2004

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Technical Report

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Summer 2004

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Abstract - This report describes a process of pigment selection for reconstructing the Gamblin Conservation Colors and various artist pigments dispersed in linseed oil. Single constant Kubelka–Munk (K-M) turbid media theory and a non-negative least square (NNLS) optimization technique were employed in this experiment. Eleven pigments were selected as representative of the 30-pigments Gamblin Conservation Colors. These were quinacridone red (PV 19), venetian red (PR 101), cadmium red medium (PR 108), cadmium yellow medium (PY 37), indian yellow (PY 83), chromium oxide green (PG 17), phthalocyanine green (PG 7), phthalocyanine blue (PB 15:2), cobalt blue (PB 28), titanium dioxide white (PW 6), and ivory black (PBK 9).
The report is classified into four sections:

A. Preparing the samples and spectral measurements
B. Pigment characterization
C. Color matching and pigment selection
D. Verification of selected pigments with unknown samples

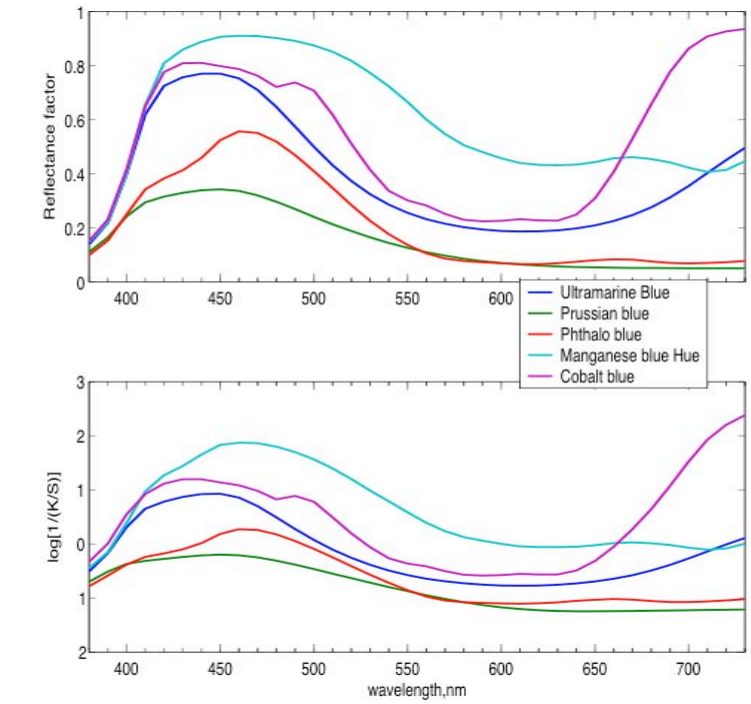
A. Preparing the samples and spectral measurements

All samples in this study were prepared from the Gamblin Conservation Colors. The 30 pigments were grouped into three sets, chromatic, earth, and achromatic, shown in Table I. These paints were made from aldehyde resin (Laropal A81), petroleum distillate mixture, and lightfast pigments. Most of them are transparent or semi transparent. More details can be found on the Gamblin webside, http://www.gamblincolors.com.

Since the masstone of an individual pigment is dark, it is difficult to determine its characteristic absorption bands. Therefore pigments were characterized relative to one particular spectrally–nonselective pigment. In this experiment each pigment was mixed with a white pigment (TiO_2) at two different ratios. The formulations are summarized in Table I in Appendix B. Titanium white is a highly reflective and scattering pigment so by adding it to the other pigments it is possible to make an opaque film. Figures 1-3 show spectral reflectance spectra of the three groups of Gamblin colors. The measurements were performed using a GretagMacbeth SpectroEye with 45/0 geometry measuring in the wavelength range from 380 to 730 nm in intervals of 10 nm with a 4.5 mm circular aperture.

Table I. *Gamblin Conservation Colors used in K/S building process.*

	Pigment name	*Chemical name*	*Color Index number*
chromatic	Viridian	Hydrated chromium oxide	PG 18
	Ultramarine blue	Complex silicate of sodium & aluminum with sulfur	PB 29
	Quinacridone red	Quinocridone red b	PV 19
	Prussian blue	Ferri-ammonium ferrocyanide	PB 27:1
	Phthalo green	Chlorinated copper phthalocyanine	PG 7
	Phthalo blue	Copper phthalocyanine	PB 15:2
	Dioxazine purple	Carbazol dioxazine	PV 23
	Hansa Yellow Medium	Arylide yelow	PY 74
	Cadmium Orange	Concentrated cadmium sulfo-selenide	PO 20
	Manganese blue Hue	Copper phthalocyanine	PB 15:4
	Cadmium Yellow Light	Concentrated cadmium zinc sulfide	PY 35
	Cadmium Yellow Medium	Concentrated cadmium sulfide	PY 37
	Chromium Oxide Green	Chromium oxide green	PG 17
	Cobalt blue	Oxides of cobalt & aluminum	PB 28
	Cobalt Green	Oxides of cobalt & zinc	PG 19
	Cobalt Violet	Cobalt phosphate	PV 14
	Indian Yellow	Diarylide yellow HR70	PY 83
	Cadmium Red Light	Concentrated cadmium sulfo-selenide	PR 108
	Cadmium Red Medium	Concentrated cadmium sulfo-selenide	PR 108
earth	Venetian Red	Synthethic red iron oxide	PR 101
	Transparent Earth Yellow	Transparent Mars yellow	PY 42
	Transparent Earth Red	Transparent Mars red	PR 101
	Raw Umber	Natural iron oxide containing manganese	PBr 7
	Yellow Ocher	Natural hydrated iron oxide	PY 43
	Indian Red	Synthetic red iron oxide	PR 101
	Burnt Sienna	Calcinated natural iron oxide	PBr 7
	Burnt Umber	Natural iron oxide containing manganese	PBr 7
	Raw Sienna	Natural iron oxide	PBr 7
achromatic	Titanium White	Titanium dioxide	PW 6
	Ivory Black	Bone black	PBk 9
	Black Spinel	Copper chromite black spinel	PBk 28



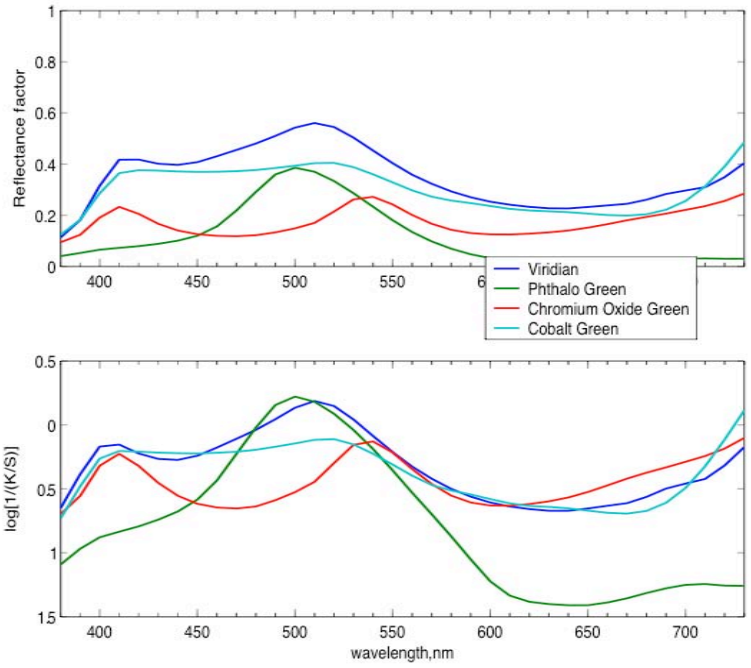


Figure 1a. *Spectral reflectance and logarithm [1/(K/S)] of Gamblin chromatic colors.*

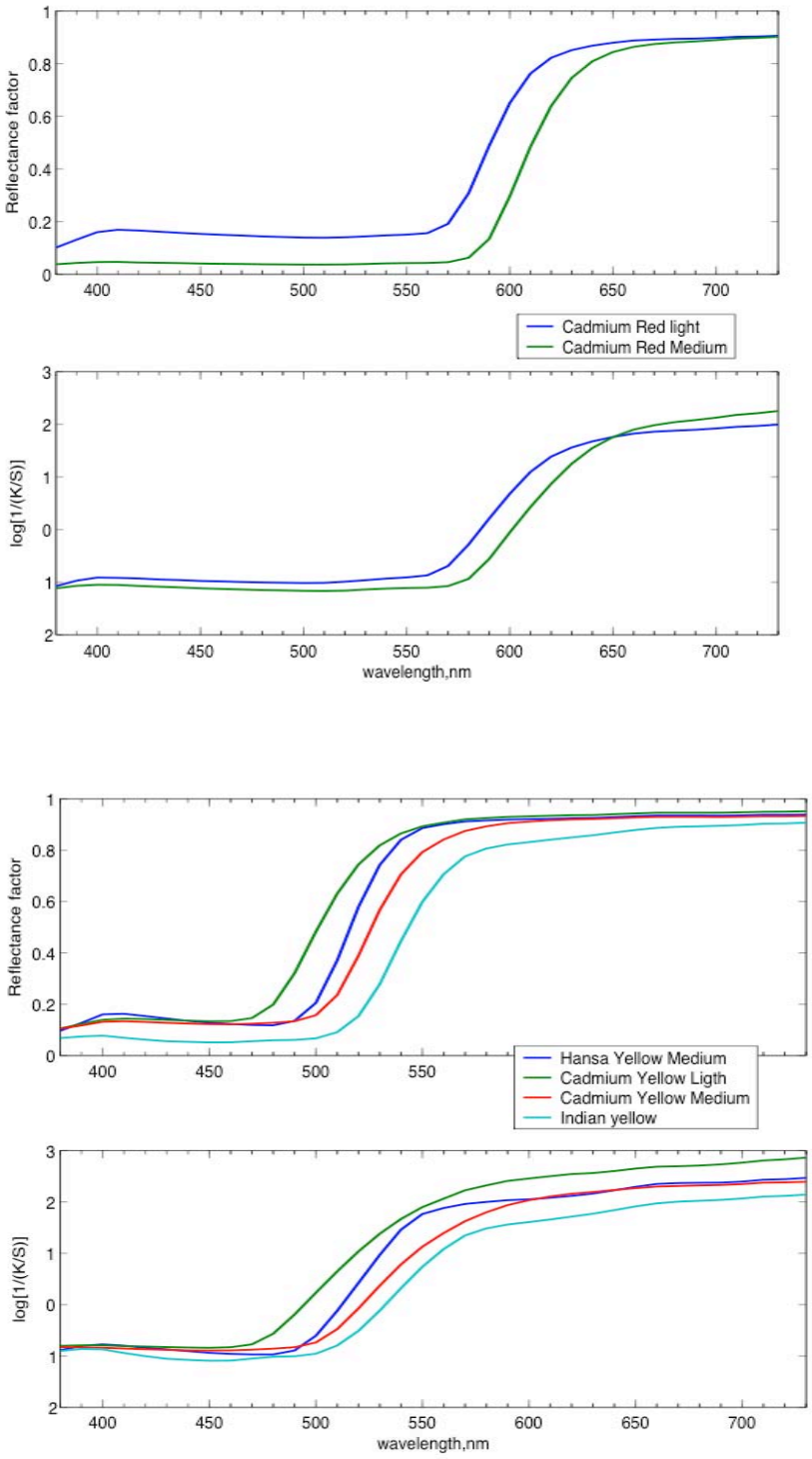


Figure 1b. *Spectral reflectance and logarithm [1/(K/S)] of Gamblin chromatic colors.*

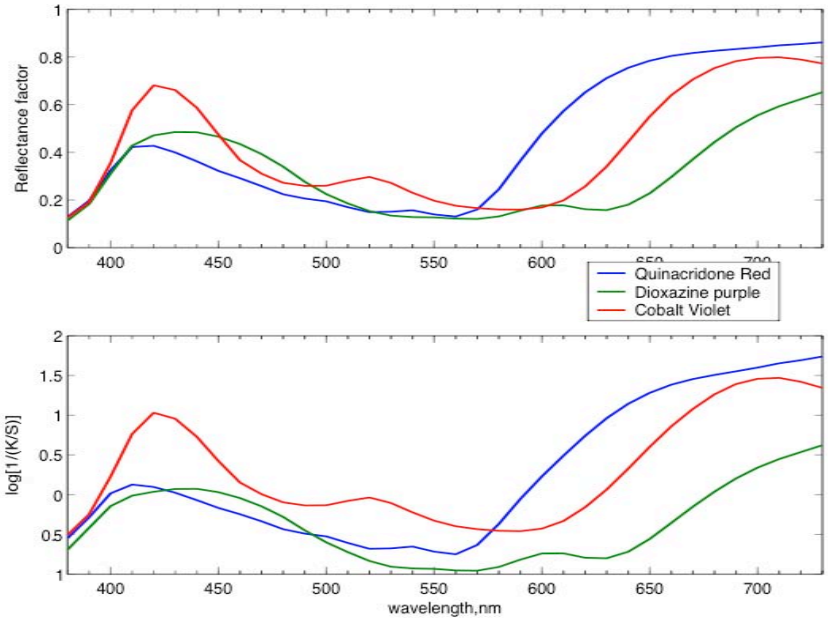


Figure 1c. *Spectral reflectance and logarithm [1/(K/S)] of Gamblin chromatic colors.*

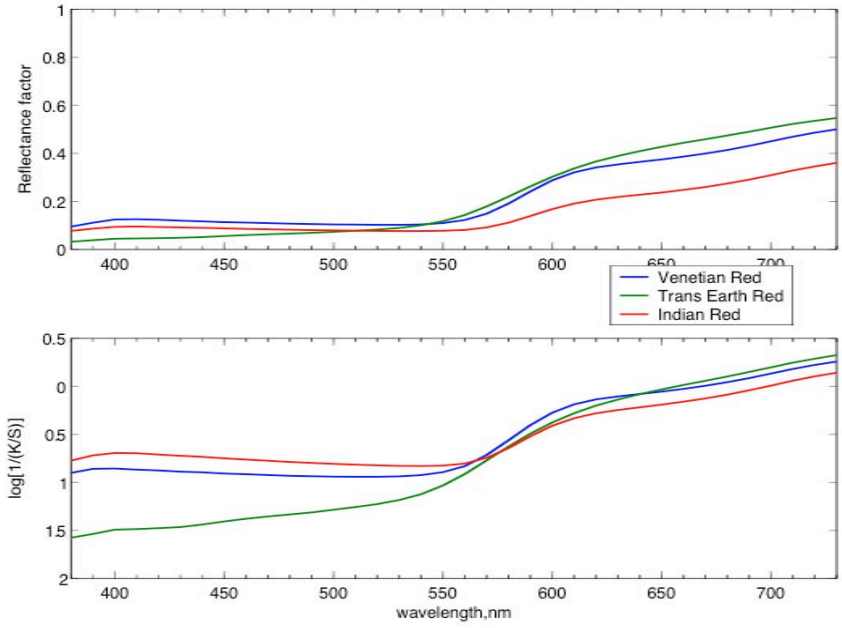


Figure 2a. *Spectral reflectance and logarithm [1/(K/S)] of Gamblin earth colors.*

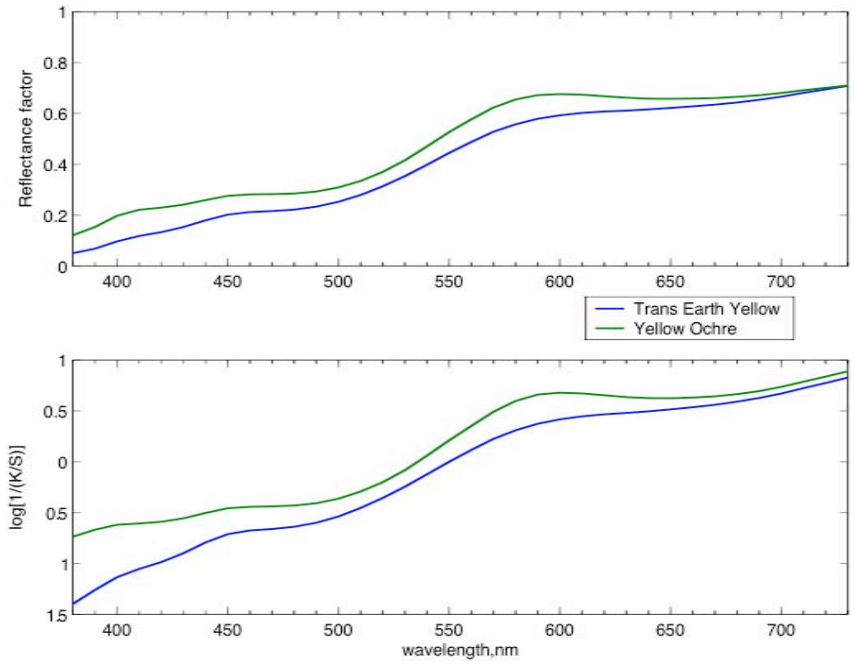


Figure 2b. *Spectral reflectance and logarithm [1/(K/S)] of Gamblin earth colors.*

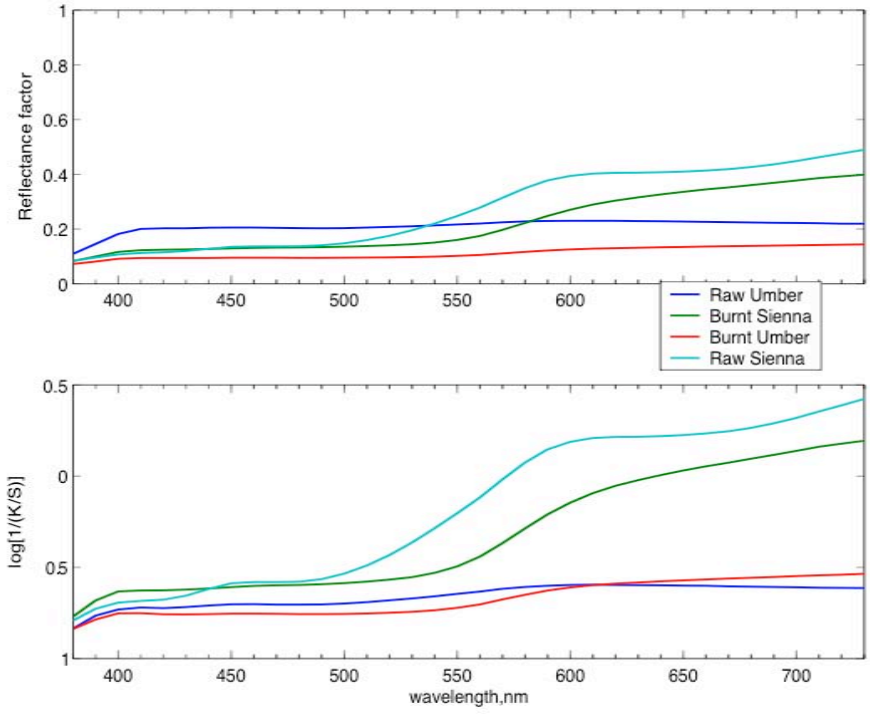


Figure 2c. *Spectral reflectance and logarithm [1/(K/S)] of Gamblin earth colors.*

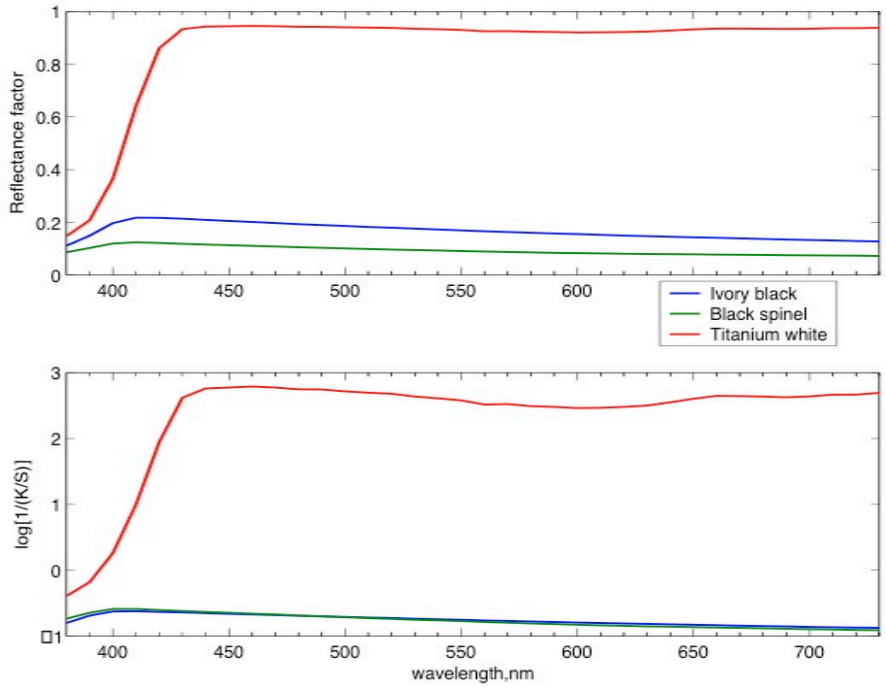


Figure 3. *Spectral reflectance and logarithm [1/(K/S)] of blacks and white (TiO_2).*

Since spectral reflectance at lower wavelengths was not so precise due to noisy data in this range of spectrum, these data were truncated to avoid differential absorption of TiO_2 versus the other pigment; hence all calculations were performed between 430-730 nm. Matlab 5.2 was used as a toolbox for all calculations.

