Estimation of spectral bands of metallic coatings assessed by multi-angle spectrophotometers

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Abstract

Using three commercial multi-angle spectrophotometers, we have measured the reflectance spectra over catalogues from the automotive industry that contain metal and interference pigments and involve changes in hue and lightness at certain viewing angles. We have used principal-component analysis to determine the spectral distribution of their constituents in order to compare between the basis functions assessed by each instrument and common measurement geometry and to examine differences between multi-angle spectrophotometers. Our results corroborate that at least a minimum of 8 basis vectors are needed to explain 99.99% of the total variance. Comparisons conclude the existence of differences in those vectors associated with interference pigments. Reconstruction of the original reflectance spectra suggest that those detection geometries close to the specular reflection provide the least accurate results.

Introduction

Metallic, pearl-like and interference pigments has produced a new class of coloring materials during the past fifty years [1-3]. In comparison with conventional absorbing pigments, a wider range of varying colors is observed when the illumination position, the viewing angle or both are changed. The spectral behavior of these special pigments come from processes based on physical optics, namely, multilayer interference reflectors, diffraction and light scattering by small structures or particles. They imitate two- and three-dimensional natural photonic structures such as the wings of certain insects and minerals [4, 5] (e.g. morpho butterflies, opals, etc.). These synthetic materials are useful. Goniochromism is very important in many industrial activities, such as automotive coatings, cosmetics, plastics, security inks, building materials and visual simulation of virtual environments [6, 7]. Certainly, measuring and modeling goniochromatic materials will be of great interest in the future for many more applications. In addition, the remarkable development of these special effect pigments has necessitated a new variety of instruments. Modern multi-angle spectrophotometers have designed to measure the bidirectional reflectance distribution function (BRDF) over a limited number of illumination and detection or viewing positions [8, 9]. The measurement of the spectral BDRF is not easy if it is done sampling metallic and pearlescent color samples [10]. Therefore, some instruments are designed to measure the spatial distribution of the reflectance factor in different geometrical configurations. In most of them, three or five geometry configurations are implemented, as established by standards DIN-6175-2 [11] and ASTM E2175-02 [12], respectively (see Table 1).

Table 1: Illumination and observation angles of a commercial multi-angle-spectrophotometer compared in this work.

Geometries					
Incident angle	45°	45°	45°	45°	45°
Detection angle (aspecular)	120° (+15°)	110° (+25°)	90° (+45°)	60° (+75°)	25° (+110°)

This kind of multi-goniospectrophotometer has been used in several industrial sectors (coatings, automotive industry, etc.) for some years, but in other sectors more complete multi-gonio-spectrophotometers have appeared in recent years. Studies about the inter-comparison between spectrophotometers have appeared in the last years [13, 14]. However, relative little attention has been focused in the study of multi-gonio-spectrophotometers. The work of Chorro et al., [15] has applied suitable test for repeatability and reproducibility to examine their accuracy, measurement errors, significance and acceptability [15]. The repeatability [16] is the capability of an instrument for repeating identical measurements under the same conditions and, in general, it can be evaluated as the standard deviation of several measures of the same object. On the other hand, the reproducibility [17] is the capability of an instrument for reproducing the expected value when the conditions have changed, for example, when the object, the instrument or the operator is not the same.

In this sense, the aim of this study is to examine differences between multi-angle spectrophotometers using spectral correlation analysis. We investigate their intrinsic variability by principal component analysis (PCA). In color technology, PCA is a useful data analysis method that project raw reflectance spectra onto few vector functions [18, 19]. PCA expansion provides a linear decomposition. Each spectral reflectance function can be approximated by the linear addition of a small number of vector functions. The number of vectors will depend on the accuracy of the color application. One of the motivations is dimensionality reduction. Large datasets can be significantly reduced selecting those vectors functions that account most of the variance. A second reason is the estimation of colorants in the statistical sense. PCA provides valuable information on their spectral bands when they added together. We propose to examine possible differences between commercial multi-angle spectrophotometers by PCA. We compare their derived basis functions over a common goniochromatic database for identical measurement geometries. This simplified the analysis to few vector functions. We restrict our analysis to those illumination-detection geometries established in the DIN 6175-2 [11] and in the ASTM E2175-02 [12] standards. This also summarized the study to key geometries that takes into account the measurement of gonio-appearance.

