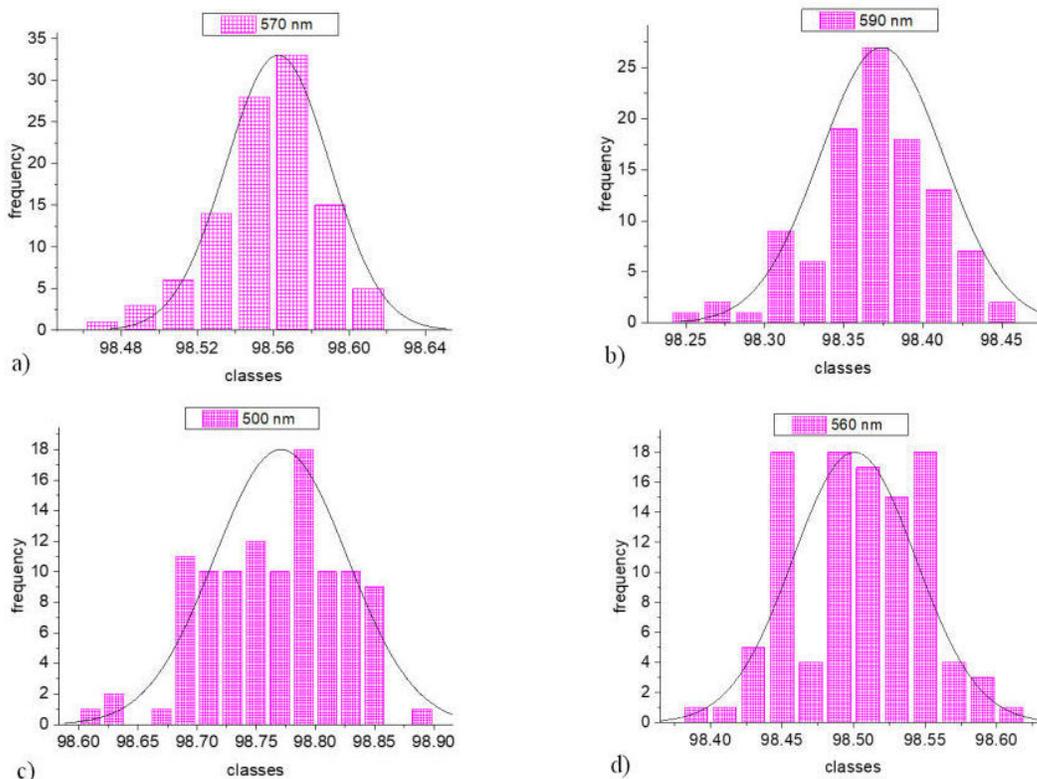


FIGURE 6. Histograms of the Minolta 2600d spectrophotometer for the following wavelengths: a) 570 nm, b) 590 nm, c) 500 nm, and d) 560 nm.

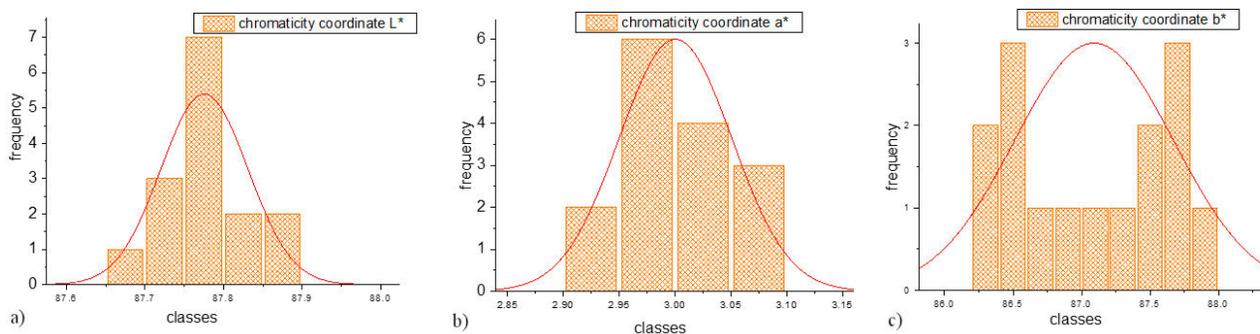


FIGURE 7. Histograms of the chromatic coordinates $L^*a^*b^*$ for the reference material with yellow hue measured with the Macbeth 7000A spectrophotometer.