B. Pigment characterization

Kubelka-Munk turbid media theory is a practical theory for the prediction of the relationship between pigment concentration and spectral reflectance of paint films [1-3]. In this research, it was assumed that the samples were opaque and the opacity was related to the white pigment (TiO_2). Therefore the single constant K-M theory was employed for pigment characterization and pigment selection and the following equations were used:

$$R_{\lambda,mix} = 1 + \left(\frac{K}{S}\right)_{\lambda,mix} - \sqrt{\left(\frac{K}{S}\right)^2_{\lambda,mix} + 2\left(\frac{K}{S}\right)_{\lambda,mix}} \qquad (1)$$

where

$$\left(\frac{K}{S}\right)_{\lambda,mix} = \sum_{i=1}^{n} C_i \left(\frac{k}{s}\right)_{\lambda,i} \qquad (2)$$

and $R_{\lambda,mix}$ is the spectral reflectance factor of a mixture, $(K/S)_{\lambda,mix}$ is the spectral absorption (K) and scattering (S) ratio of a mixture, $(k/s)_{\lambda,i}$ is the unit $(k/s)$of a pigment,

C_i is the amount of a pigment, and n is the number of pigments in a mixture. By having $(K/S)_{\lambda,mix}$ properties of a mixture of the colored pigment and white at known concentrations, unit $(k/s)_{\lambda,i}$ for all pigments were calculated using Eq. (2). In order to have a curve shape independent of concentration for the pigments, $\log[1/(K/S)]$ was calculated [1]. Since $\log[1/(K/S)]$ was plotted, the maximum corresponds to the maximum of the reflectance curve. This is a ''signature'' of a pigment and it can be determined how the spectral characteristics of the pigments in each group are similar or dissimilar with each other. Of course it should be noted that the unit (k/s) values at each wavelength are specific for the particular vehicle system and white pigment used [8]. The $\log[1/(K/S)]$ spectra of each pigment are plotted in Figures 1-3. For example, cobalt blue has a very characteristic spectrum. It exhibits a sharp rise in reflectance in the red region and has a slight band in the middle of the spectrum. The cobalt blue has characteristic curve shape in the region of maximum reflectance that would be another clue for identification of this special pigment. Chromium oxide green, sometimes called Vert Emeraude Dull, is known since the early nineteenth century [8]. The double absorption bands at 465 nm and 600 nm of the pure chrome oxide are characteristic of this pigment. Since yellows absorb in the short-wavelength violet region and reflect almost all wavelengths, there is no minimal absorption characteristic for these pigments. The flatness in the absorption region of cadmium reds is characteristic. Reflectance of cadmium red light rises at a shorter wavelength than cadmium red medium. Quinacridone red is categorized as violet pigment in color index. It's two or more absorption bands are specific to quinacridone red. Earth pigments do not have characteristic absorption bands that are as well defined as chromatic pigments.

B. Color matching and pigment selection

In this part of experiment, each sample of the Gamblin database (60 samples) was used as a target and it was hypothesized that the target is a combination of the pigments in the database:

$$\left(\frac{K}{S}\right)_{\lambda,unknown} - \left(\frac{k}{s}\right)_{\lambda,white} = \sum_{j=1}^{n} C_i \left(\frac{k}{s}\right)_{\lambda,j} \qquad (3)$$

Equation (3) can be written using statistical notation [4].

$$Y_i = \beta_1 X_{i,1} + \beta_2 X_{i,2} + \ldots \quad \beta_n X_{i,n} \qquad (4)$$

where the independent variable, $X_{i,n}$, represent the unit (k/s) of a pigment in which i represents wavelength, Y is the dependent variable and represents the K/S properties of the unknown mixture minus unit (k/s) of white, and β_n represents the pigment amounts. The constraint of having non-negative concentration was also considered in the regression (NNLS). The above equations can be shown using vector-matrix notation:

$$\mathbf{b} = (\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}'\mathbf{Y} \qquad (5)$$

where

$$\mathbf{b} = \begin{bmatrix} C_1 \\ C_2 \\ . \\ . \\ C_n \end{bmatrix} \quad \mathbf{X} = \begin{bmatrix} \left(\frac{k}{s}\right)_{430,1} & . & . & . & \left(\frac{k}{s}\right)_{430,n} \\ . & . & . & . & \\ . & . & . & . & \\ \left(\frac{k}{s}\right)_{730,1} & . & . & . & \left(\frac{k}{s}\right)_{730,n} \end{bmatrix}$$

and

$$\mathbf{Y} = \begin{bmatrix} \left(\frac{K}{S}\right)_{430,unknown} & \left(\frac{k}{s}\right)_{430,w} \\ . & \\ . & \\ . & \\ \left(\frac{K}{S}\right)_{730,unknown} & \left(\frac{k}{s}\right)_{730,w} \end{bmatrix}$$

If the unknown is metameric, minimizing (K/S) differences does not minimize either reflectance differences or visual differences [1]. A weighting function, d_λ, can be introduced to improve correlation [11].

$$d_\lambda = \frac{\partial R_{\lambda,unknown}}{\partial \left(\frac{K}{S}\right)_{\lambda,unknown}} = \frac{2R^2_{\lambda,unknown}}{\left(\frac{K}{S}\right)_{\lambda,unknown}\left(1 - R^2_{\lambda,unknown}\right)} \qquad (6)$$

All the spectral data in equation (5) were premultiplied by the weighting function. This led to differences in weighted (K/S) being better correlated with differences in spectral reflectance factor.

All three, four, and five combinations of thirty pigments were made computationally:

$$\binom{n}{r} = \frac{n!}{(n-r)!r!} \qquad (7)$$

Therefore $\binom{30}{3} = 4{,}060$, $\binom{30}{4} = 27{,}405$, and $\binom{30}{5} = 142{,}506$ recipe were generated, respectively. It should be noted that white pigment was included in all recipes and it was assumed that the total amount of material is $\left(1 + \sum_{i=1}^{n} C_i\right)$. This means that the amount of white pigment was set equal by one and the amount of the other pigments were added up. Every recipe was employed to predict all the chromatic and earth Gamblin samples. Since

there is no single metric that can express the accuracy of spectral matching, a group of metrics was used. These included:

1. Spectral difference, root mean square error (RMS).
2. Color difference, $\Delta E_{00}\left(D_{65},2^{o}\right)$.
3. Metamerism index($MI_{00}\left(D_{65}\right.$, $\left.A\right)$,
4. GFC metric.

Details of these metrics are presented in Appendix A.

It should be noted that the earth and chromatic pigments were analyzed separately. The results of the predicted samples were rearranged in ascending order and the top thirty recipes were selected for further analysis. It was not guaranteed that the first recipe was the best one.

C.1. Color gamut evaluation

The range of colors produced by a coloration system is called its color gamut [1]. In this experiment the coloration system is a set of pigments. The volume of a color solid was calculated using corrected CIELAB values based on the CIE94 color difference equation, similar to Luo's LLAB [7]. The color gamuts of the first thirty sets were calculated. For each pigment a logarithmic range of concentration (between zero and one) at seven levels was designed. For each set, the full factorial of seven levels of concentrations was considered. It should be noted that white pigment was always included in a recipe. Therefore $7^4 = 2{,}401$, $7^5 = 16{,}807$, $7^6 = 117{,}649$ points in CIELAB color space were generated as concentrations for 3-pigment, 4-pigment, and 5-pigment recipes, respectively. By having unit (k/s) of the pigments and the generated concentrations, the spectral reflectance of each recipe was synthesized. The corrected CIELAB was calculated using equations (8), designated by L_{94}, a_{94}, and b_{94}. These values comprise a three dimensional solid that is the color gamut in CIE94 corrected CIELAB space:

$$\begin{aligned} L_{94} &= L^{*} \\ C_{94} &= \frac{\ln\left(1+0.045C^{*}\right)}{0.045} \\ h_{94} &= \arctan\left(b^{*}/a^{*}\right) \\ a_{94} &= C_{94}\cos\left(h_{94}\right) \\ b_{94} &= C_{94}\sin\left(h_{94}\right) \end{aligned} \qquad (8)$$

Outer shells of the generated color gamut were found using the ''convhulln'' function in matlab and the corresponding volume generated by the pigments were saved. A set from the first thirty top recipes with larger color gamut was selected as the best recipe at each error criterion. The same procedure was performed for chromatic and earth pigments. The results are tabulated in Tables II and III.

Table II*-Three, four, and five- pigment sets based on the spectral matching of chromatic samples using different criteria.*

3-pigment sets				
□	RMS (%)	□E_{00}	GFC	MI_{00}
pigment 1	Cadmium red medium	Cadmium red medium	Indian yellow	Indian yellow
pigment 2	Hansa yellow medium	Hansa yellow medium	Phthalocyanine green	Phthalocyanine green
pigment 3	Phthalocyanine blue	Ultramarine blue	Dioxazine purple	Dioxazine purple
Volume	56307	52276	56975	56975
4-pigment sets				
pigment 1	Quinacridone red	Cadmium red medium	Quinacridone red	Quinacridone red
pigment 2	Indian yellow	Hansa yellow medium	Hansa yellow medium	Indian yellow
pigment 3	Phthalocyanine green	Phthalocyanine green	Phthalocyanine green	Phthalocyanine green
pigment 4	Cobalt blue	Cobalt blue	Cobalt blue	Cobalt blue
Volume	71405	77660	73147	71405
5-pigment sets				
pigment 1	Quinacridone red	Cadmium red medium	Cadmium red medium	Cadmium red medium
pigment 2	Cadmium yellow medium	Cadmium orange	Hansa yellow medium	Indian yellow
pigment 3	Phthalocyanine green	Hansa yellow medium	Phthalocyanine green	Phthalocyanine green
pigment 4	Manganese blue hue	Phthalocyanine green	Manganese blue hue	Cobalt blue
pigment 5	Cobalt blue	Cobalt blue	Cobalt blue	Ultramarine blue
Volume	71238	80401	79248	80601

The projection of three-dimensional color spaces for the selected pigments onto $a_{94}b_{94}$ axes at different L_{94} levels is shown in Figures 4a-4d.

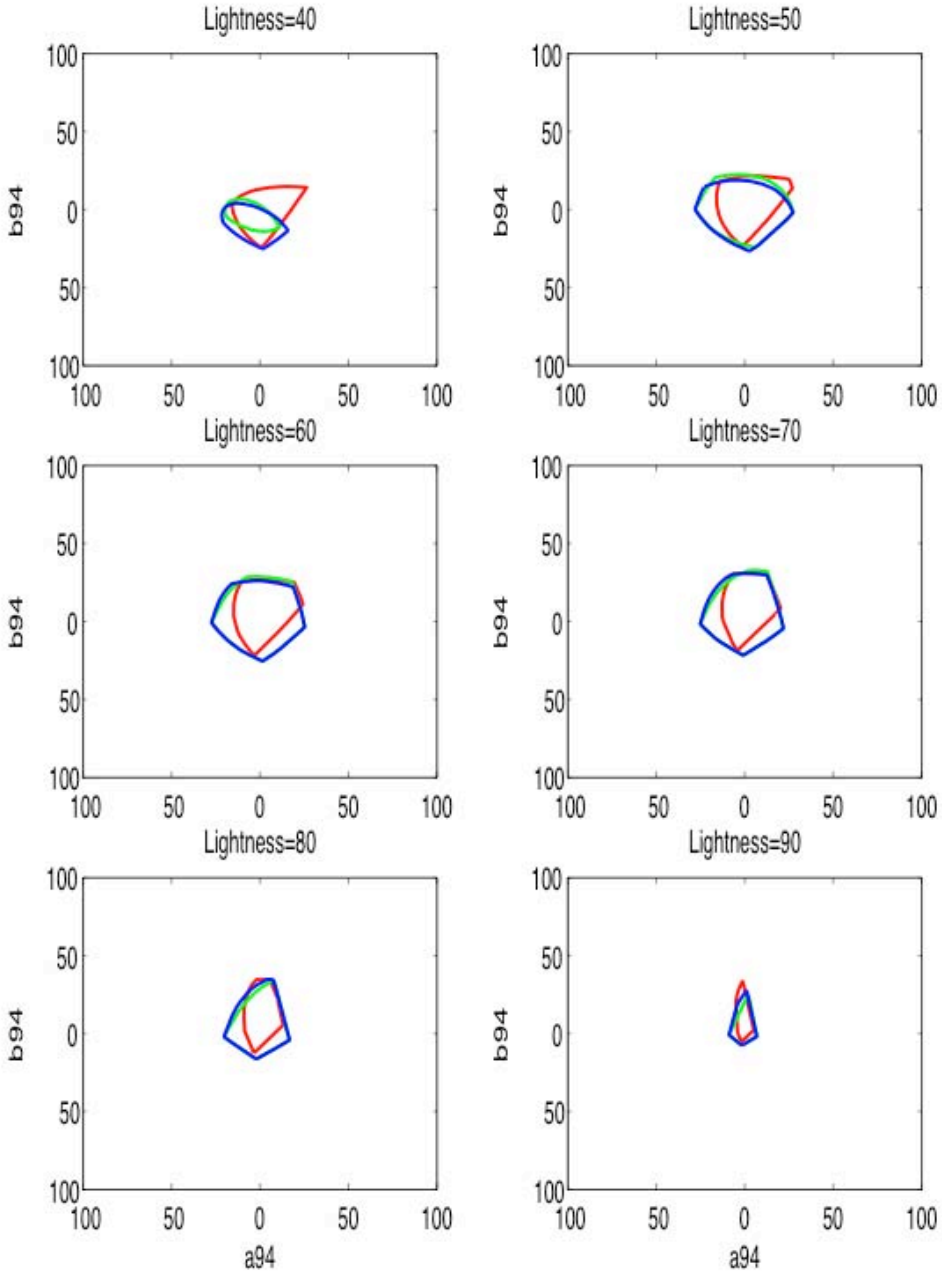


Figure 4a. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching of chromatic samples using RMS criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

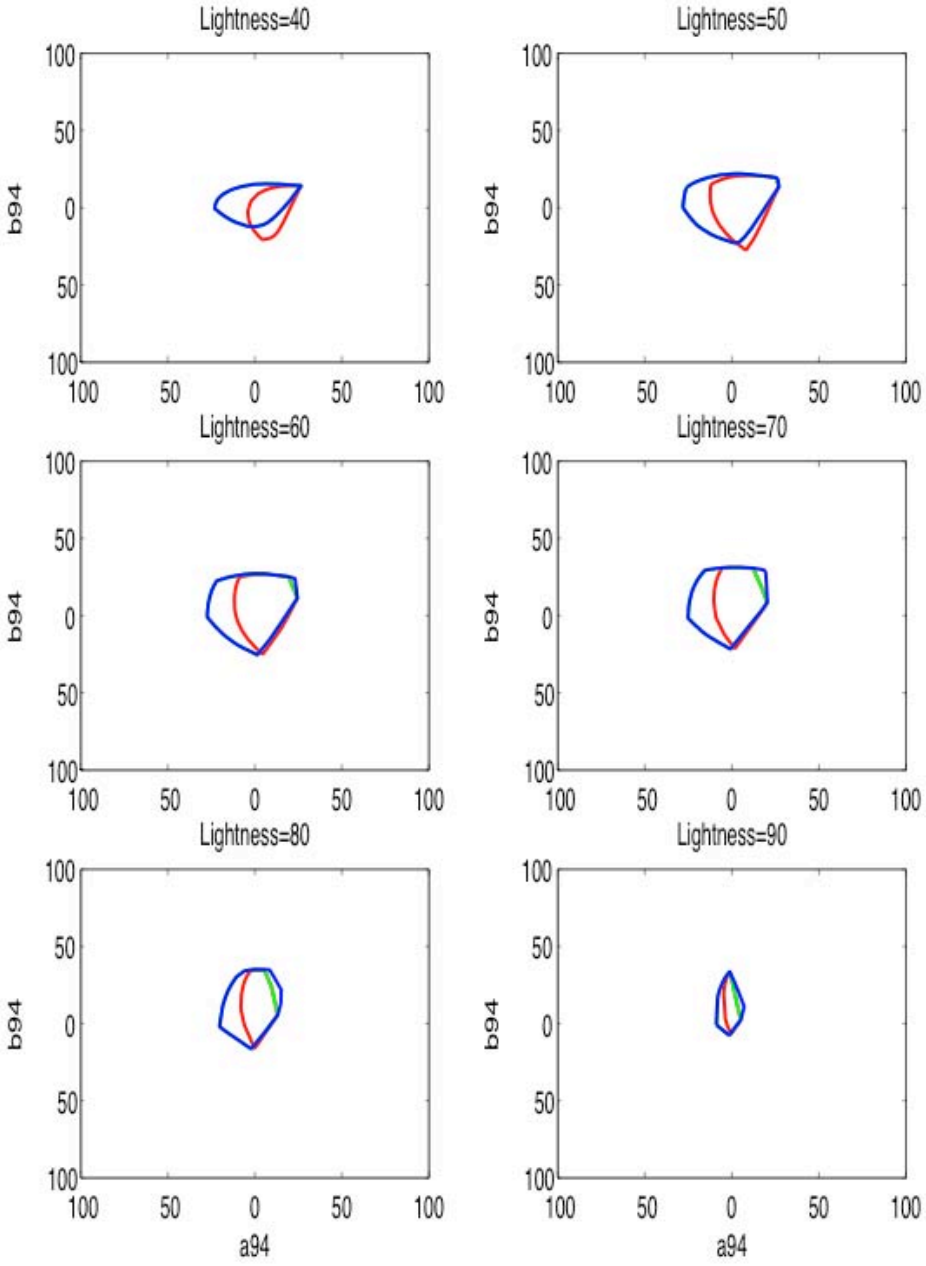


Figure 4b. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching of chromatic samples using ΔE_{00} criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