The work is organized as follows. Firstly, we describe the synthetic goniochromatic database and the multi-angle spectrophotometers. We also briefly describe PCA. After that, we derive the basis functions in each instrument by PCA. At each measurement geometry, we analyze the possible differences between instruments. We also construct the reflectance spectra from a limited number of basis functions. Furthermore, at the end a discussion can be found with the main conclusion of this work.

Methods

Spectral database

We have 91 metallic, interference, luster and pearlescent samples, collected by different manufacturers. They belong to catalogues from the automotive industry. The 91 goniochromatic samples were measured by three multi-gonio-spectrophotometers, after a long time of stand-by (higher to 20 min), using their corresponding matte white standards. The temporal interval between the measurements done in each laboratory was not longer to 2 months. Relative reflectance factors from each sample and colorimetric coordinates under illuminant D65 and CIE-1931 XYZ standard observer in the CIELAB color space were obtained (Figure1).

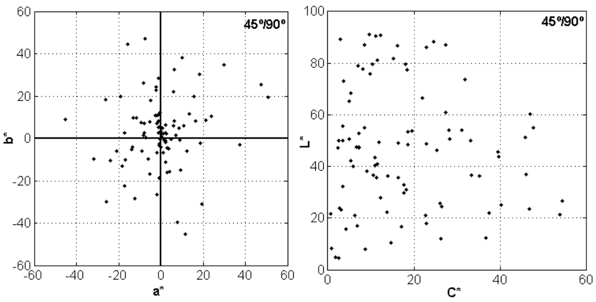


Figure 1. Colorimetric data under the illuminant D65 and the CIE-XYZ 1931 standard observer in the CIELAB colour space measured by the X-Rite MA98 multi-angle spectrophotometer.

Instrument description

The three multi-gonio-spectrophotometer used in this work were:

- The multi-gonio-spectrophotometer X-Rite MA68II. It is a portable device and has 5 geometries of illumination/observation, following the ASTM 2194 and DIN 6175-2 standards. These geometries are summarized in the Table 1. This instrument belongs to the Technological Institute of Optics, Color and Imaging-AIDO (Valencia, Spain).
- The multi-gonio-spectrophotometer Datacolor FX10. It is a desktop device and has 10 different geometries of illumination/observation (Table 1), including the 5 standard geometries of the MA68II. These geometries are also summarized in the Table 1. This instrument belongs to the Color & Vision Group of the University of Alicante (Spain).
- The multi-gonio-spectrophotometer X-Rite MA98. It is a portable device and has 19 different geometries of illumination/observation, including 8 geometries of the FX10 and 5 of the MA98. This instrument also belongs to the Color & Vision Group of the University of Alicante (Spain).

Therefore, in this work we worked with the 5 common geometries: 45º/120º, 45º/110º, 45º/90º, 45º/60º and 45º/25º, which fulfill the recent recommendations (ASTM E2539-08) for measurement of gonio-appearance of metallic coatings.

Principal component analysis

PCA analyzes the covariance or the correlation matrix $\mathbf{C}$ of the reflectance measurements described above. To uncover the basis functions that summarize the reflectance dataset in the uncorrelated components, $\mathbf{C}$ must be transformed to a diagonal matrix $\mathbf{D}$ by eigenanalysis. The elements of $\mathbf{D}$ off-diagonal are all zero whereas as, $\mathbf{D}_{ii} = \sigma_i^2$, where σ_i^2 is the *i*-th eigenvalue. The total variance is therefore the sum of the diagonal elements. Let $\boldsymbol{\lambda}$ the eigenvalue matrix and $\mathbf{x}$ the eigenvector matrix:

$$\mathbf{Dx} = \boldsymbol{\lambda}\mathbf{x} \quad (1)$$

There are as many eigenvalues as dimensions are in the original reflectance dataset (i.e. in our case, wavelengths). Each spectral reflectance function R_j is the weighted linear combination of $\mathbf{x}_i$:

$$R_j \cong \alpha_1\mathbf{x}_1 + \alpha_2\mathbf{x}_2 + ... + \alpha_n\mathbf{x}_n \quad (2)$$

The coefficients α_i indicate the coordinates or the principal components in the new basis vectors. For example, $\mathbf{x}_2$ is uncorrelated with $\mathbf{x}_1$ and contributes to maximize the total variance accounted for and so on. It is expected that few eigenvectors $\mathbf{x}_i$ will provide an accurate description of the entire goniochromatic database.