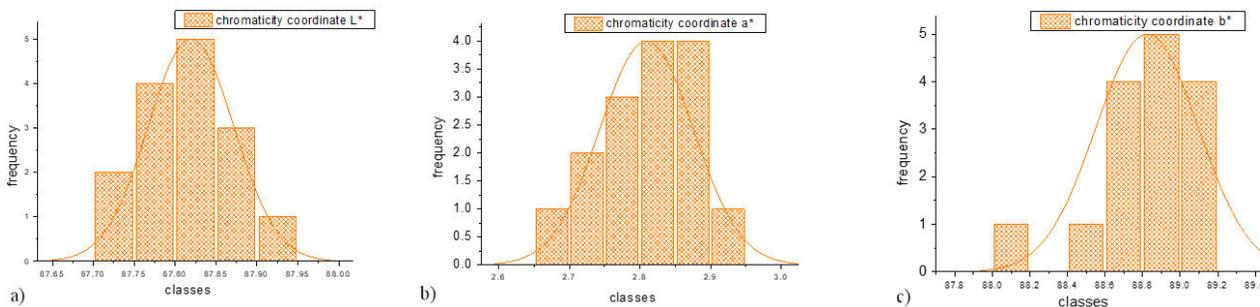


FIGURE 8. Histograms of the chromatic coordinates $L^*a^*b^*$ for the reference material with yellow hue measured with the Minolta 2600d spectrophotometer.

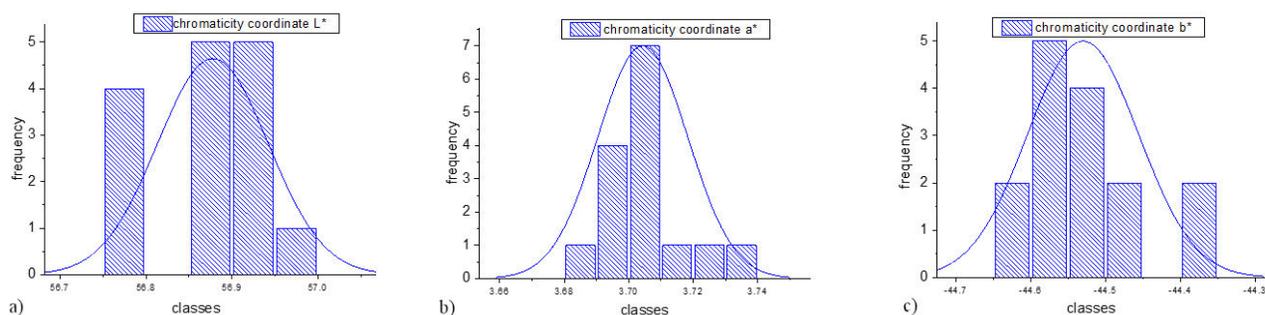


FIGURE 9. Histograms of the chromatic coordinates $L^*a^*b^*$ for the reference material with blue hue measured with the Macbeth 7000A spectrophotometer.

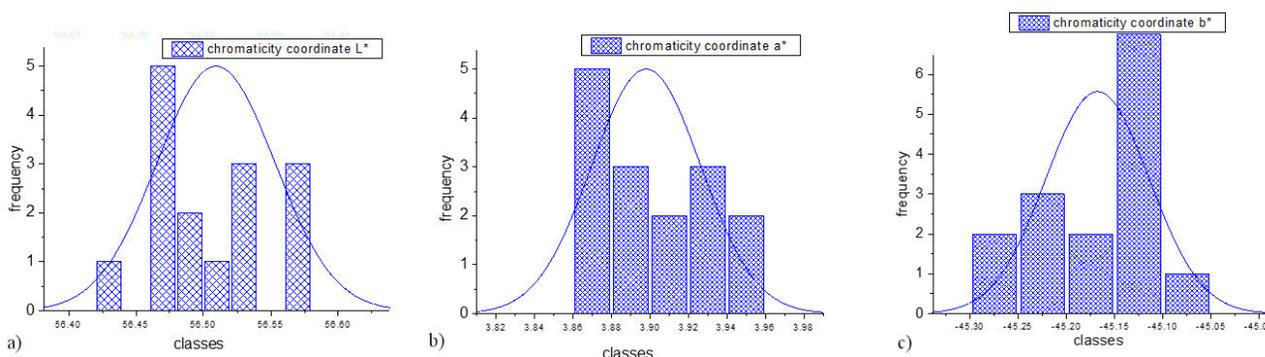


FIGURE 10. Histograms of the chromatic coordinates $L^*a^*b^*$ for the reference material with blue hue measured with the Minolta 2600d spectrophotometer.

In the case of the three reference materials with different hue, as already mentioned, the measurements of their chromatic coordinates were made under the same conditions as the ones used to measure the white ceramics. The results are shown in Figures from 7 to 12.

It can be seen from Figs. 7 and 8, which show the measurements made to the reference material with yellow hue, that those made with the Macbeth 7000A equipment do not have a Gaussian distribution, while those made with the Minolta 2600d have a better behavior. Figures 9 and 10 show that, for both devices, the measurements of the chromatic co-

ordinates of the reference material with blue hue do not have a Gaussian distribution.