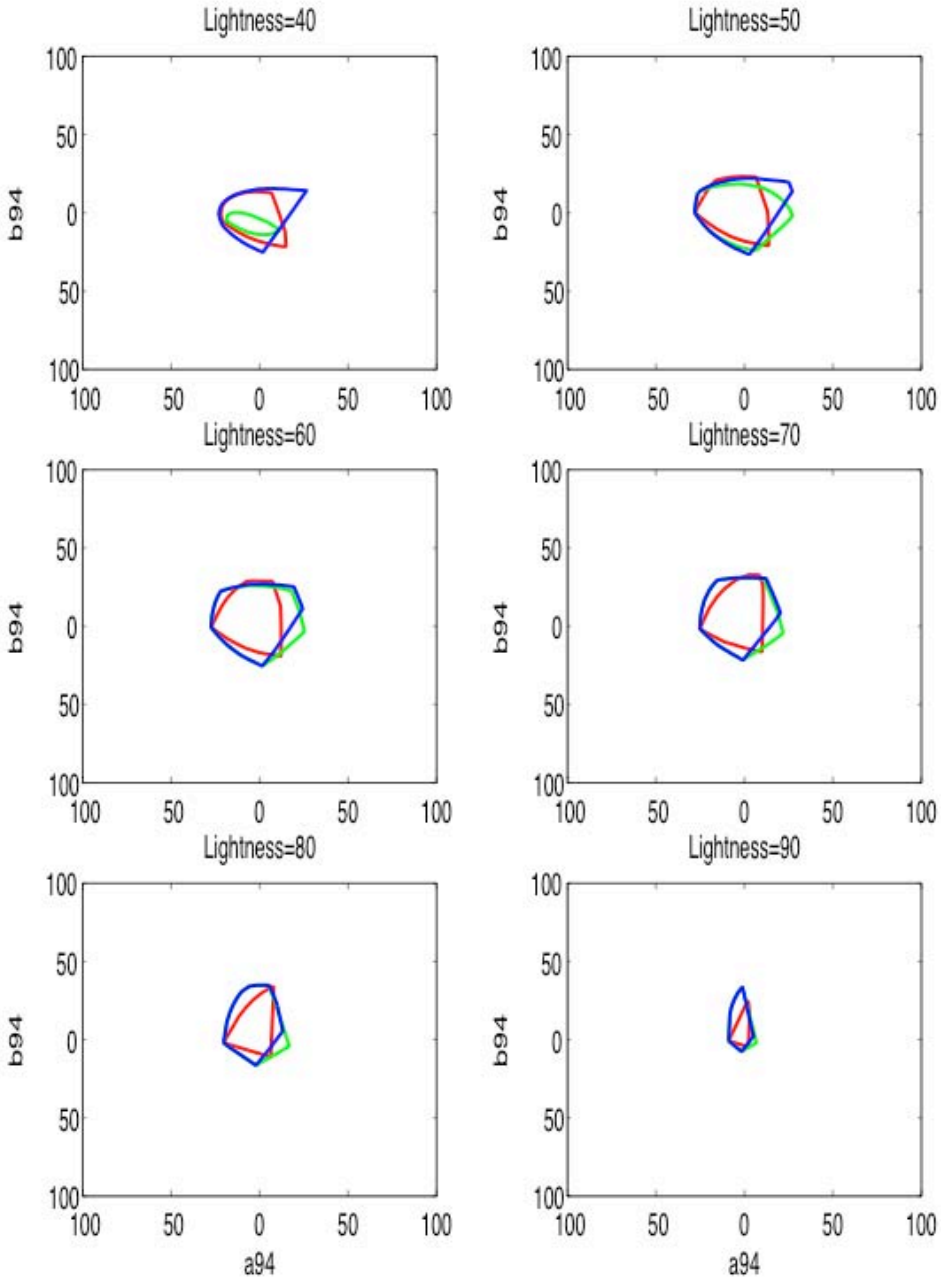


Figure 4c. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching of chromatic samples using GFC criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

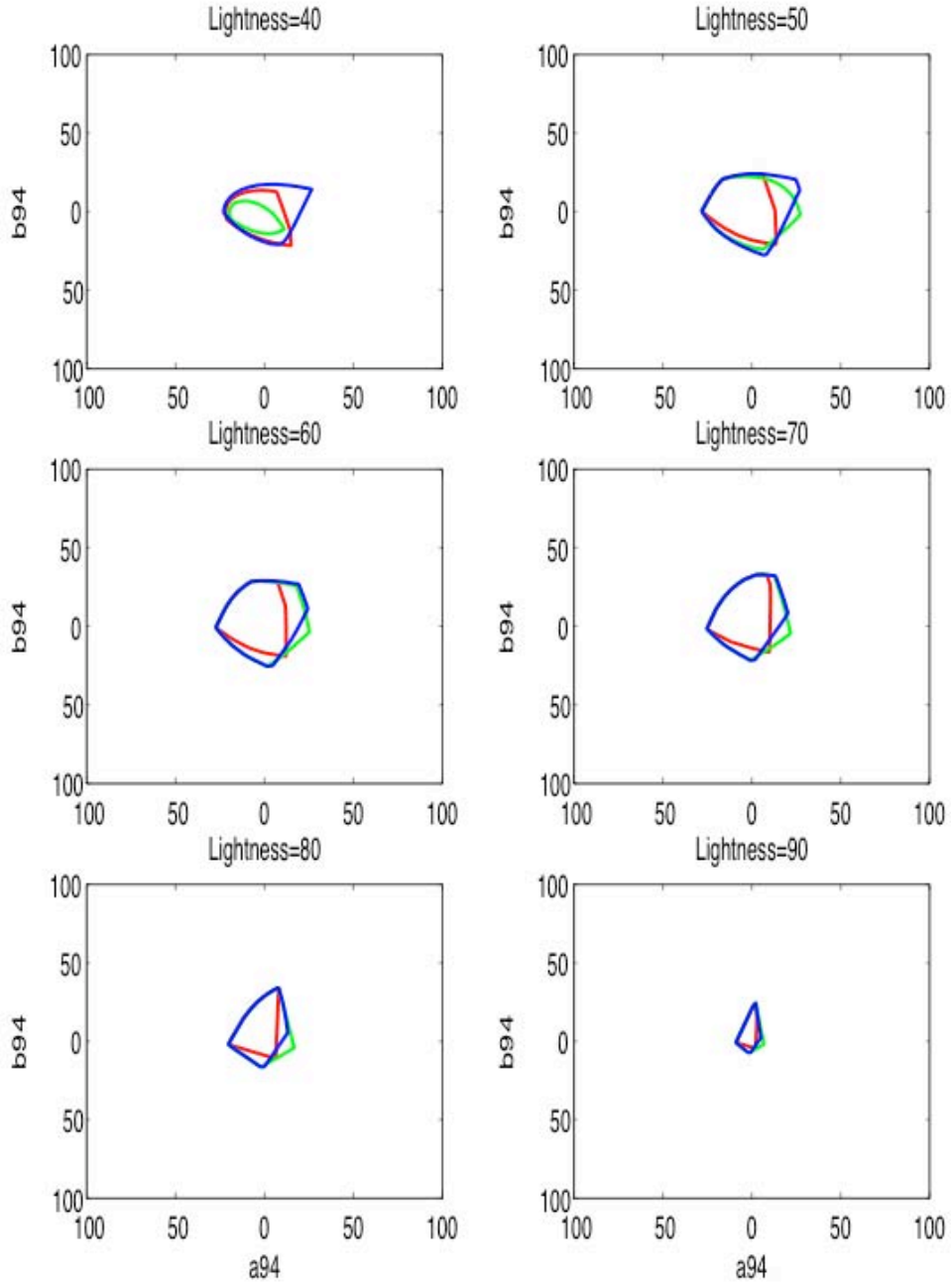


Figure 4d. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching of chromatic samples using $MI_{00}(D65 \square A)$ criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

As can be seen from the above figures and tables, adding one pigment to the system from three to four made a significant improvement in color gamut at all error criteria. Moving

from four pigments to five does not have the same improvement effect as moving from three to four pigments. The selected pigments at the different criteria are not exactly the same but the generated color gamuts almost have the same range of volume for three, four, and five pigments. The area size of slices of color gamuts depends on the pigments used in generating the color solid. In this study, for the case of pigments selected based on RMS criterion, the area corresponding to the three pigments is larger than areas of four and five pigments. Color gamut of the selected pigments for matching the earth pigments was also calculated and shown in Figures 5a-5d and Table III.

Table III. *Three, four, and five-pigment sets based on the spectral matching of earth samples using different criteria.*

3-pigment sets				
□	RMS (%)	□E_{00}	GFC	MI_{00}
pigment 1	Venetian red	Cadmium red medium	Venetian red	Venetian red
pigment 2	Indian yellow	Indian yellow	Indian yellow	Indian yellow
pigment 3	Prussian blue	Phthalocyanine green	Prussian blue	Manganese blue hue
Volume	37702	45624	37702	24362
4-pigment sets				
pigment 1	Indian red	Indian red	Indian red	Quinacridone red
pigment 2	Cadmium red light	Cadmium red light	Trans. Earth red	Yellow ocher
pigment 3	Yellow ocher	Indian yellow	Indian yellow	Manganese blue hue
pigment 4	Prussian blue	Phthalocyanine green	Prussian blue	Cobalt blue
Volume	27649	47598	40502	31736
5-pigment sets				
pigment 1	Quinacridone red	Quinacridone red	Quinacridone red	Cadmium red medium
pigment 2	Trans. Earth red	Cadmium orange	Trans. Earth red	Trans. Earth red
pigment 3	Yellow ocher	Cadmium yellow light	Yellow ocher	Cadmium orange
pigment 4	Black spinel	Phthalocyanine green	Black spinel	Manganese blue hue
pigment 5	Ultramarine blue	Cobalt violet	Ultramarine blue	Ultramarine blue
Volume	37482	73512	37482	41005

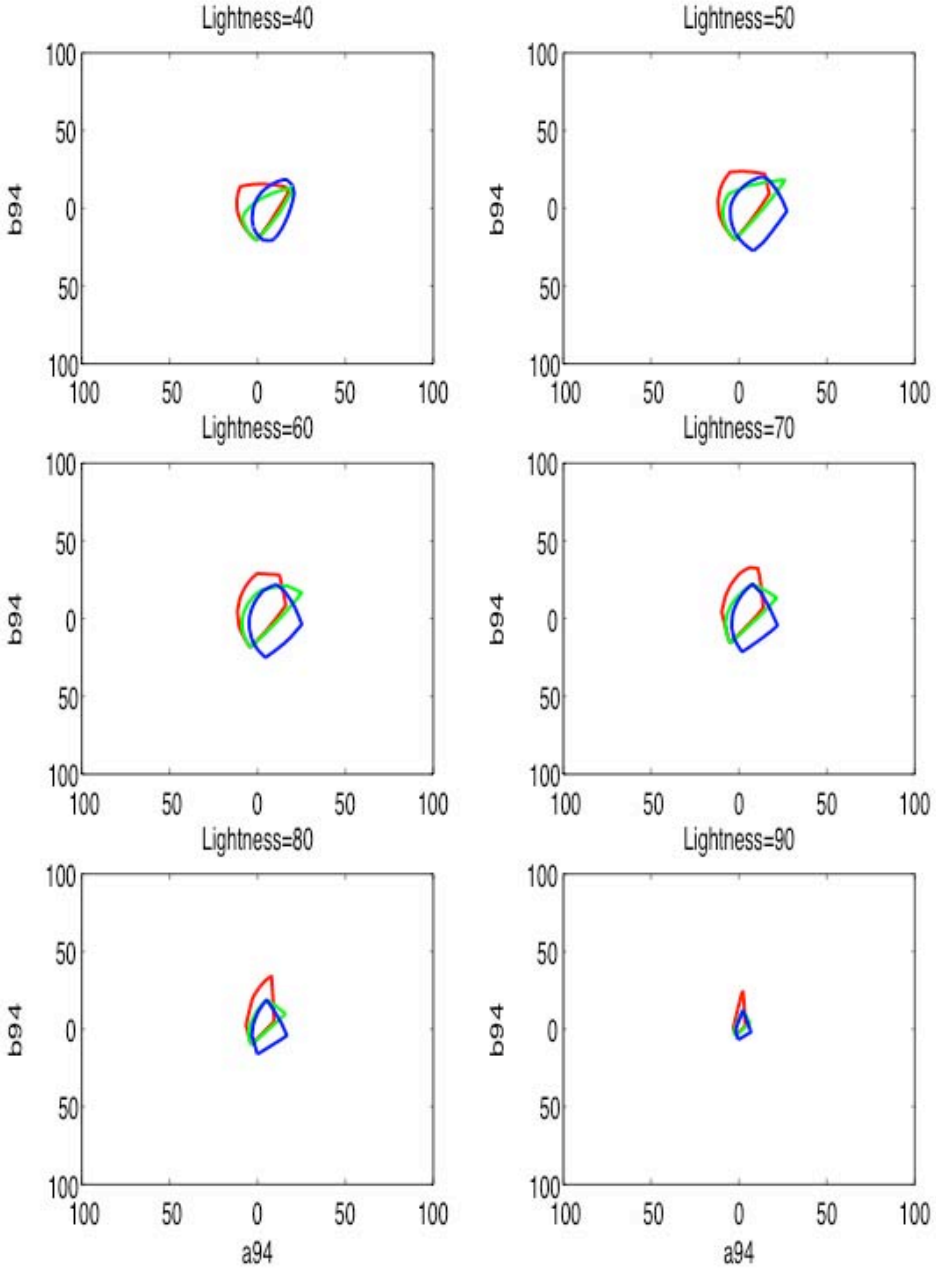


Figure 5a. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching for earth samples using RMS criterion. Red lines indicate 3-pigment set, green lines indicate 4- pigment set, and blue lines indicate 5-pigment set.*

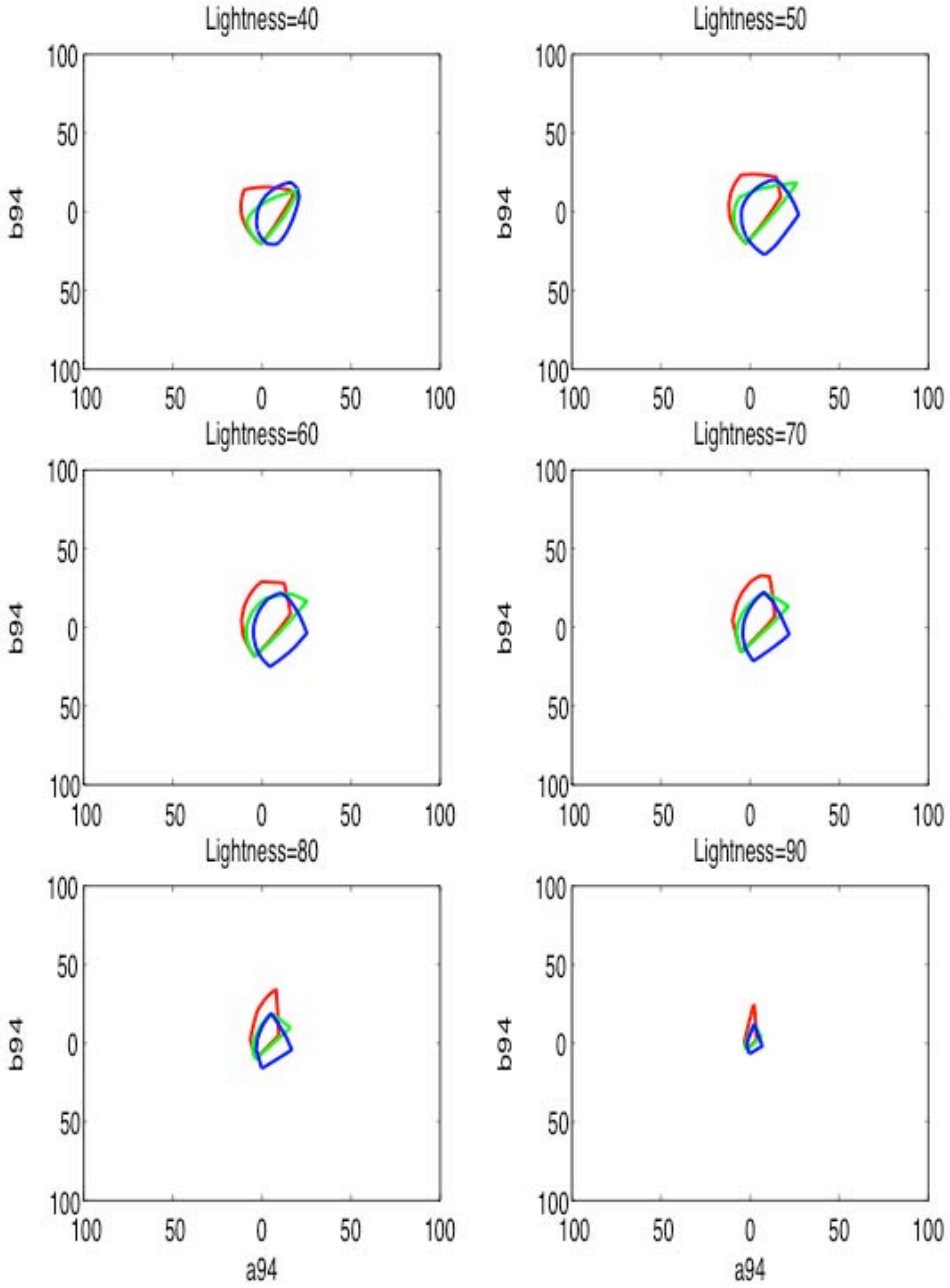


Figure 5b. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching for earth samples using ΔE_{00} criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