Results

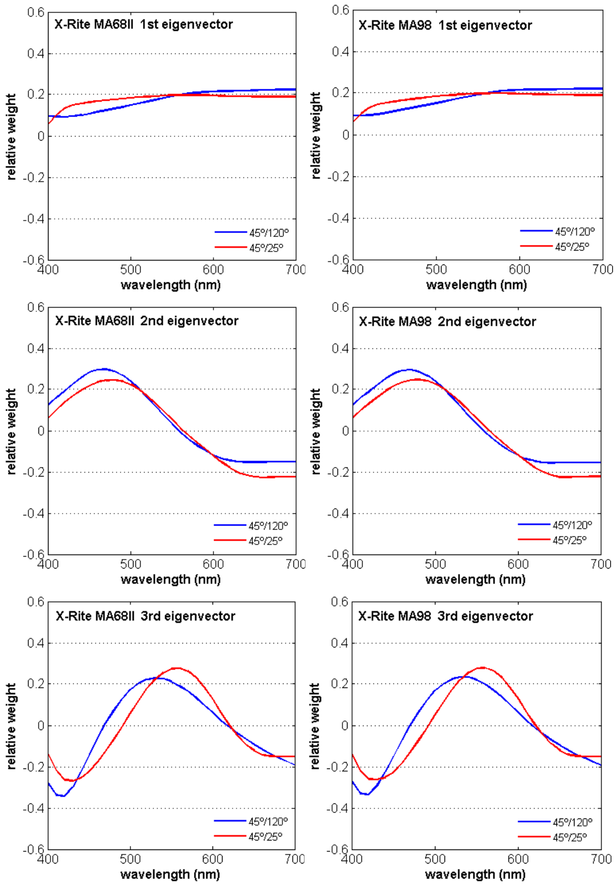
Basis functions

We first have calculated PCA over the entire spectral database taking all the detection geometries together (i.e. global basis). Then, we have separately repeated PCA for every measurement geometry, (i.e. local basis). The results confirm that, for each multi-angle spectrophotometer, a minimum of 3 basis function can take into account 99% of the total variance. A minimum of 8 basis functions are need to reach 99.99% of the total variance. Percentages for the global basis are shown in Table 2.

Table 2. Percentages for the global basis for the three instruments evaluated in this work.

Eigenvector order	Variance (%)		
	FX10	MA98	MA68II
1	85.85	86.73	86.49
2	95.90	96.09	95.78
3	99.06	99.11	99.14
4	99.61	99.64	99.64
5	99.85	99.86	99.87
6	99.94	99.94	99.95
7	99.97	99.97	99.98
8	99.99	99.99	99.99
9	99.99	99.99	99.99
10	99.99	99.99	99.99

Figure 2 represents the first 8 basis functions near (45º/120º) and far (45º/25º) from the specular reflection. Examples correspond to the local basis of the X-Rite MA68II and X-Rite MA98. Data are normalized to the mean reflectance of the entire dataset. The first basis function indicates a quasi-flat curve except in the blue-green part of spectrum and can be associated with metal flakes [20]. Basis functions from 2 to 8 present dependence with the measurement geometries and can be associated with interference pigments.