Figures 11 and 12 show that the measurements of the chromatic coordinates of the reference material with red hue do not have a Gaussian distribution in either one of the two equipment. The existing variability is due only to the fact that the measurements are being performed with different equipment, since all measurements were made under the same conditions of both repeatability and environmental, the latter were controlled. The reference materials used are certified.

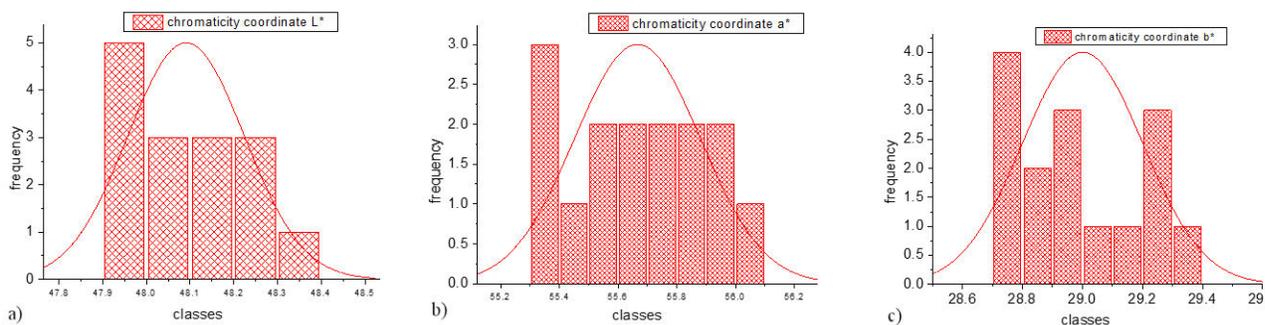


FIGURE 11. Histograms of the chromatic coordinates $L^*a^*b^*$ for the reference material with red hue measured with the Macbeth 7000A spectrophotometer.

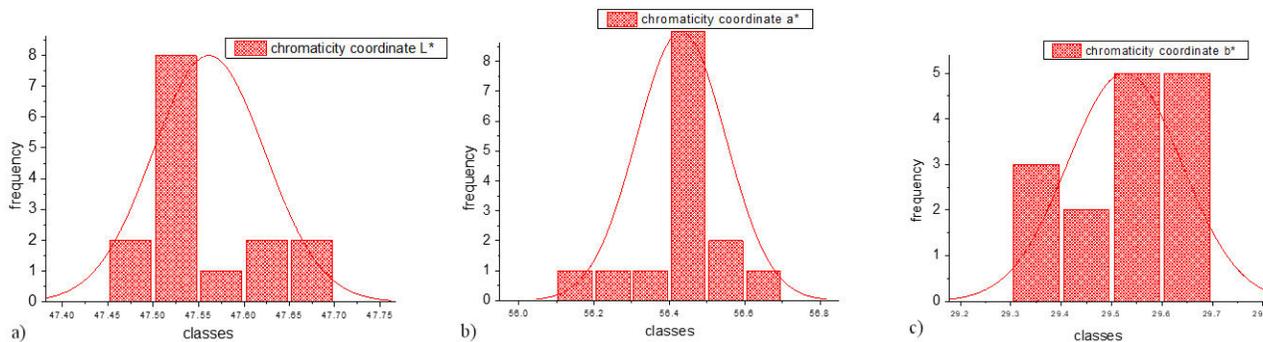


FIGURE 12. Histograms of the chromatic coordinates $L^*a^*b^*$ for the reference material with red hue measured with the Minolta 2600d spectrophotometer.

4. Conclusions

The histograms of the chromatic coordinates for the white ceramic of each equipment show that the variability for both of them does not have a Gaussian distribution in every wavelength. In some cases, denominated as “best cases”, the distributions are Gaussian, but there are others in which their distributions are practically square. As it has been mentioned before, the histograms were obtained by performing 105 measurements for each sample, which is sufficient to statistically determine the shape of the population distribution.

In the case of the reference chromatic materials, it is observed that the distributions of the chromatic coordinates are not the same from one hue to another, and also, that only in some cases Gaussian distributions are found.

Since, the current calibration from this kind of equipment

is carried out in chromatic coordinates, and, as it is observed not all of them have a Gaussian distribution, it is concluded that the calculation of the statistical uncertainty should not be performed in this magnitude to avoid using correlated variables. The calculation should be made only in the wavelength scale and only in those where there is a better concordance with the Gaussian distribution, in order to be able to use the parametric statistics and, thus, establish the acceptable level of confidence; otherwise, non-parametric statistics would have to be used.

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