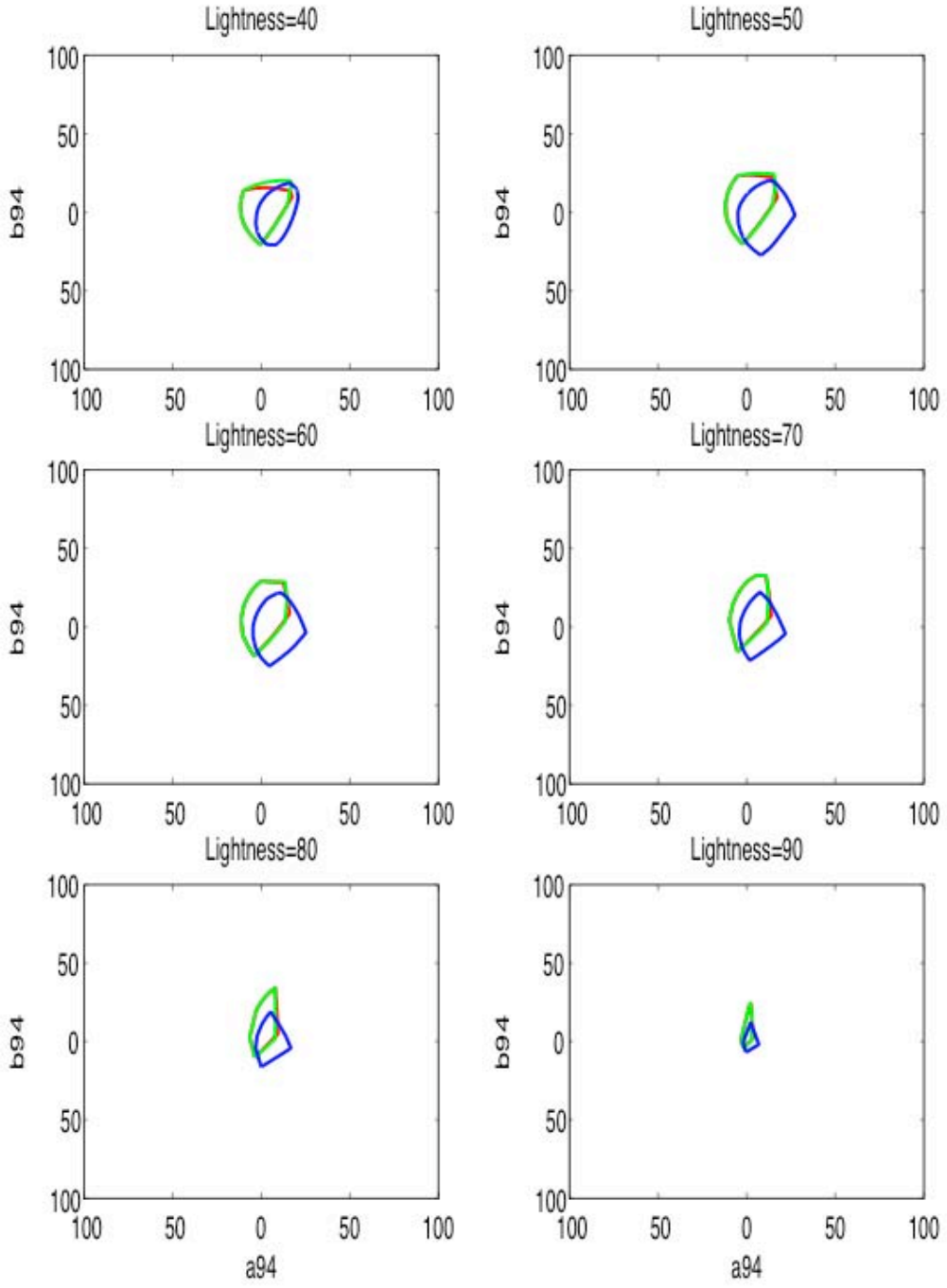


Figure 5c. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching of earth samples using GFC criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

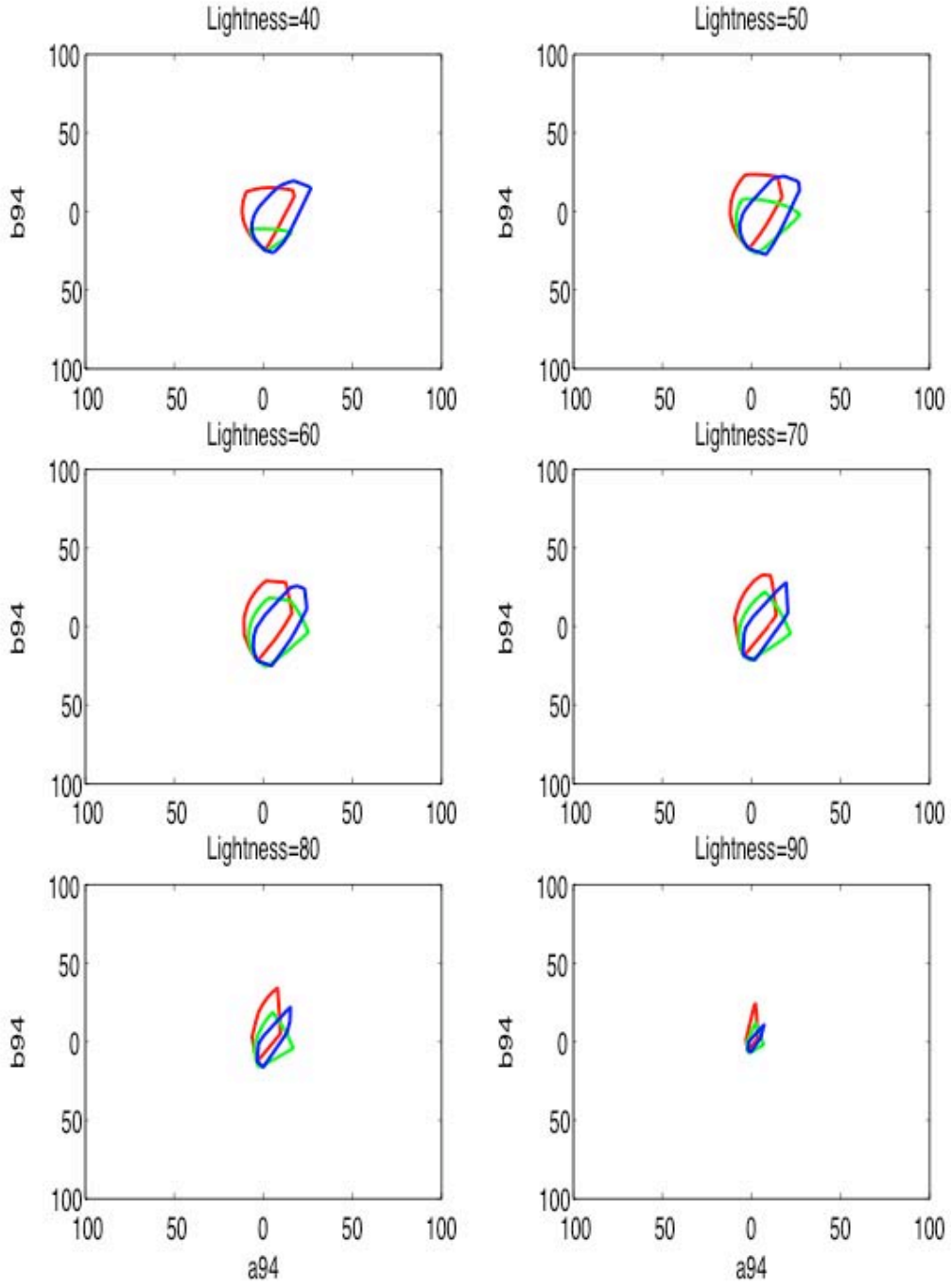


Figure 5d. *b_{94} versus a_{94} at different L_{94} levels for three, four, and five-pigment recipes based on the spectral matching of earth samples using $MI_{00}(D65 \square A)$ criterion. Red lines indicate 3-pigment set, green lines indicate 4-pigment set, and blue lines indicate 5-pigment set.*

As can be seen from the Tables II and III and Figure 4-5, in most cases the volume of color solid generated by the sets for matching the earth pigments were smaller than the corresponding volumes in the chromatic pigments. In the cases that chromatic pigments were used in predicting the earth samples, the color gamut gets larger than those sets containing only earth pigments. Therefore having a large color gamut is highly dependent on the selected pigments and not just on to the number of pigments in the set. It means that three chromatic pigments can make a larger color gamut than four earth pigments.

In order to investigate which pigments have more influence on making a larger color gamut, the volume of generated color gamut using the first thirty top sets was calculated and plotted against the corresponding error criterion (Figures 6a-6d). As can be seen, some plots in Figure 6 are clustered into two groups. The sets corresponds to each group was investigated and it was found that those sets containing phthalocyanine green make the color gamut significantly bigger than the other sets and the top clusters contain this pigment.

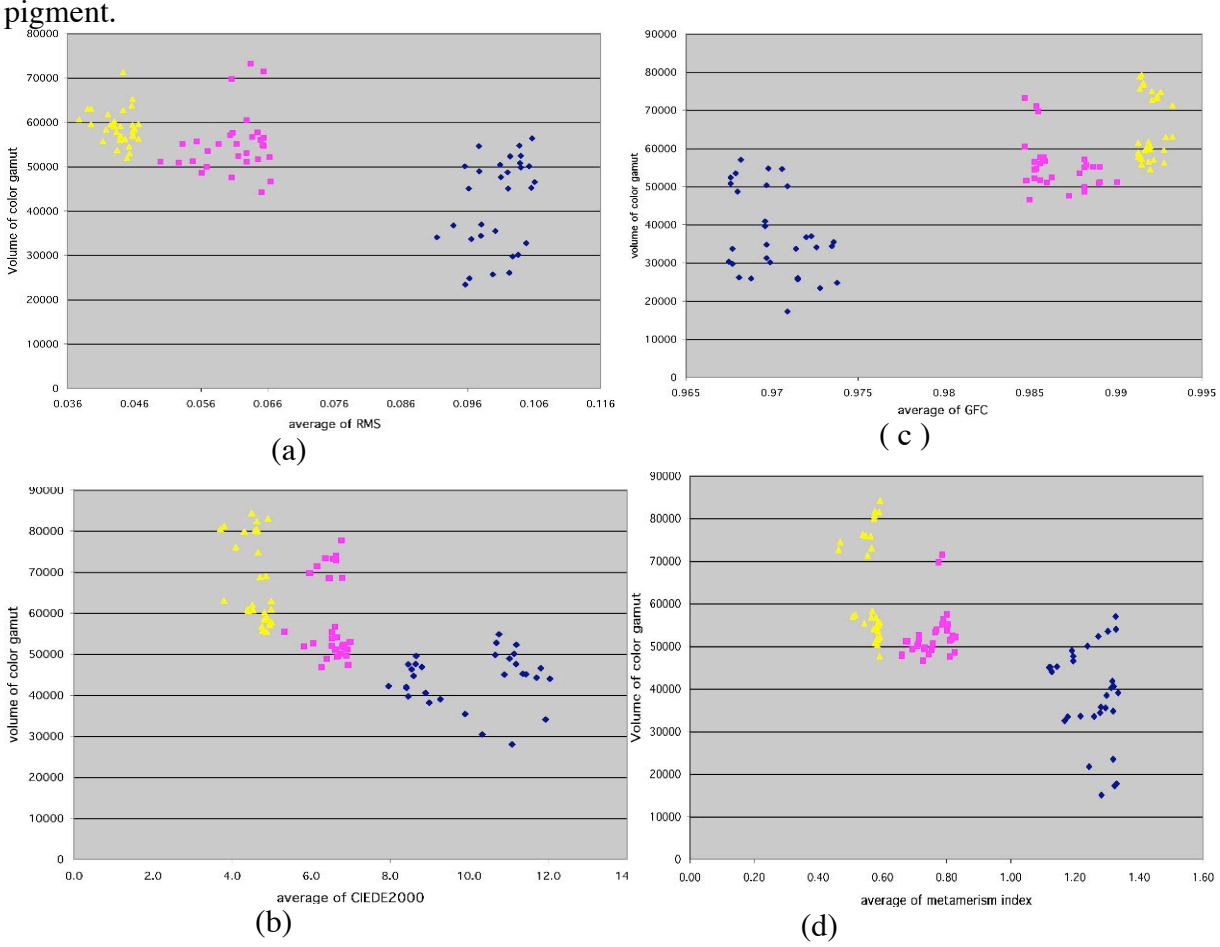


Figure 6. *Volume of color gamut generated by the first thirty top sets sorted in different error criteria: a) spectral RMS, b) ΔE_{00}, c) GFC, d) $MI_{00}(D65 \Delta A)$. Blue lines indicate 3-pigment sets, red lines indicate 4-pigment sets, and yellow lines indicate 5-pigment sets.*

The performance of spectral matching of chromatic and earth samples using the selected set of pigments based on different error criteria is summarized in Tables IV and V, respectively.

Table IV. *Statistical results of performance of predicting the chromatic samples.*

Results	Three-pigment	Four- Pigment	Five-Pigment
RMS (%)			
Average	10.6	6.5	4.4
Minimum	0.1	0.1	0.0
Maximum	42.6	16.7	13.5
Standard Deviation	10.1	5.2	4.2
ΔE_{00}			
Average	11.2	6.8	4.6
Minimum	0.1	0.1	0.0
Maximum	32.9	24.8	18.6
Standard Deviation	9.2	6.9	5.6
GFC			
Average	0.9682	0.9847	0.9915
Minimum	0.8991	0.9314	0.9615
Maximum	1.0000	1.0000	1.0000
Standard Deviation	0.0296	0.0176	0.0100
$MI_{00}(D65 \quad A)$			
Average	1.3	0.8	0.6
Minimum	0.0	0.0	0.0
Maxiumum	5.0	3.9	2.6
Standard Deviation	1.5	0.8	0.6

The average performance of 10.6% spectral RMS and 11.2 ΔE_{00} of 3-pigment sets are large enough to convince one that three pigments could not be sufficient for spectral matching. The average performance of 1.3 metamerism is not so high but the associated ΔE_{00} are in the range of 8 to 17 ΔE_{00}, which are high. In other words, the prediction error does not change so much under different illumination. Since the associated ΔE_{00} is large the average prediction error would be large for other illumination. Hence small average metamerism index is not an indication of good color matching unless it is associated with the small average ΔE_{00}.

The spectral plots of measured and predicted chromatic Gamblin samples using the selected sets based on spectral RMS are shown in Figures 7-11. In most cases the three-pigment set could not match the pigments well and at least the shape were not the same as original except in those cases that the target pigment was one of the pigments of the selected set. Four and five-pigment set could take the pattern of the original shape and they are almost acceptable but not as a perfect spectral matching.

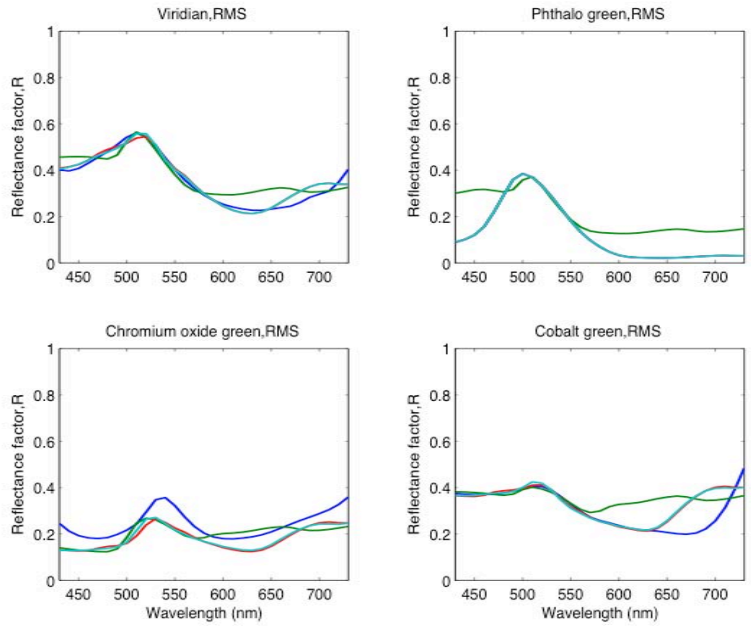


Figure 7. *Spectral reflectance of green pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

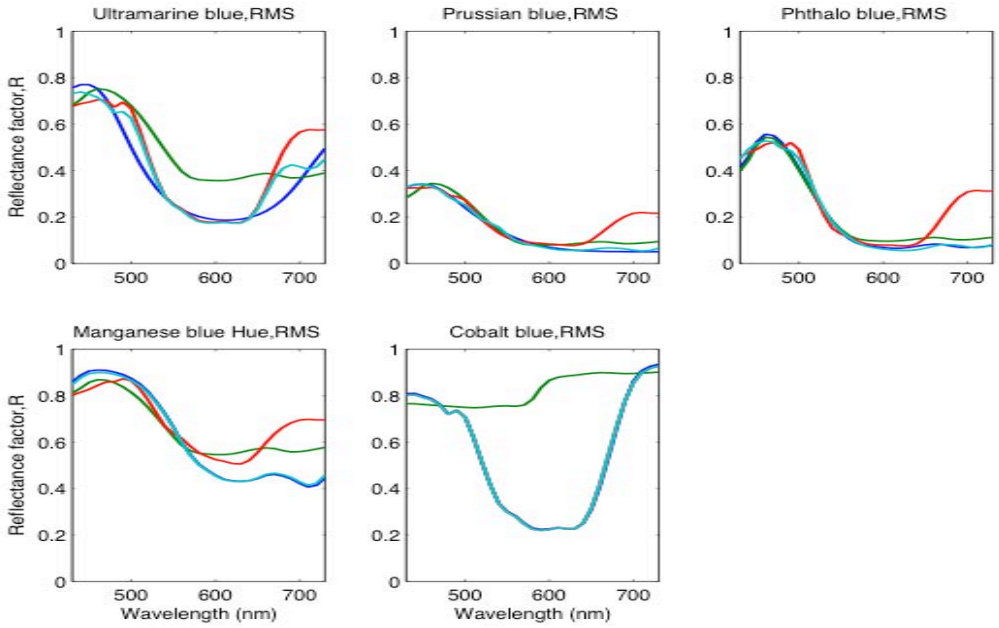


Figure 8. *Spectral reflectance of blue pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