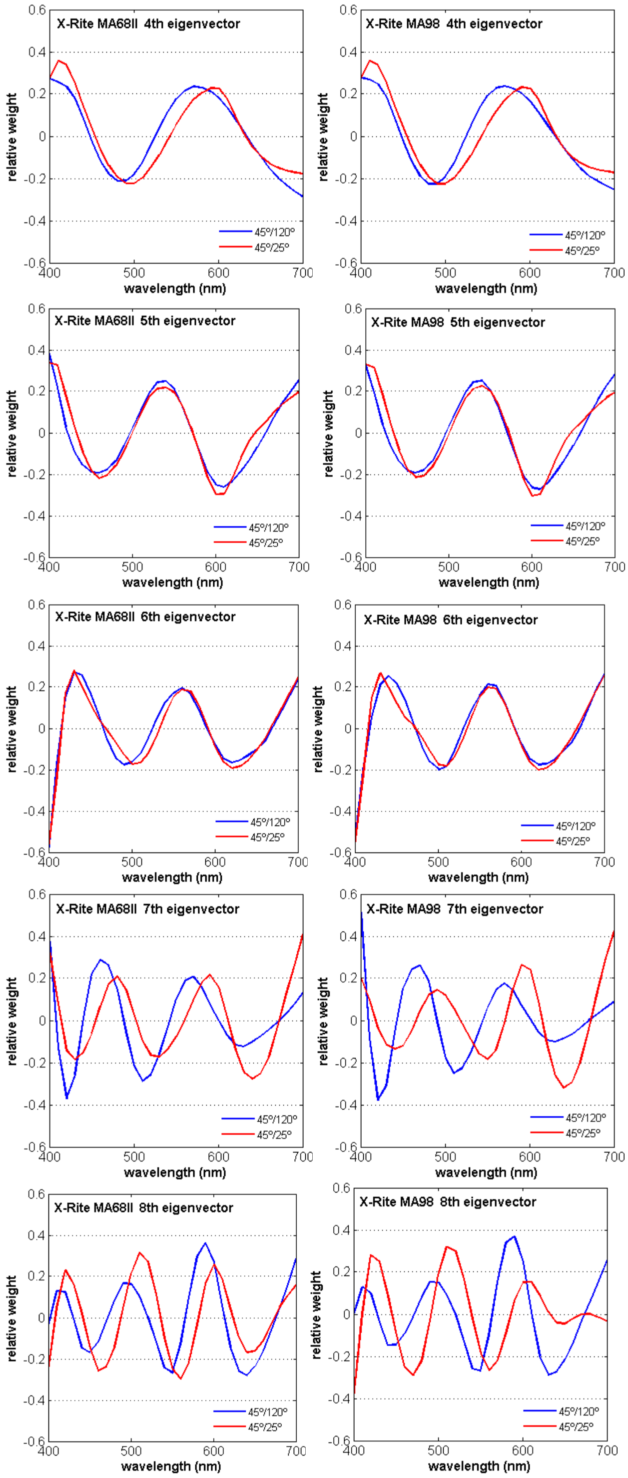
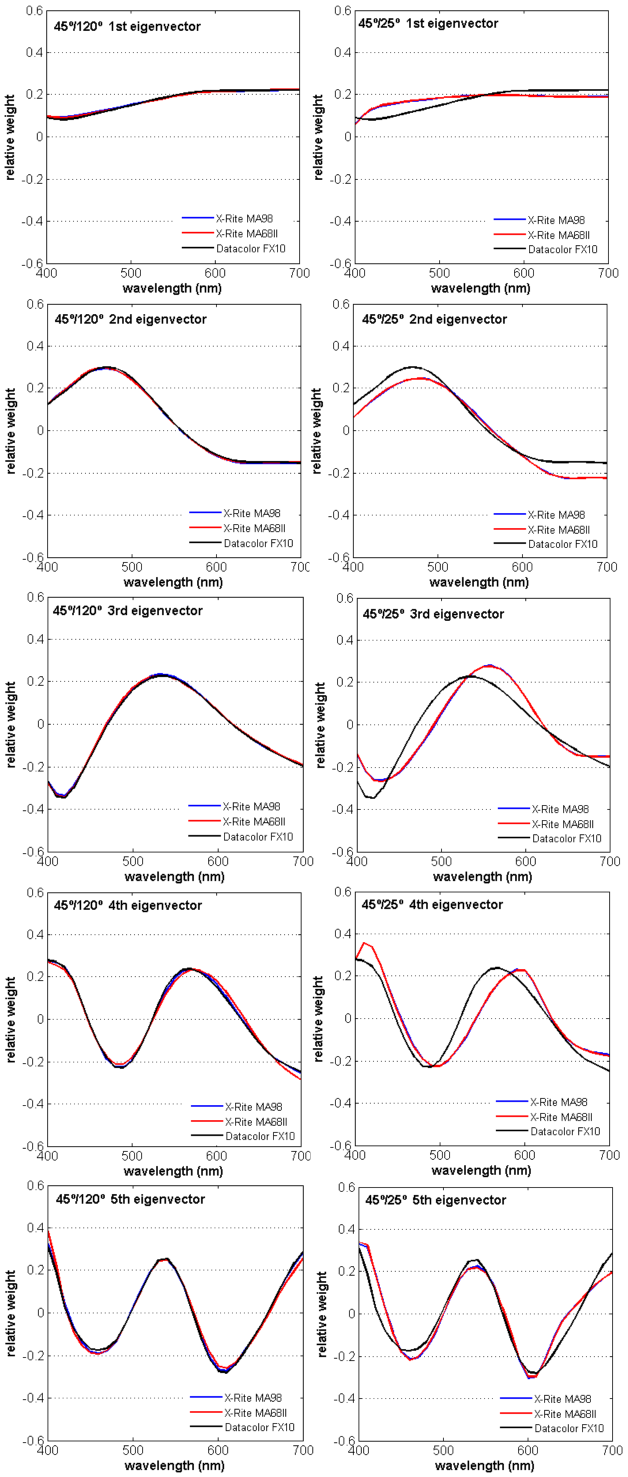


Figure 2. *First 8 basis functions near to (45º/120º) and far (45º/25º) from the specular reflection for the local basis of the X-Rite MA68II and X-Rite MA98.*

To compare between instruments, Figure 3 again represents the above basis vectors in each geometry, separately. There are differences in the basis functions from 6 to 8 near to 45º/120º but also far from the specular at 45º/25º in all the basis functions.



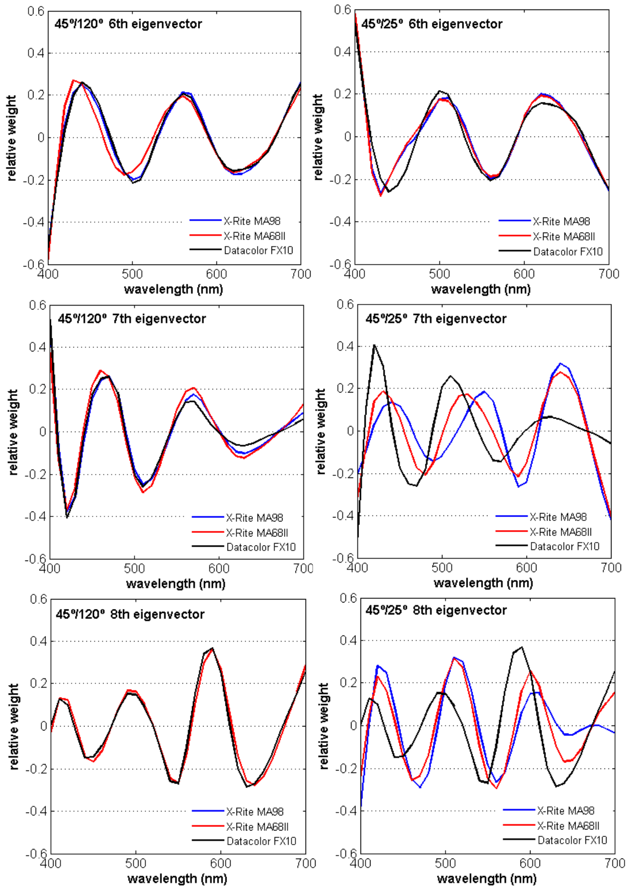


Figure 3. *Comparison among the instruments X-Rite MA68II, X-Rite MA98 and Datacolor FX10 based on the first 8 basis functions for the geometries (45º/120º) and (45º/25º).*

For each basis function, we also have estimated the cross-correlation function between the vector functions provided by each instrument. If the vector functions are equal, the cross-correlation should match with the autocorrelation function and be equal to the unity at lag 0 (i.e. directly superposed). Table 3 summarizes, for the first 8 basis functions, all pairwise comparisons at lag 0. Near the specular reflection, correlation values drop until 97% for the basis functions 6 and 7 at 45º/120º or 45º/110º (MA68 vs. MA98). Correlation coefficients were even lower far from the specular reflection. For the basis functions 7 and 8, values reached 79% at 45º/25º (FX10 vs. MA68).