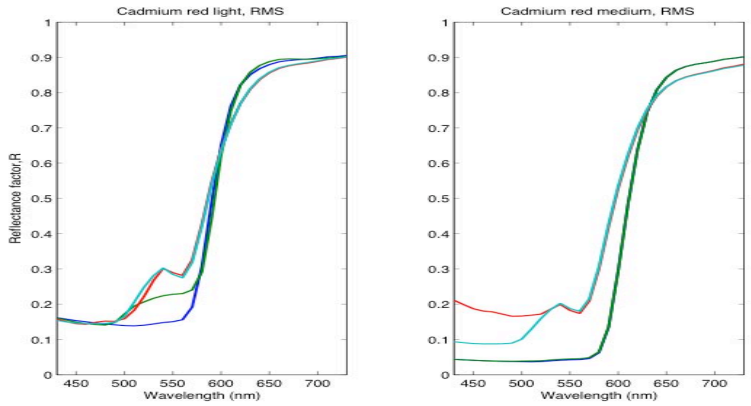


Figure 9. *Spectral reflectance of red pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

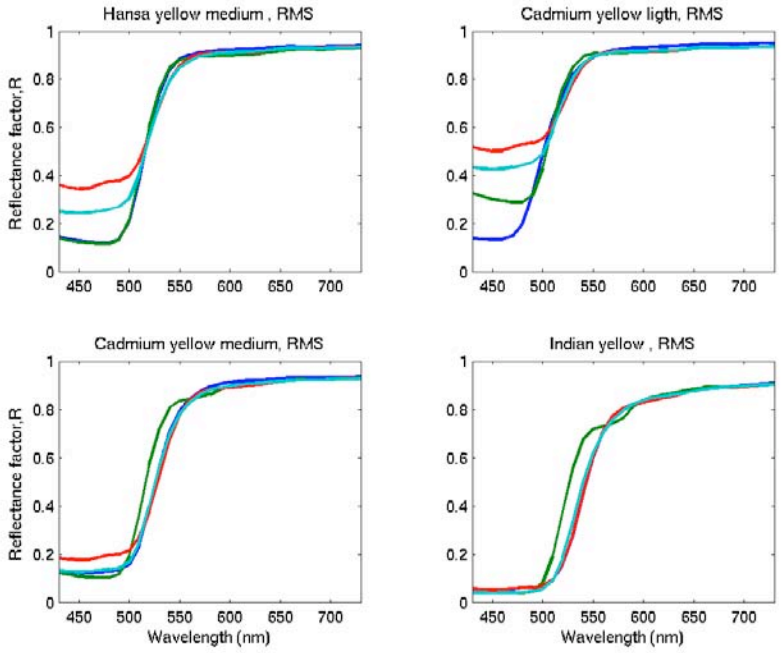


Figure 10. *Spectral reflectance of yellow pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

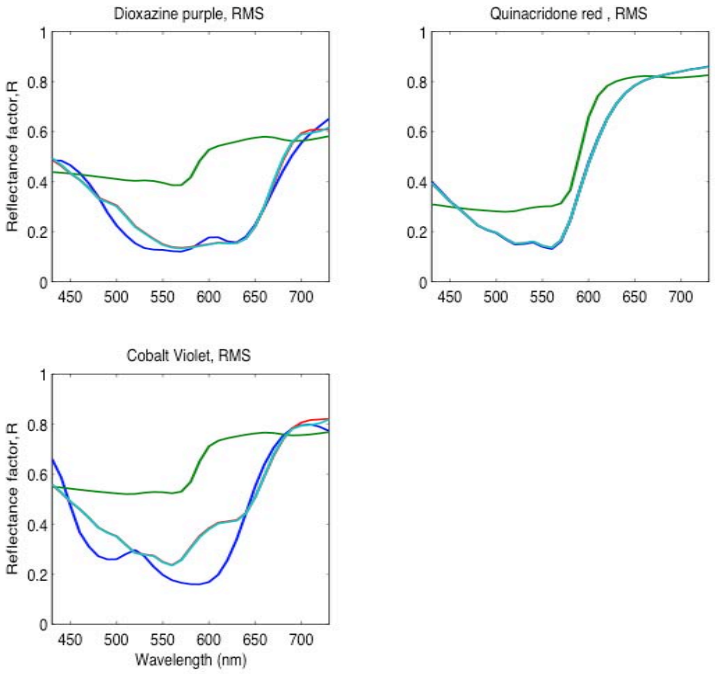


Figure 11. *Spectral reflectance of violet pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

The lower averages of spectral RMS, ΔE_{00}, and higher average of GFC indices for the prediction of earth pigments indicates better spectral matching performance than for chromatic samples. The five-pigment recipes have reasonably small averages. The performances of predictions are improved by moving from three to four and then to five pigments. Again, there is greater improvement from three to four pigments than from four to five pigments. The performance of spectral matching of earth samples using the selected set of pigments based on different error criteria is summarized in Table V.

The spectral plots of measured and predicted earth Gamblin samples using the selected sets based on spectral RMS are shown in Figures 12-14. In most cases all three, four, and five pigments could match the pigments very well and they are almost acceptable. Therefore in order to reduce the number of pigments in the set, the set containing three pigments was selected as the best set of pigments for matching earth samples.

Table V. *Statistical results of performance of predicting the earth samples.*

Results	Three-pigment	Four- Pigment	Five-Pigment
RMS (%)			
Average	1.3	0.7	0.4
Minimum	0.0	0.0	0.1
Maximum	2.9	2.4	1.5
Standard Deviation	0.8	0.7	0.4
$\square E_{00}$			
Average	2.3	1.1	0.5
Minimum	0.6	0.0	0.1
Maximum	6.5	2.8	1.3
Standard Deviation	1.6	0.7	0.3
GFC			
Average	0.9988	0.9996	0.9999
Minimum	0.9948	0.9991	0.9993
Maximum	1.0000	1.0000	1.0000
Standard Deviation	0.0014	0.0003	0.0002
$MI_{00}(D65 \square A)$			
Average	0.2	0.1	0.1
Minimum	0.0	0.0	0.0
Maximum	0.4	0.4	0.1
Standard Deviation	0.1	0.1	0.0

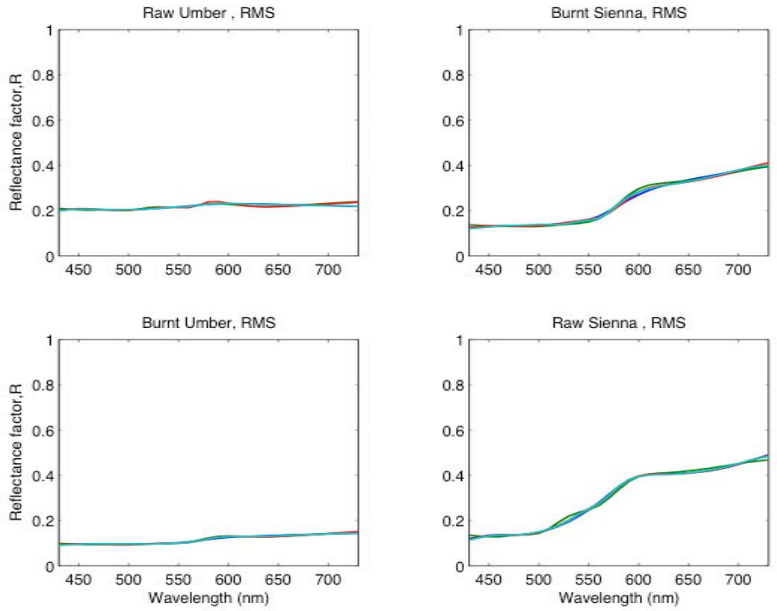


Figure 12. *Spectral reflectance of brown pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

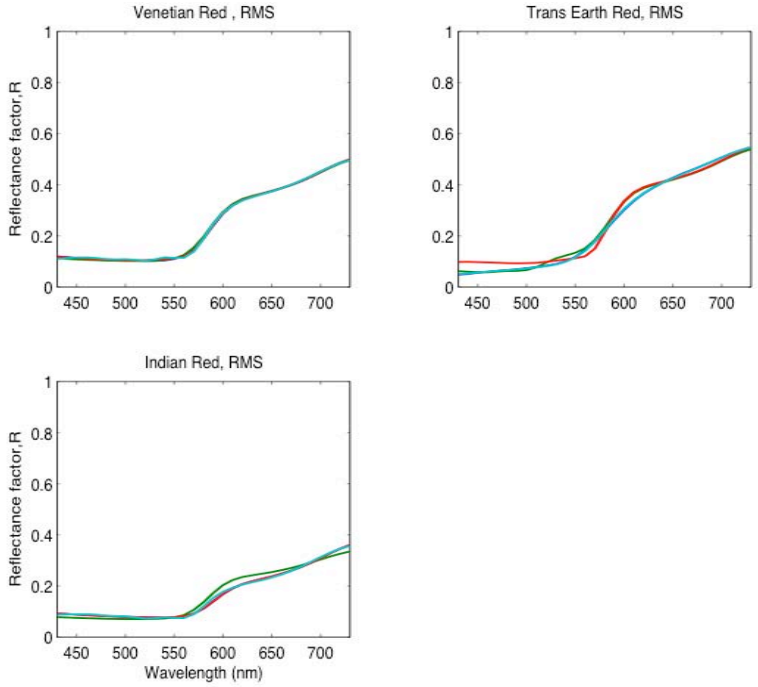


Figure 13. *Spectral reflectance of red earth pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

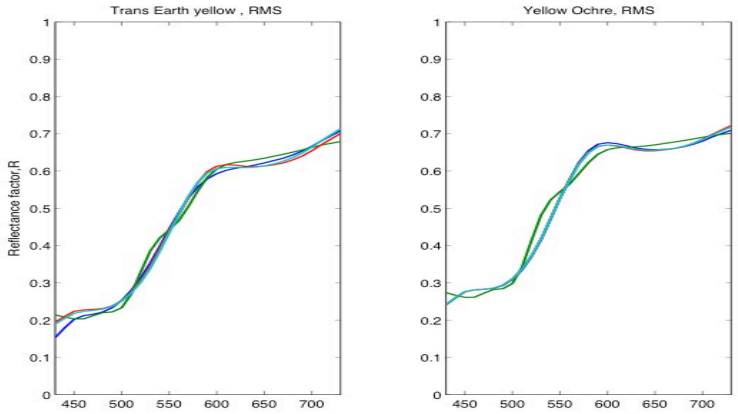


Figure 14. *Spectral reflectance of yellow earths pigments using the sets sorted based on RMS. Green lines indicate using 3-pigment set, red lines indicate using 4-pigment set, cyan lines indicate using 5-pigment set, and blue lines indicate the measured spectral reflectance.*

As a conclusion, the five-pigment sets had better performance for predicting the chromatic samples and three-pigment sets were sufficient for predicting the earth samples

at different criteria. Therefore a data set containing eight pigments could be a representative of Gamblin Conservation Colors. Since RMS optimization was employed for predicting the samples, the selected three earth and five chromatic pigments based on this criteria (Table VI) were chose as the selected set. The spectral plots of the pigments included in the selected set are shown in Figure 15.

Table VI. Selected pigments based on spectral RMS optimization

Pigment #	Pigment name
1	Quinacridone red
2	Cadmium yellow medium
3	Phthalocyanine green
4	Manganese blue hue
5	Cobalt blue
6	Venetian red
7	Indian yellow
8	Prussian blue

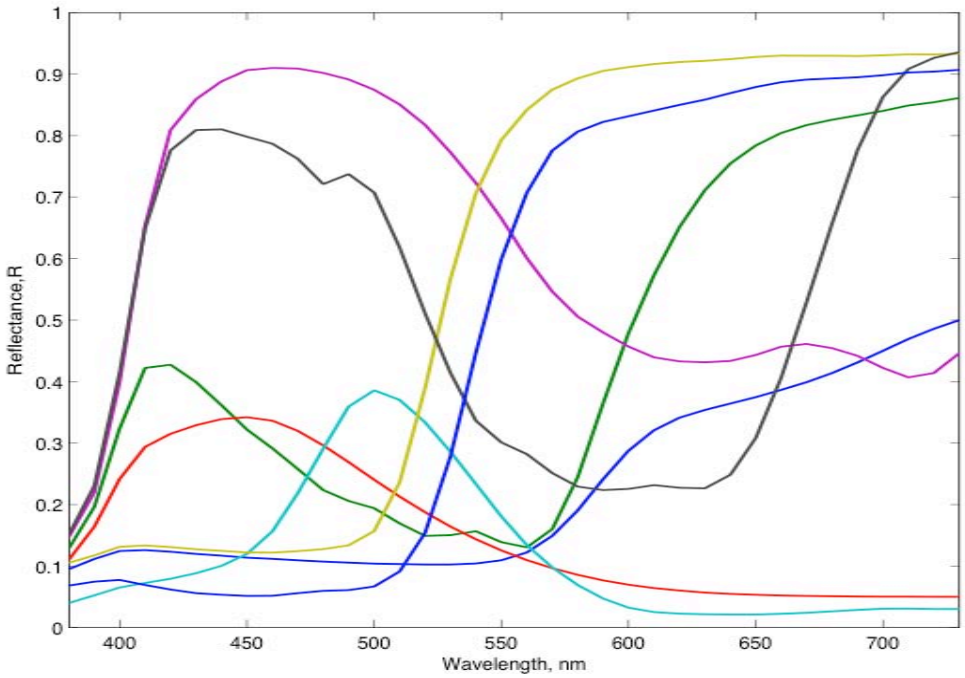
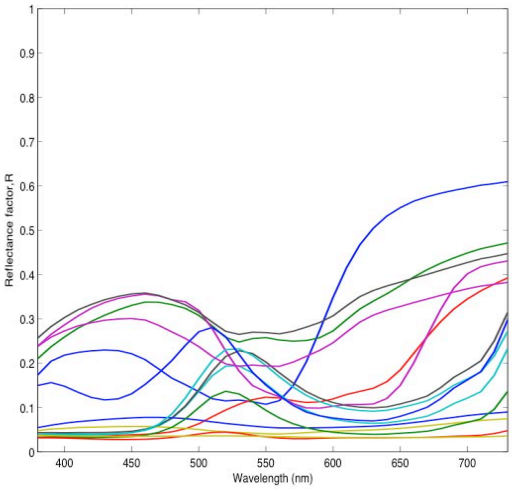


Figure 15. *Spectral reflectance of the selected pigments based on RMS criterion.*

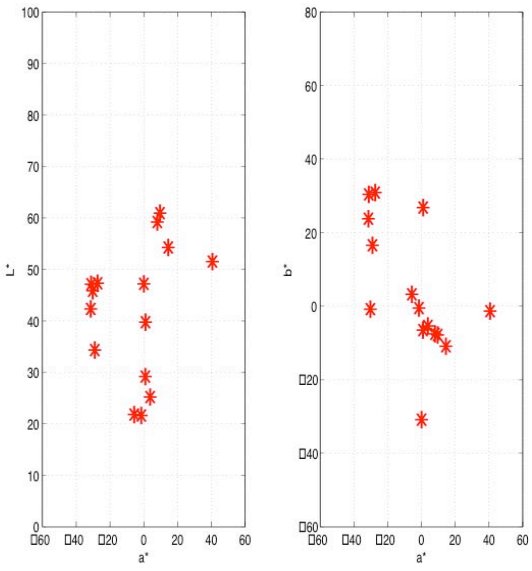
D. Verification of selected pigments with unknown samples

In this part of the experiment the quality of the selected set based on RMS criteria of part C was examined. Several verification targets were selected. The first was Matisse's Pot of Geraniums, an oil painting on linen painted by Henri Matisse in 1912. The second was four panels of painted patches contain 64, 61, 32, and 64 oil painted patches, respectively. Since there were some repeated samples in the Matisse group so the 15 samples of them were selected as the verification target. Patches of panels were made of mixing a colored pigment with TiO_2 dispersed in poly-vinyl acetate (PVA). The samples prepared at NGA by painting conservation department. The measurements were performed using spectroEye measuring in the wavelength range from 380 nm to 730 nm in interval of 10 nm. The CIELAB colorimetric attributes were also calculated for the targets using D65 illuminant and 2° observer. The verification targets, their spectral reflectance factors and color distribution are shown in Figures 16-20.

(a)



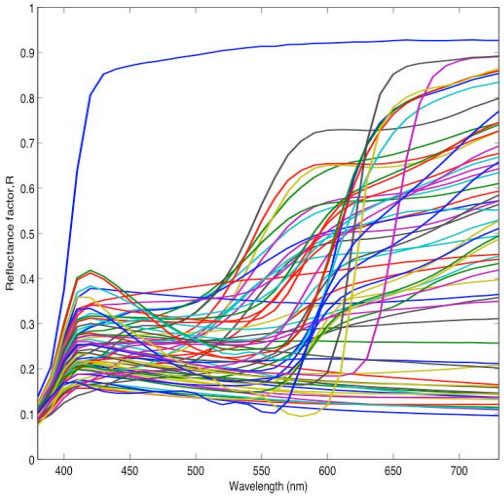
(c)



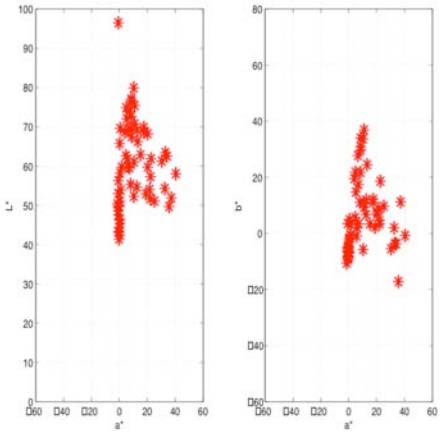
(b)

Figure 16. *(a) Henri Matisse, Pot of Geraniums, 1912 (b) Colorimetric plot (under D65 illuminant, 2□), (c) In situ measurement.*

(a)



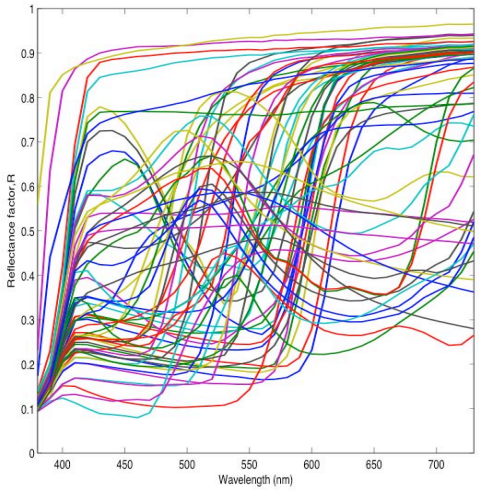
(c)