Table 3. Percentage of the autocorrelation function for the first 8 basis functions and for all pair wise comparisons at lag 0 for all the geometries.

45º/120º								
	1	2	3	4	5	6	7	8
MA98 vs. MA68	100	100	100	100	100	97	97	99
MA98 vs. FX10	100	100	100	100	100	100	99	100
FX10 vs. MA68	100	100	100	99	99	96	96	99
45º/110º								
	1	2	3	4	5	6	7	8
MA98 vs. MA68	100	100	100	100	99	99	98	99
MA98 vs. FX10	100	100	100	100	100	100	100	100
FX10 vs. MA68	100	100	99	99	99	99	99	99
45º/90º								
	1	2	3	4	5	6	7	8
MA98 vs. MA68	100	100	100	100	100	100	100	100
MA98 vs. FX10	100	100	100	100	100	100	100	100
FX10 vs. MA68	100	100	100	100	100	100	100	100
45º/60º								
	1	2	3	4	5	6	7	8
MA98 vs. MA68	100	100	100	100	100	100	100	100
MA98 vs. FX10	100	100	100	100	100	100	100	100
FX10 vs. MA68	100	100	100	100	100	100	100	100
45º/25º								
	1	2	3	4	5	6	7	8
MA98 vs. MA68	100	100	100	100	100	100	90	90
MA98 vs. FX10	100	100	100	100	100	100	98	98
FX10 vs. MA68	100	100	100	100	100	100	80	80

Reconstruction of the reflectance spectra

To evaluate the implications of the above differences and resemblances, we have reconstructed the reflectance spectra as a function of the number of basis functions. The spectral reflectance function was calculated for the 91 samples of the database. For example, we show the results for a characteristic sample (Figure 4).

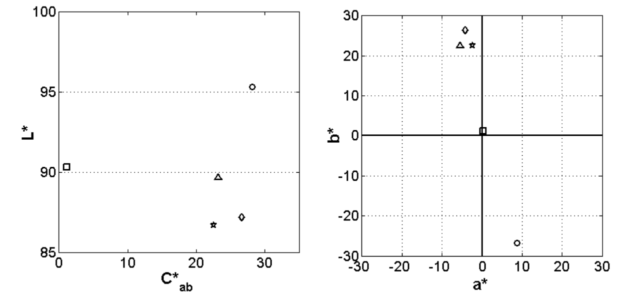


Figure 4. Colorimetric characterization in the b vs. a* and L* vs. C* colorimetric diagram under the illuminant D65 and the CIE-XYZ 1931 standard observer of the chosen sample for the different geometries studied in this work: circle (45º/120º); square (45º/110º); hexagram (45º/90º); diamond (45º/60º); triangle (45º/25º).*

Figure 5 shows the results for this sample taking into account the first 5, 6, 7 and 8 basis function for the geometries (45º/25º) and (45º/120º) with each instrument.