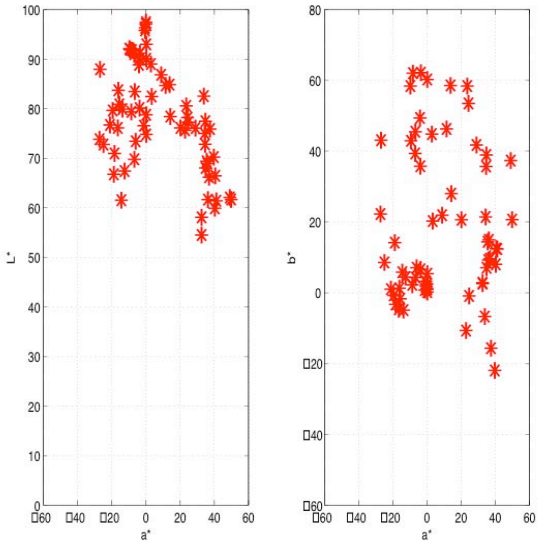
(b)

Figure 17*. (a) panel I, (b) Colorimetric plot (under D65 illuminant, 2□), (c) Spectral reflectance factors.*

(a)



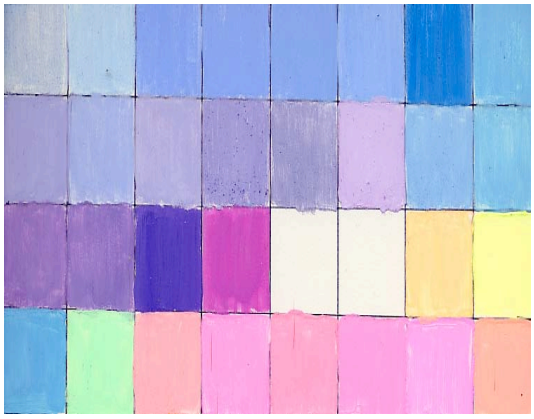
(c)



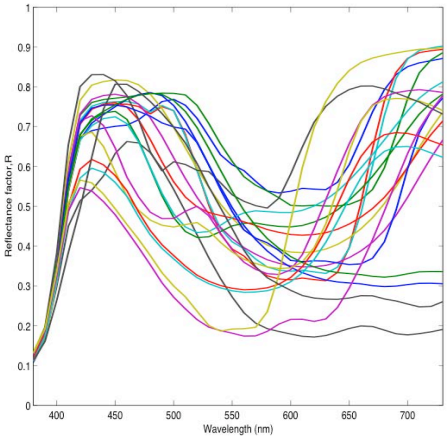
(b)

Figure 18. *(a) panel II, (b) Colorimetric plot (under D65 illuminant, 2□),(c) Spectral reflectance factors*

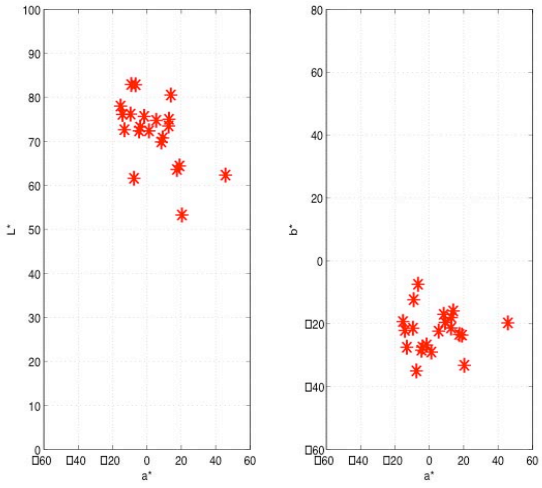
.



(a)

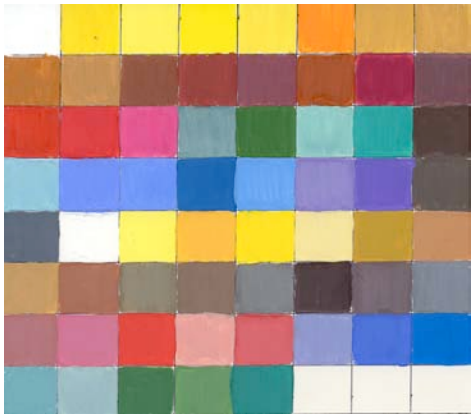


(c)

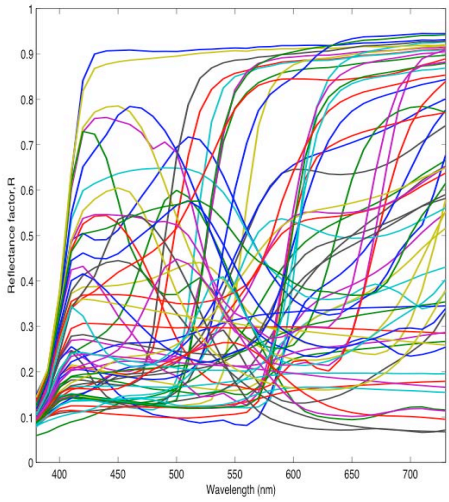


(b)

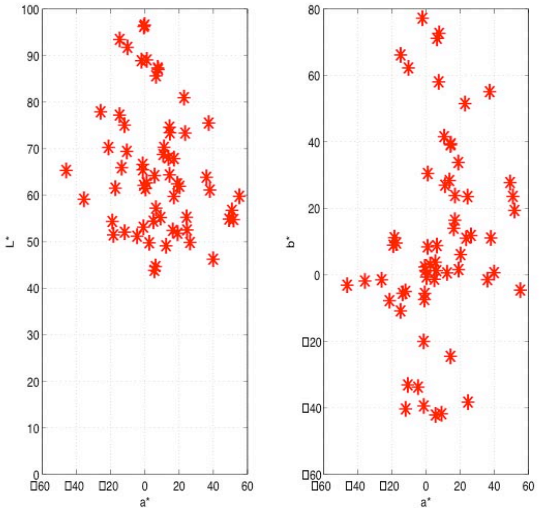
Figure 19. *(a) panel III, (b) Colorimetric plot (under D65 illuminant, 2□), (c) Spectral reflectance factor.*



(a)



(c)



(b)

Figure 20. *(a) panel IV, (b) Colorimetric plot (under D65 illuminant, 2□),(c) Spectral reflectance factors.*

It was assumed that having three pigments plus a black and white was sufficient to match any target. Based on this assumption, the selected three earth and five chromatic pigments based on RMS optimization and RMS sorted list (Table VI) were used as a group of pigments. All three-combinations of this database plus white and black pigments were employed for matching every sample of the Matisse target.

In order to verify that if these 10 pigments would be sufficient for matching the targets, all the three pigment combinations of the 28 Gamblin pigments, which were used for building the K/S database in part A, plus black and white were also examined for matching the Matisse target. The goal was finding a series of sets that could match each sample of the target with high spectral accuracy. Therefore for every sample of each target a recipe with minimum spectral RMS was selected as a recipe for matching that sample. In other words, 15 recipes were determined for 15 samples of the Matisse target. Optimization was based on minimizing spectral RMS values between the estimated and

measured spectral reflectance factors. It was assumed that the total amount of material is $\sum_{i=1}^{n} C_i$. Therefore unit $(k/s)_{\lambda}$ for each pigment was recalculated using the real amount of white pigment. Since every optimization is sensitive to the initial values, the concentration values was initialized to zero for all pigments except white and one for white pigment. That is because mixing a white with a color pigment makes the white darker and the color pigments lighter than before mixing. Aged lead was used as a white pigment for spectral matching of the Matisse, because it has less absorption than TiO_2 at low wavelengths (Figure 21).

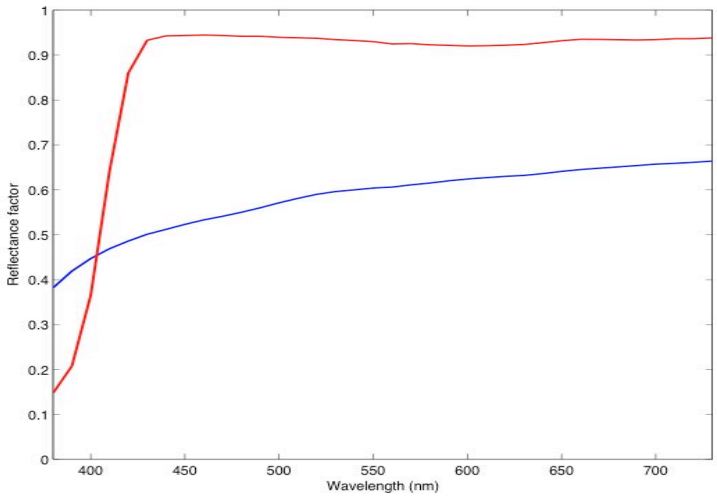


Figure 21. *Spectral reflectance factors of TiO_2 and aged lead white.*

The spectral plots of the estimated and measured 15 samples of Matisse using all three combinations out of the 8-pigment and 28-pigment databases are shown in Figure 22. The spectral and colorimetric accuracy for both groups are summarized in Table VII. The spectral plots and tables show that the overall shapes of the spectral curves were reasonably predicted with both databases. The selected pigments for matching the Matisse's samples are summarized in Tables VIII and IX. Although the selection of pigments of two groups was not exactly the same, the trend of selection was similar. For example venetian red and quinacridone red were selected for both groups for predicting sample 1. The selection of pigments for predicting sample 3 is the same because the transparent earth red and venetian red both are iron oxide with the same color index name except that venetian red is opaque and transparent earth red is transparent.

Table VII. *Colorimetric and spectral performance of estimation of Pot of Geraniums using the 8 and 28- pigment databases.*

	8-pigment database		28-pigment database	
sample	RMS (%)	ΔE_{00}	RMS (%)	ΔE_{00}
1	1.3	1.4	1.2	1.3
2	2.2	5.6	1.4	1.5
3	2.6	11.1	1.4	9.0
4	3.3	6.0	3.0	5.5
5	2.1	2.0	2.1	1.8
6	0.7	4.0	0.5	2.3
7	3.4	4.4	2.8	6.4
8	0.9	4.7	0.3	2.6
9	2.5	6.1	2.2	5.1
10	0.5	7.7	0.5	6.6
11	3.6	5.1	2.8	7.0
12	1.4	1.7	1.5	3.2
13	0.1	1.5	0.1	1.9
14	1.5	1.1	1.1	1.9
15	3.4	4.0	2.2	4.2

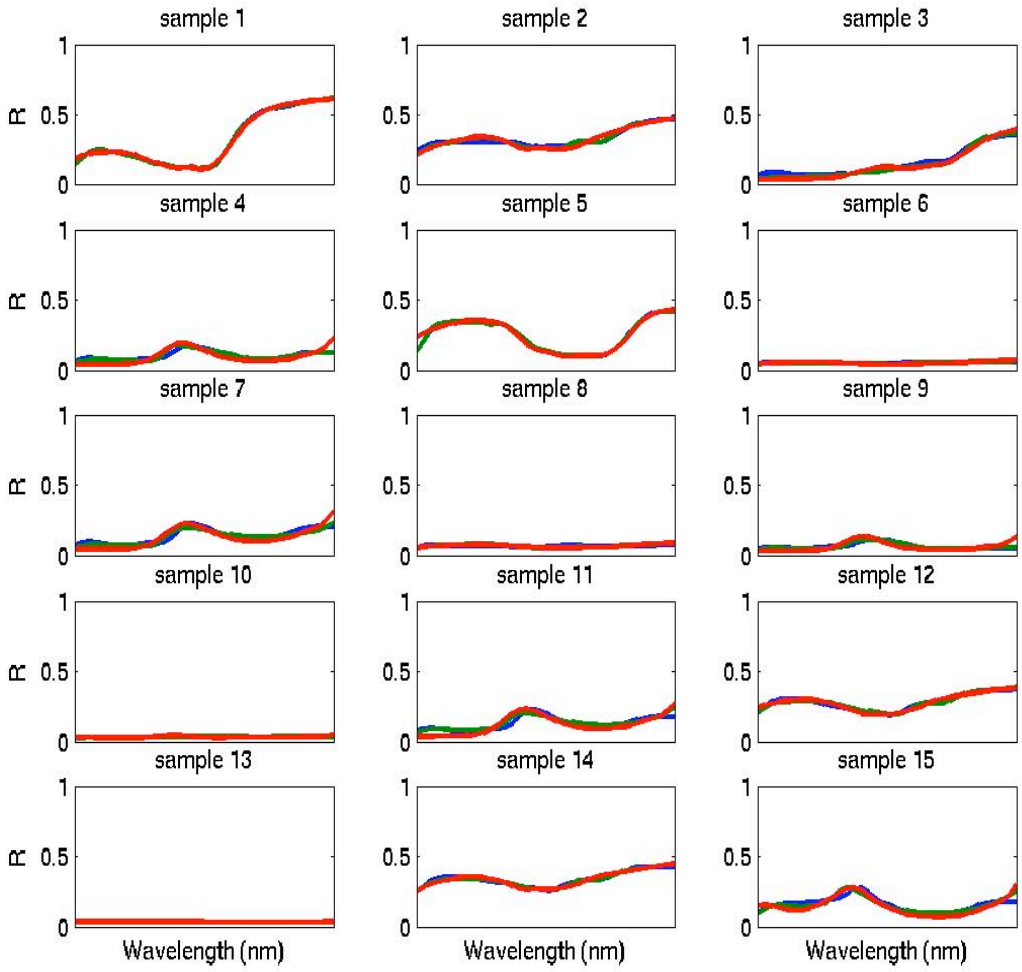


Figure 22. *Spectral reflectance factors of Pot of Geraniums. Blue lines indicate estimation based on 8-pigment database, green lines indicate estimation based on 28-pigment database, and red lines indicate in-situ spectrophotometry. Wavelength range is 380-730 nm.*

Table VIII. *Selected pigments for spectral matching of samples of Matisse using 8- pigments database. Pigments 1 and 5 are white and black, respectively.*

sample	pigment 2	pigment 3	pigment 4
1	Venetian red	Quinacridone red	Manganese blue hue
2	Venetian red	Prussian blue	Cobalt blue
3	Venetian red	Cobalt blue	Indian yellow
4	Phthalocyanine green	Cobalt blue	Indian yellow
5	Venetian	Phthalocyanine green	Cobalt blue
6	Venetian	Prussian blue	Phthalocyanine green
7	Phthalocyanine green	Cobalt blue	Indian yellow
8	Venetian	Prussian blue	Phthalocyanine green
9	Venetian	Phthalocyanine green	Indian yellow
10	Venetian red	Prussian blue	Phthalocyanine green
11	Phthalocyanine green	Cobalt blue	Indian yellow
12	Venetian red	Quinacridone red	Cobalt blue
13	Venetian red	Prussian blue	Phthalocyanine green
14	Quinacridone red	Cobalt blue	Indian yellow
15	Phthalocyanine green	Cadmium yellow medium	Cobalt blue

Table IX. *Selected pigments for spectral matching of samples of Matisse using 28- pigments database. Pigments 1 and 5 are white and black, respectively.*

sample	pigment 2	pigment 3	pigment 4
1	Venetian red	Quinacridone red	Phthalocyanine blue
2	Trans earth red	Phthalocyanine blue	Dioxazine purple
3	Trans earth red	Cadmium yellow medium	Cobalt blue
4	Phthalocyanine green	Dioxazine purple	Hansa yellow medium
5	Phthalocyanine green	Indian red	Cobalt blue
6	Phthalocyanine green	Phthalocyanine blue	Cadmium red medium
7	Viridian	Trans earth red	Hansa yellow medium
8	Trans earth red	Prussian blue	Dioxazine purple
9	Phthalocyanine green	Hansa yellow medium	Cadmium red medium
10	Trans earth red	Prussian blue	Phthalocyanine blue
11	Viridian	Trans earth red	Hansa yellow medium
12	Phthalocyanine blue	Dioxazine purple	Cadmium red medium
13	Trans earth red	Prussian blue	Cadmium red medium
14	Phthalocyanine blue	Dioxazine purple	Indian red
15	Viridian	Ultramarine blue	Cadmium yellow light

In order to compare the performance of the two groups of database (8 and 28 pigments), the different values between the colorimetric accuracy for predicting each sample using the two groups of databases were calculated. The same calculation was performed for spectral accuracy. The statistical for 15 samples of Matisse are summarized in Table X. The average difference of 1.3 ΔE_{00} and 0.4% spectral RMS between the two group shows that the database containing 28-pigment estimate the Matisse more accurate than 8-pigment database. But by considering the number of pigments in the database it would be worth to reduce it to a smaller number of pigments.

Table X. *Colorimetric and spectral difference of 8-pigment database and 28-pigment database for spectral matching the Pot of Geraniums.*

	ΔE_{00}	RMS (%)
Average	1.3	0.4
Minimum	0.1	0
Maximum	4.1	1.2
Std Dev	1.1	0.4

Since some pigments have the same reflectance and absorption characteristics, they can be replaced by each other. For example phthalocyanine blue and manganese blue hue are both copper phthalocyanine with the same color index number might be give the same characteristic to a mixture. Since phthalocyanine blue is a popular pigment among the artists, it was selected instead of manganese blue hue. Cobalt blue is a cobalt-alumina oxide pigment that is also a major blue on the artist's palette in every medium [8]. Finally by existence of phthalocyanine blue and cobalt blue in the pigment database, the contribution of prussian blue would not be very significant. Two reds in the selected set, quinacridone red and venetian red, have their own specific characteristic. Quinacridone red has two distinctive absorption bands that is unique fingerprint for this pigment. Even when red is mixed with other pigments the pattern remains intact [8]. Venetian red as an iron oxide exhibits a characteristic reflectance in the red region rising continuously after 620 nm. It is a dull red pigment that possesses excellent lightfastness [8]. A real red still needed in the pigment database. Cadmium red medium with its flat characteristic in the absorption region and moderately bright appearance could be a real red. Therefore it was appended to the pigment database. Finally a new group named as set A was nominated for matching the panel series. The existence of double reflectance bands at 425 nm and 545 nm in spectral plot of chromium oxide green led us to think more about the selection of green pigments. Therefore two other sets were created by adding chromium oxide green into set A to make set B and removing phthalocyanine green from set B to make set C. The three sets are shown in Table XI.

Table XI. *Three nominated pigment database*

Pigment number	Set A	Set B	Set C
1	Quinacridone red	Quinacridone red	Quinacridone red
2	Cadmium red medium	Cadmium red medium	Cadmium red medium
3	Phthalocyanine blue	Phthalocyanine blue	Phthalocyanine blue
4	Cobalt blue	Cobalt blue	Cobalt blue
5	Cadmium yellow medium	Cadmium yellow medium	Cadmium yellow medium
6	Indian yellow	Indian yellow	Indian yellow
7	Venetian red	Venetian red	Venetian red
8	Phthalocyanine green	Phthalocyanine green	Chromium oxide green
9	□	Chromium oxide green	□

All three-pigments combinations of sets A, B, and C; 56, 84, and 56 combinations respectively; along with white and black were employed for spectral matching the panel series. Again it was assumed that the summation of concentrations of all pigments should be equal to one and the other considerations that were mentioned for matching the Matisse were applied for estimation the panel series, though in this case, titanium white was used. For each patch, a set with minimum spectral RMS was selected as a best set of pigments for matching that selected patch. The concentrations of the selected pigments after spectral matching were saved as initial values for colorimetric matching. The idea of colorimetric matching using the output of spectral matching with the same selected pigments for each patch was converging to a minimum ΔE_{00} for D65 and the 2^o observer. Therefore another optimization based on minimizing ΔE_{00} was performed for matching the panel series. It was assumed that ΔE_{00} after the second optimization has to converge to zero. Of course Kubelka-Munk limitation, error caused by NNLS technique for building unit $(k/s)_{\square}$, experimental error during making Gamblin samples for building unit $(k/s)_{\square}$, different process of production of same pigments by different manufacturer, and some unexpected errors might be sources of error for the patches with non-zero ΔE_{00} value. The results of panel series were analyzed based on different color clusters. The patches with the same spectral overall shape were clustered in a one group. The color index number of the pigments was also considered for clustering the panel series. Table XII and XIV show the chromatic and earth samples as verification targets.