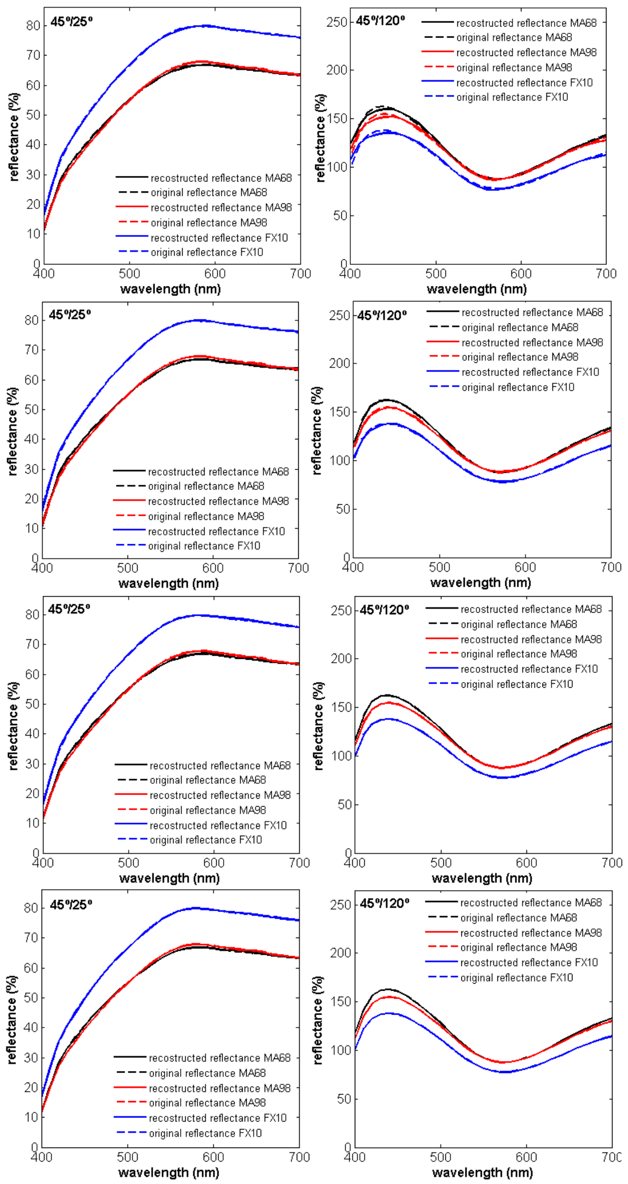


Figure 5. Comparison between the reconstructed and original reflectance spectrum of a sample for the instruments X-Rite MA68II, X-Rite MA98 and Datacolor FX10 with 5, 6, 7 and 8 (from top to bottom) basis functions for the geometries (45º/120º) and (45º/25º).

Far from the specular reflection (45º/25º), both instruments from X-Rite instruments are very similar. However, close to the specular reflection (45º/120º), there are marked differences in the measured spectral reflectance function between any of the three instruments specially in the blue-green part of the spectrum.

The number vector functions added in Eq. (2) will depend on the accuracy of the specific color application. The mean squared error (MSE) between the original and reconstructed reflectance was calculated [18] as a function of the number of vectors added. To compare between pairs of instruments, the absolute difference of the MSE (ΔMSE) was calculated. Figure 6 shows the comparison between instruments near (45º/120º) and far (45º/25º) from the specular reflection. The magnitude of ΔMSE was higher close to (45º/120º) than far from the specular reflection (45º/25º). In the former, differences between MA68II vs. MA98 were close to 0.3 in the basis function nº6 which was associated with interference pigments (see Figure 6). At 45º/25º, maximum ΔMSE values were lower than 0.06 and corresponded to the pair comparison between MA98 vs. FX10 in all the basis function added.

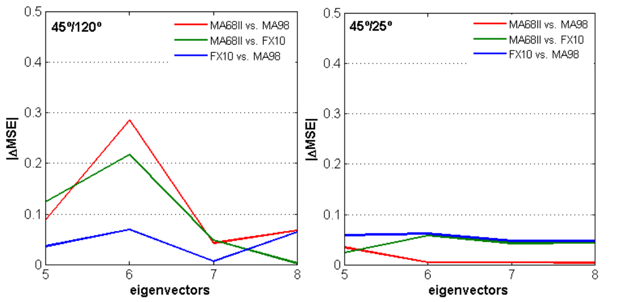
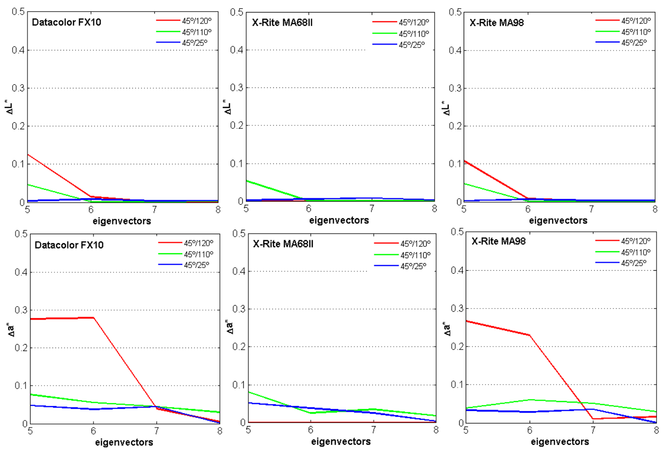


Figure 6. *Comparison between instruments using the mean squared error (MSE) for the geometries 45º/120º and 45º/25º.*

Figure 7 represents the partial color differences (ΔL*, Δa*, Δb*, illuminant D65 and CIE 1931 standard observer) as a function of the number of basis functions added. In all the cases, differences decrease as the number of eigenvectors increases. Maximum values were lower than 0.5 CIELAB units. They were higher near the specular reflection (45º/120º) until the basis functions nº6 or nº7 except for the X-Rite MA68II which shows smaller color differences for this geometry.



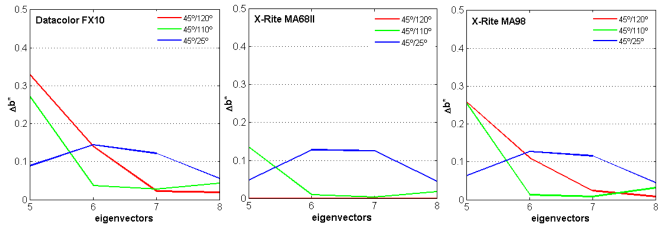


Figure 7. *Partial color differences ΔL*, Δa*, Δb* between the reconstructed and original colorimetric data under the illuminant D65 and the CIE-XYZ 1931 standard observer corresponding to the Datacolor FX10, X-Rite MA68II and X-Rite MA98 instruments and for different geometries.*

Figure 8 summarizes the total CIELAB color difference (ΔE*) as a function of the number of basis function added. In this example, comparisons between instruments have indicated a maximum difference of 0.45 CIELAB units at the eigenvector nº5 between the MA68 vs. FX10 for the geometry 45º/120º, however the instrument X-Rite Ma68II shows a smallest color difference at this geometry. For the other geometries the behavior of the three instruments are similar with a maximum difference of 0.15 CIELAB units at the eigenvector nº6 at the geometry 45º/25º and a maximum difference of 0.3 CIELAB units at the eigenvector nº5 for the geometry 45º/110º

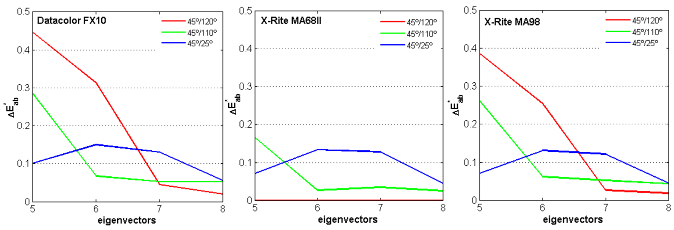


Figure 8. *Total color differences ΔE* between the reconstructed and original colorimetric data under the illuminant D65 and the CIE-XYZ 1931 standard observer corresponding to the Datacolor FX10, X-Rite MA68II and MA98 instruments and for different geometries.*

Conclusions

We have measured the reflectance function of a goniochromatic database using three different multi-angle spectrophotometers. For each instrument, we have estimated the spectral composition of their constituents by PCA. Comparisons between instruments have indicated the existence of differences in both the RMS square error and the CIELAB color coordinates. They were associated with the characterization of interference pigments. These results should be taken into those spectral and colorimetric techniques that attempt to analyze the inter-instrument agreement. Our study confirms PCA as a useful tool in the characterization of goniochromatism.

Acknowledgements

This research was supported by the Spanish Ministry of Science and Innovation under grant DPI2008-06455-C02-02 and by the Fundação para a Ciência e Tecnologia and by the Center for Physics, University of Minho, Portugal. Esther Perales also would like to thank the Ministry for Education and Science for the PhD grant that she has received.

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