Table XII. *Chromatic samples used as verification target.*

	Pigment name	*Color Index number*
Blue	Cobalt blue	PB 28
	Ultramarine blue	PB 29
	Manganese blue	PB 33
	Cerulean blue	PB 35
	Phthalocyanine blue (Winsor blue)	PB 15
	Hoggar blue	□
	Prussian blue	PB 27
Yellow	Aureolin yellow	PY 40
	Cadmium yellows	PY 37 & 37
	Lemon yellow deep	PY 31
	Winsor yellow	□
	Indian yellow	PY 83
	Hansa yellow medium	PY 74
Orange	Cadmium orange	PO 20
Green	Cobalt green	PG 19
	Viridian	PG 18
	Chromium oxide green	PG 17
	Chrome green light	PG 15
	Phthalo green	PG 7
	Hooker's green	PG 8
Red	Cadmium reds	PR 108
	Vermilion	PR 106
	Rose madder Genuine	C.I natural red 9
	Alizarin permanent	□
	Red lead	PR 105
Violet	Ultramarine violet	PV 15
	Cobalt violet	PV 14
	Manganese violet, Minearl violet	PV 16
	Blue violet	□
	Rose violet	□
	Quinacridone red	PV 19
	Dioxazine purple	PV 23

The spectral and colorimetric accuracy is listed in Table XIII and spectral plots are shown in Figures 23-28.

Table XIII. *Comparison between colorimetric, spectral, and converged colorimetric accuracy of chromatic samples used as verification target.* $\Delta E_{00}1$ *and* $\Delta E_{00}2$ *are associated to the spectral and converged prediction, respectively.*

□	□	Set A	□	□	□	Set B	□	□	□	Set C	□	□
Results	RMS (%)	$\Delta E_{00}1$	$\Delta E_{00}2$	MI_{00}	RMS (%)	$\Delta E_{00}1$	$\Delta E_{00}2$	MI_{00}	RMS (%)	$\Delta E_{00}1$	$\Delta E_{00}2$	MI_{00}
Blues												
Average	3.2	2.1	1.0	0.7	3.2	2.1	1.0	0.7	3.5	3.2	1.7	0.7
Min	0.7	0.3	0.0	0.0	0.7	0.3	0.0	0.0	0.8	0.3	0.0	0.0
Max	6.2	7.6	5.1	2.3	6.1	7.6	5.1	2.3	6.8	7.4	4.7	2.5
Std	1.6	2.1	1.4	0.7	1.6	2.1	1.4	0.7	1.8	2.2	1.7	0.8
Yellows												
Average	4.4	4.3	2.6	1.4	4.4	4.3	2.6	1.4	4.4	4.3	2.9	1.2
Min	0.6	0.2	0.0	0.1	0.6	0.2	0.0	0.1	0.6	0.2	0.0	0.1
Max	10.9	10.0	6.9	3.9	10.9	10.0	6.9	3.9	10.9	10.1	9.1	2.6
Std	2.9	2.8	2.3	1.1	2.9	2.8	2.3	1.1	2.9	2.8	2.7	0.9
Oranges												
Average	5.1	8.8	3.0	1.0	5.1	8.7	3.0	1.0	5.1	8.8	3.0	1.0
Min	3.0	3.0	0.0	0.2	3.0	3.0	0.0	0.2	3.0	3.0	0.0	0.2
Max	8.2	14.7	5.2	1.8	8.2	14.7	5.2	1.5	8.2	14.7	5.2	1.5
Std	2.0	3.9	1.8	0.5	2.0	3.9	1.8	0.5	2.0	3.9	1.8	0.5
Greens												
Average	3.9	3.2	0.2	0.8	3.4	2.9	0.6	0.8	5.2	6.7	4.2	0.8
Min	0.7	0.3	0.0	0.1	0.7	0.5	0.0	0.1	0.8	0.7	0.0	0.1
Max	9.2	9.1	5.0	2.5	8.9	8.6	7.1	2.5	10.5	20.6	12.9	2.6
Std	2.2	2.3	1.0	0.7	2.5	2.0	1.8	0.7	2.8	4.6	3.8	0.6
Reds												
Average	3.1	2.9	0.2	0.8	3.1	2.9	0.2	0.8	3.1	3.0	0.2	0.8
Min	0.9	0.1	0.0	0.1	0.9	0.1	0.0	0.1	0.9	0.1	0.0	0.1
Max	8.6	8.0	3.2	2.8	8.6	8.0	3.2	2.8	8.6	8.2	3.2	2.8
Std	2.2	2.2	0.7	0.7	2.1	2.2	0.7	0.7	2.1	2.4	0.7	0.7
Violets												
Average	4.7	3.8	1.3	1.3	4.6	3.8	1.3	1.3	4.6	3.8	1.3	1.3
Min	3.0	1.8	0.0	0.1	3.0	1.8	0.0	0.1	3.0	1.8	0.0	0.1
Max	6.6	6.1	4.2	2.4	6.6	6.1	4.2	2.4	6.6	6.1	4.2	2.4
Std	0.9	1.3	1.4	0.8	0.9	1.3	1.4	0.8	0.9	1.3	1.4	0.8

From Table XIII, it can be seen that the average spectral RMS and ΔE_{00} for set C are always equal or bigger than the corresponding values in sets A and B. In other words, on average, set A and B have equal or better performance in terms of spectral RMS and ΔE_{00} than set C. Since there is phthalocyanine green in set A and B that is not included in set C, one may address the presence of this pigment in recipes as the cause of differences in performances. Set B includes both phthalocyanine green and chromium oxide green while set A only includes phthalocyanine green. The performance of set B is reasonably good for red, blue, and green colors. The average performance is 3.1%, 3.2%, 3.9% spectral RMS and 0.2, 1.0, and 0.2 ΔE_{00}, respectively. All three sets had problems in prediction of yellow colors, which is indicated by average 4.4% spectral RMS and average 2.6 ΔE_{00}. This lower performance in prediction of yellow colors also leads to a low performance in prediction of orange colors. Since set B had better spectral performance in terms of average and maximum spectral RMS than set A and C, it was selected as the best set of pigments. The average metamerism indices presented in Table XIII are not so high but they should be interpreted based on the corresponding ΔE_{00}.

The spectral plots of chromatic verification patches are shown in the following figures. As can be seen from the estimated curves, the overall spectral shapes were predicted very well. The idea of converging ΔE_{00} to zero has improved the ΔE_{00} values. The average ΔE_{00} after converging process is less than average ΔE_{00} of the first optimization. But in most cases it was tried to match the short and medium wavelengths and matching at long wavelengths was not as good as the spectral matching results. Because CIE color-matching functions $\bar{x}, \bar{y}, \bar{z}$ get very close to zero at above 700 nm, 715 nm, and 555 nm, respectively. Of course practically by performing color correction process, a perfect colorimetric matching would be possible with these selected pigments.

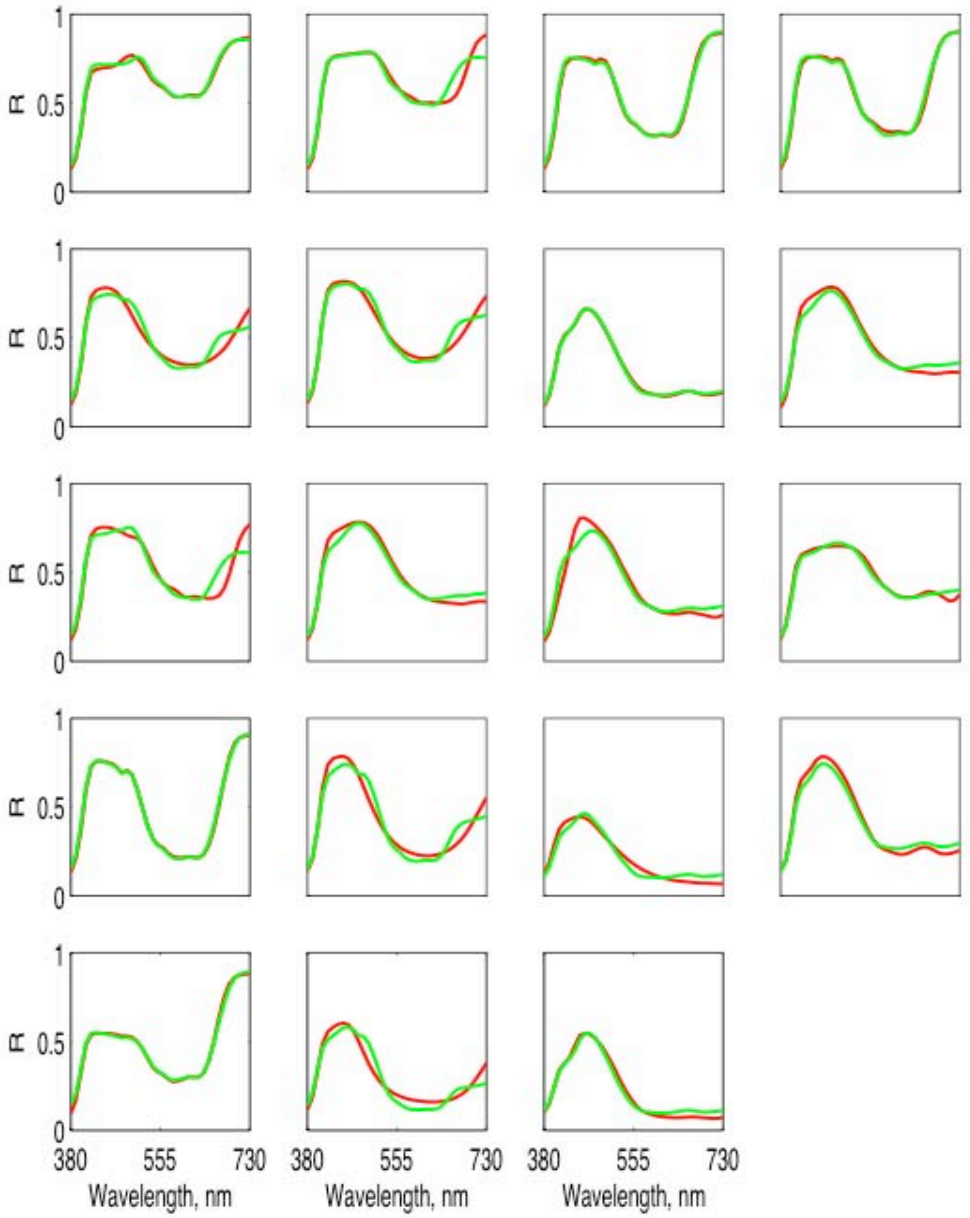


Figure 23. *Estimated spectral reflectance factors using set B compared with the measurement of blue verification targets. Red lines indicate measurement and green lines indicate prediction.*

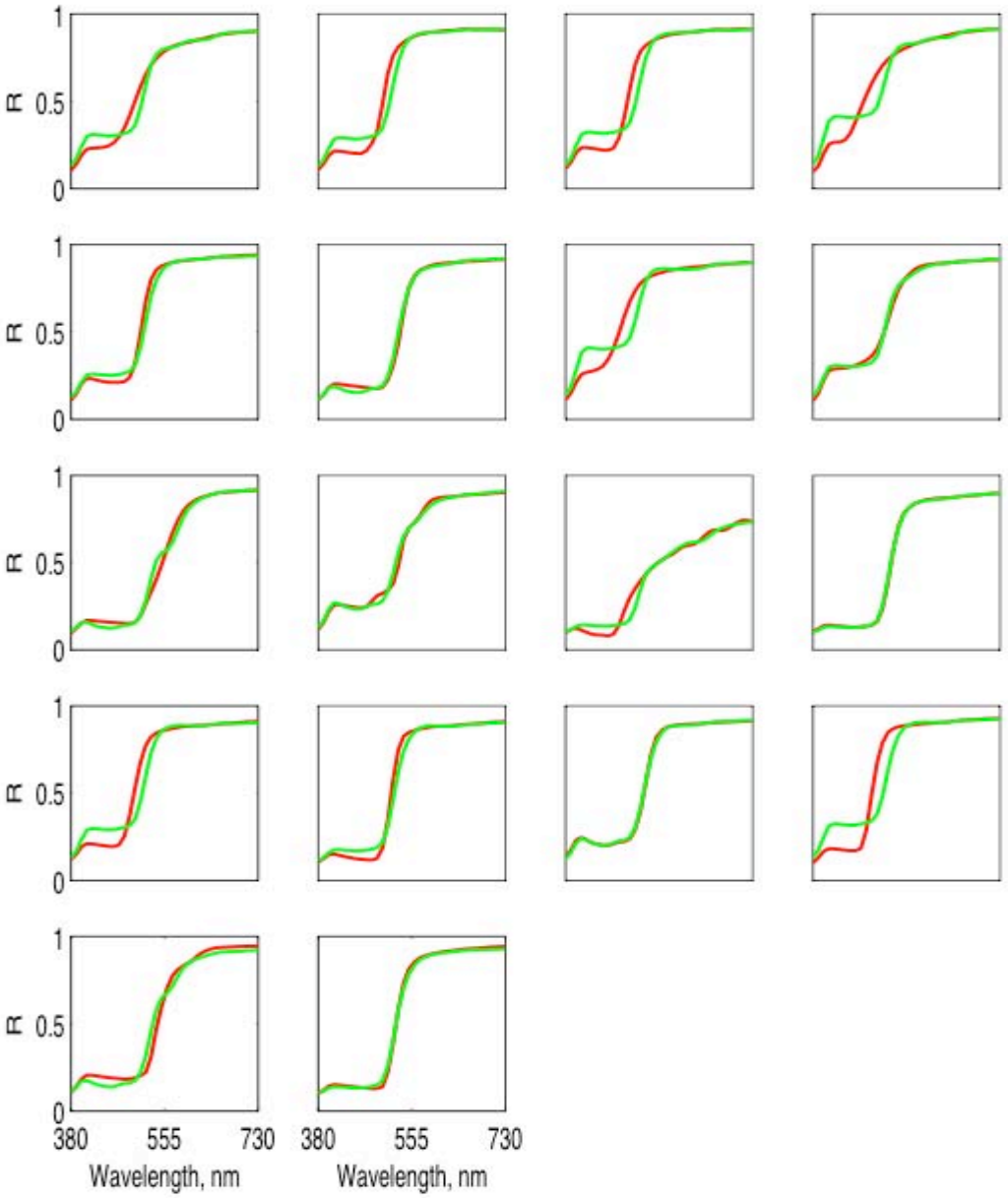


Figure 24. *Estimated spectral reflectance factors using set B compared with the measurement of yellow verification targets. Red lines indicate measurement and green lines indicate prediction.*

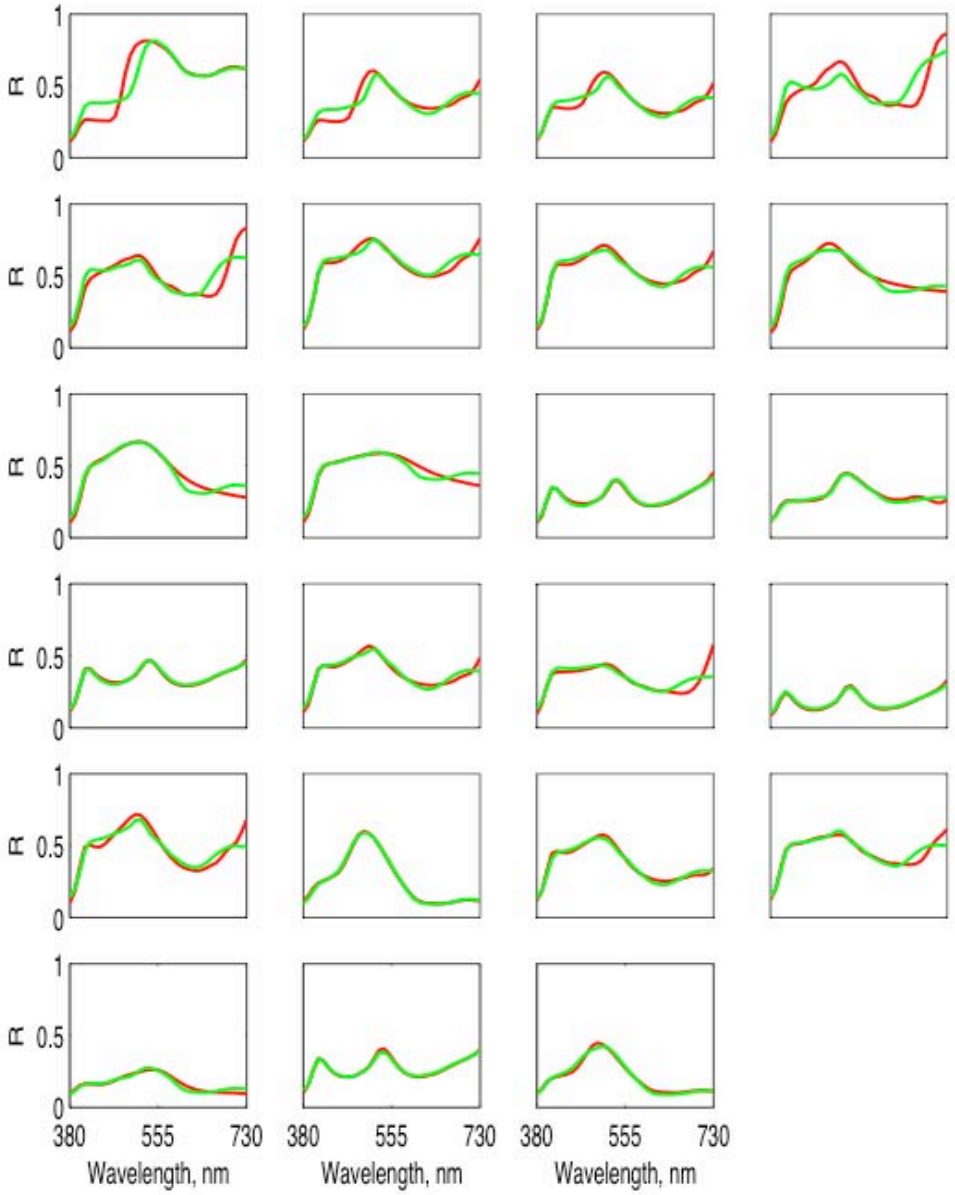


Figure 25. *Estimated spectral reflectance factors using set B compared with the measurement of green verification targets. Red lines indicate measurement and green lines indicate prediction.*

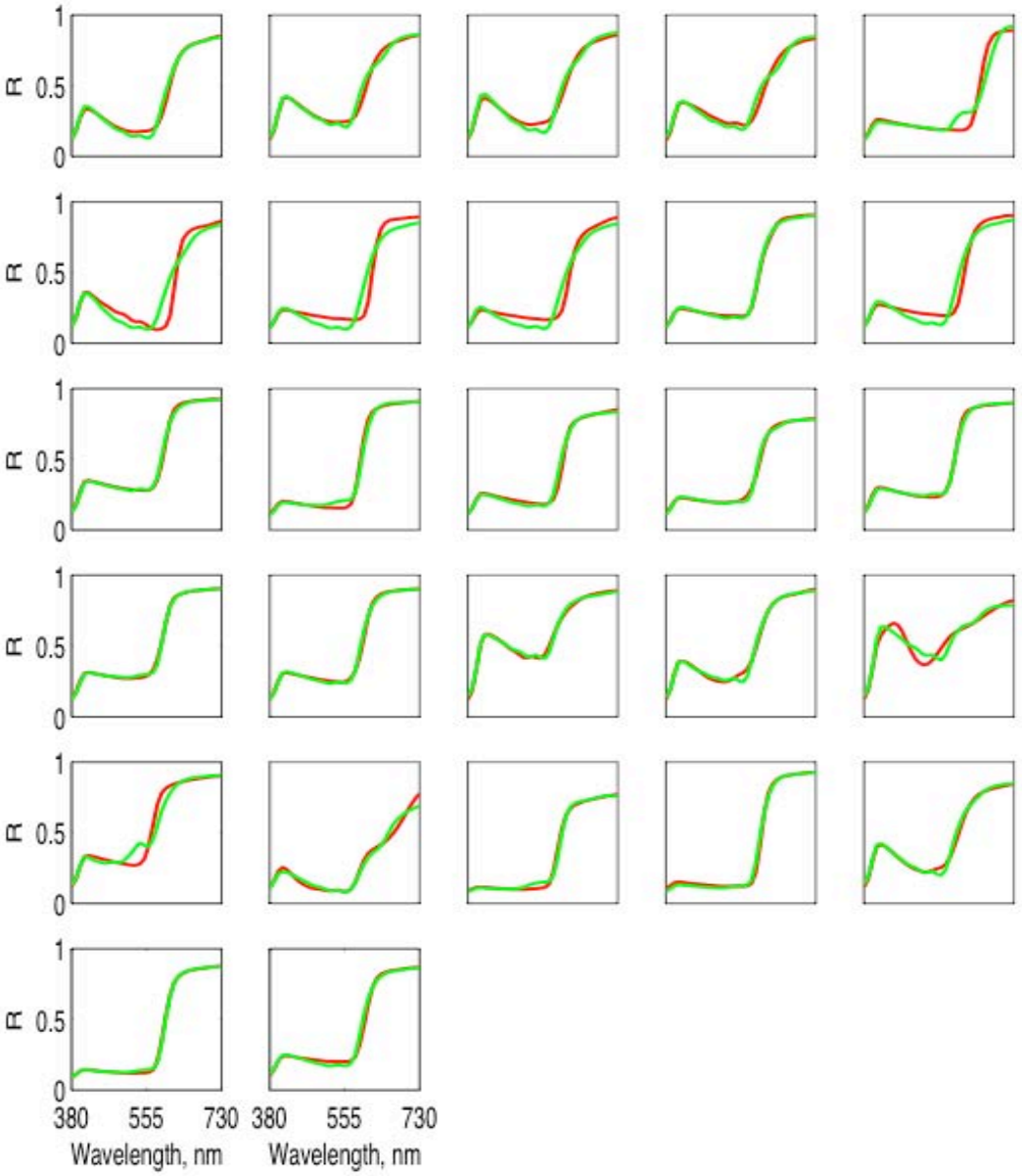


Figure 26. *Estimated spectral reflectance factors using set B compared with the measurement of red verification targets. Red lines indicate measurement and green lines indicate prediction.*

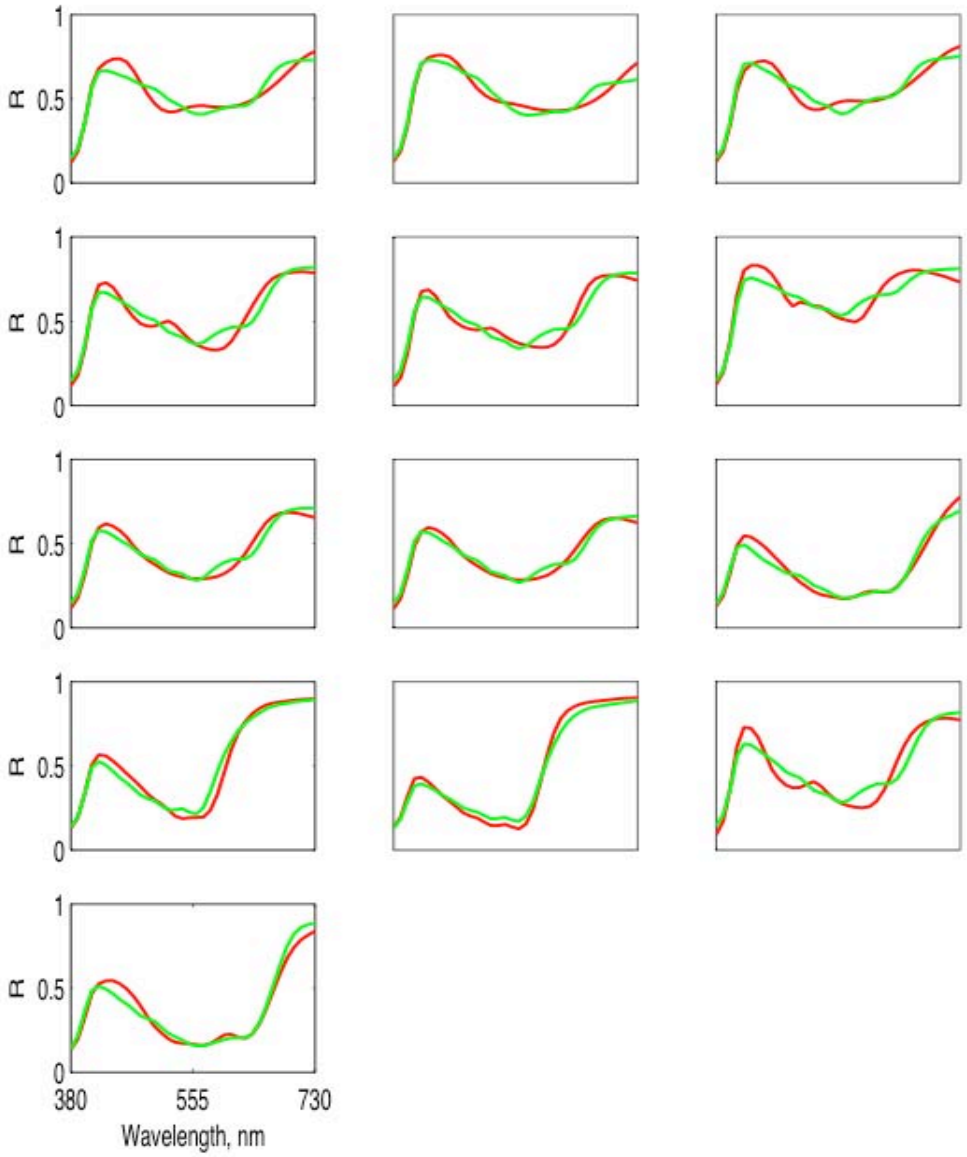


Figure 27. *Estimated spectral reflectance factors using set B compared with the measurement of violet verification targets. Red lines indicate measurement and green lines indicate prediction.*

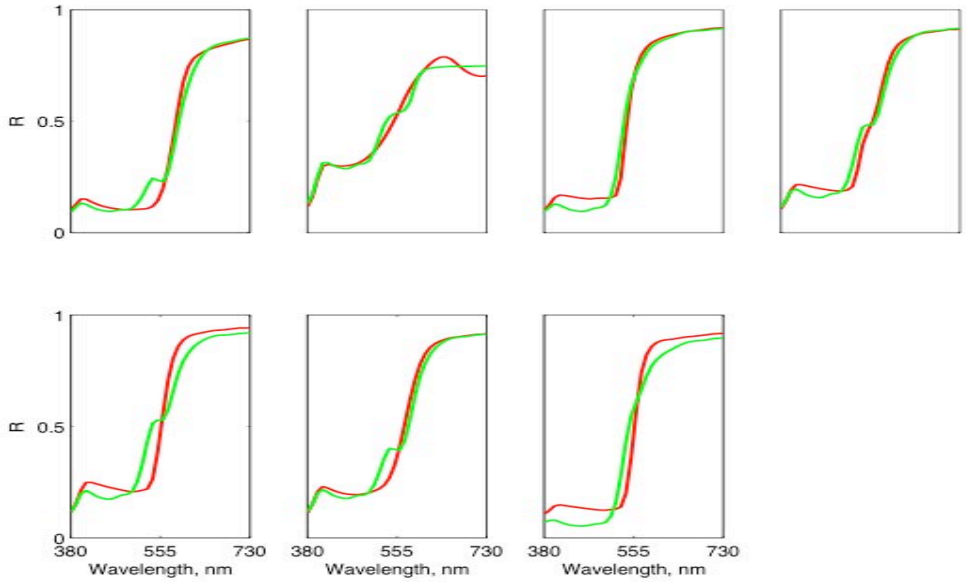


Figure 28. *Estimated spectral reflectance factors using set B compared with the measurement of orange verification targets. Red lines indicate measurement and green lines indicate prediction.*

Table XIV show the earth samples used as the verification target. Average spectral RMS for predicting the earth verification patches using sets A and B are less than 1.7% for all patches. Set C predicts the green and yellow earth samples with less accuracy than set A and B. In comparison with predicting the chromatic patches, the performance of all three sets are good. Therefore it can be concluded that the performance of spectral prediction of earth verification patches is better than chromatic verification samples. The same is true in terms of average ΔE_{00}, earth targets were predicted with lower ΔE_{00} than chromatic samples. Average ΔE_{00} values for all earth samples are less than 0.1 except for the red earth sample, which is 0.3 ΔE_{00}. The average values of most criteria, such as spectral RMS and ΔE_{00}, were almost the same for set A, B, and C. However set B usually had equal or a little bit better performance. The spectral plots of earth verification patches are shown in Figures 29-33. The good performance of prediction of earth samples using set B can be seen from these figures. Like chromatic targets set B is not perfect in the prediction of yellow colors.

Table XIV. *Earth samples used as verification target.*

	Pigment name	*Color Index number*
Black	Ivory black, Bone black	PBK 9
	Iron oxide black	PBK 11
	Vine black	PBK 8
	Manganese black	PBK 14
	Lamp black	PBK 6
Brown	Raw umber, Burnt umber	PBR 7
	Vand dyke brown	PBR 9
	Manganese brown	PBR 8
	Mars brown	PBR 6 and 7
Red	Red ocher Mars red, Indian red, Venetian red	PR 101
Yellow	Raw Sienna, Yellow ochre,Terra di Sienna, brown ocher	PY 43
	Translucent yellow	□
	Monastral fast gold	□
	Orpiment, Realgar	PY 39
	Massicot	PY 46
	Transparent earth yellow , Mars yellow	PY 42
Green	Verdigris	C.I pigment green 20
	Terra verte,Burnt Green earth	C.I pigment green 23

***Table XV**. Comparison between colorimetric, spectral, and converged colorimetric accuracy of earth samples used as verification target. $\Delta E_{00}1$ and $\Delta E_{00}2$ are associated to the spectral and converged prediction, respectively.*

□	□	Set A	□	□	□	Set B	□	□	□	Set C	□	□
Results	RMS (%)	$\Delta E_{00}1$	$\Delta E_{00}2$	MI_{00}	RMS (%)	$\Delta E_{00}1$	$\Delta E_{00}2$	MI_{00}	RMS(%R)	$\Delta E_{00}1$	$\Delta E_{00}2$	MI_{00}
Blacks												
Average	1.0	1.9	0.1	1.0	1.0	1.8	0.1	1.0	1.0	1.6	0.1	1.0
Min	0.6	0.8	0.0	0.2	0.6	0.8	0.0	0.2	0.6	0.6	0.0	0.2
Max	1.5	3.2	1.0	1.7	1.5	3.0	1.0	1.4	1.5	3.0	0.5	1.4
Std	0.3	0.9	0.4	0.5	0.3	0.9	0.4	0.4	0.3	0.8	0.2	0.5
Browns												
Average	0.7	1.2	0.0	0.3	0.7	1.1	0.0	0.3	0.7	1.1	0.0	0.3
Min	0.2	0.2	0.0	0.0	0.2	0.2	0.0	0.0	0.2	0.2	0.0	0.0
Max	1.2	4.1	0.8	0.6	1.2	3.2	0.8	0.6	1.2	3.2	0.1	0.9
Std	0.3	0.9	0.2	0.2	0.3	0.8	0.2	0.2	0.3	0.8	0.0	0.2
Red earths												
Average	1.2	2.0	1.1	0.3	1.1	2.1	0.4	0.2	1.1	2.1	0.3	0.3
Min	0.6	0.2	0.0	0.0	0.6	0.2	0.0	0.0	0.6	0.2	0.0	0.0
Max	2.1	4.2	3.8	0.8	1.9	5.0	2.1	0.6	1.9	5.0	2.1	0.6
Std	0.5	1.3	1.2	0.2	0.4	1.5	0.6	0.2	0.4	1.6	0.6	0.2
Yellow earths												
Average	2.3	1.5	0.0	0.6	2.3	1.5	0.0	0.6	2.3	1.5	0.0	0.6
Min	1.3	0.1	0.0	0.1	1.3	0.1	0.0	0.1	1.3	0.4	0.0	0.1
Max	4.8	3.0	0.6	1.9	4.8	3.0	0.6	1.9	4.8	3.0	0.6	1.9
Std	0.9	0.8	0.1	0.4	0.9	0.8	0.1	0.4	0.9	0.7	0.1	0.4
Green earths												
Average	1.7	1.5	0.0	0.3	1.7	1.5	0.0	0.3	2.2	1.6	0.0	0.8
Min	1.1	1.2	0.0	0.2	1.1	1.2	0.0	0.2	1.1	0.8	0.0	0.4
Max	2.7	2.1	0.0	0.5	2.7	2.1	0.0	0.5	3.7	2.7	0.0	1.4
Std	0.7	0.3	0.0	0.1	0.7	0.3	0.0	0.1	1.1	0.9	0.0	0.4

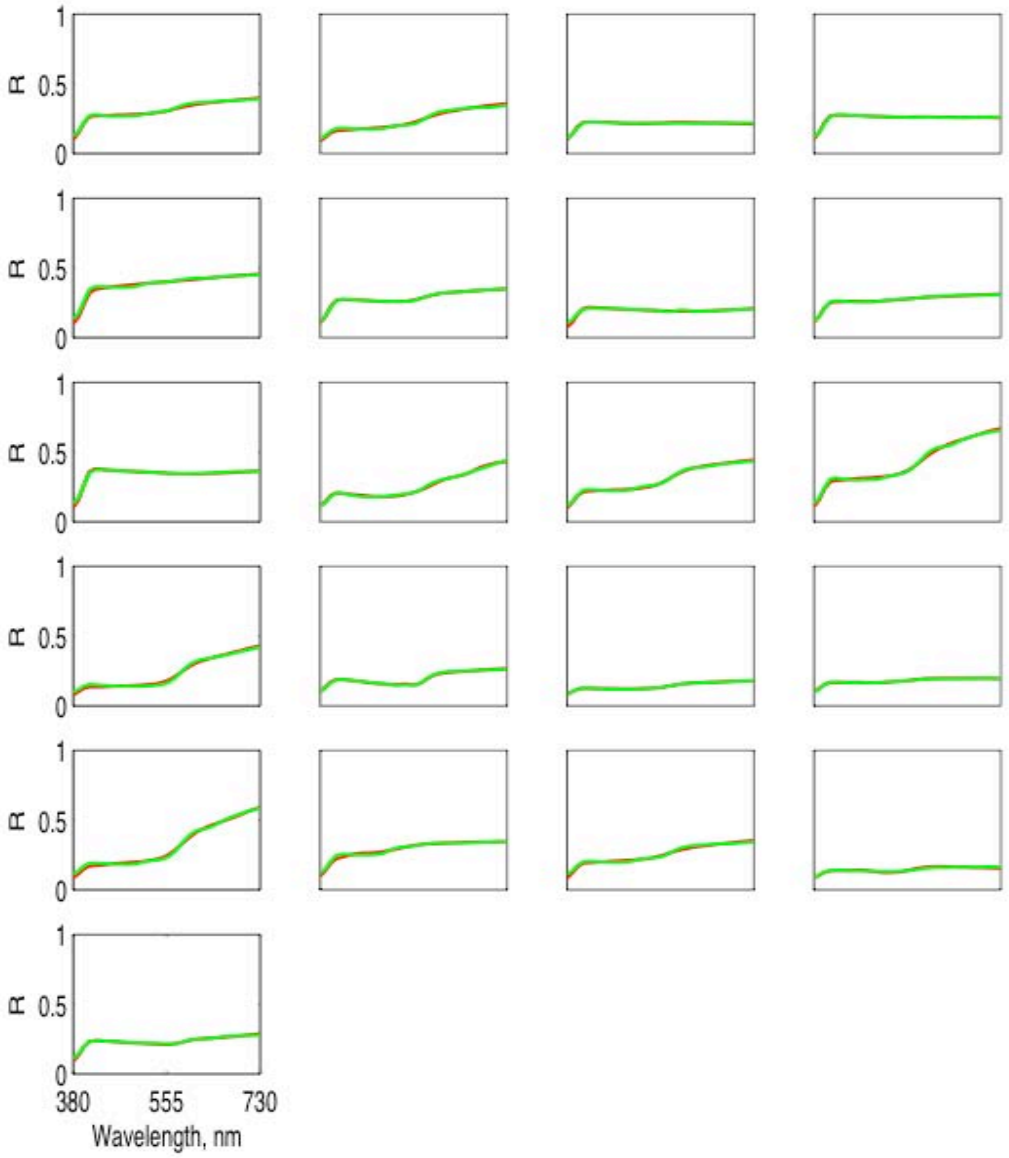


Figure 29. *Estimated spectral reflectance factors using set B compared with the measurement of brown verification targets. Red lines indicate measurement and green lines indicate prediction.*

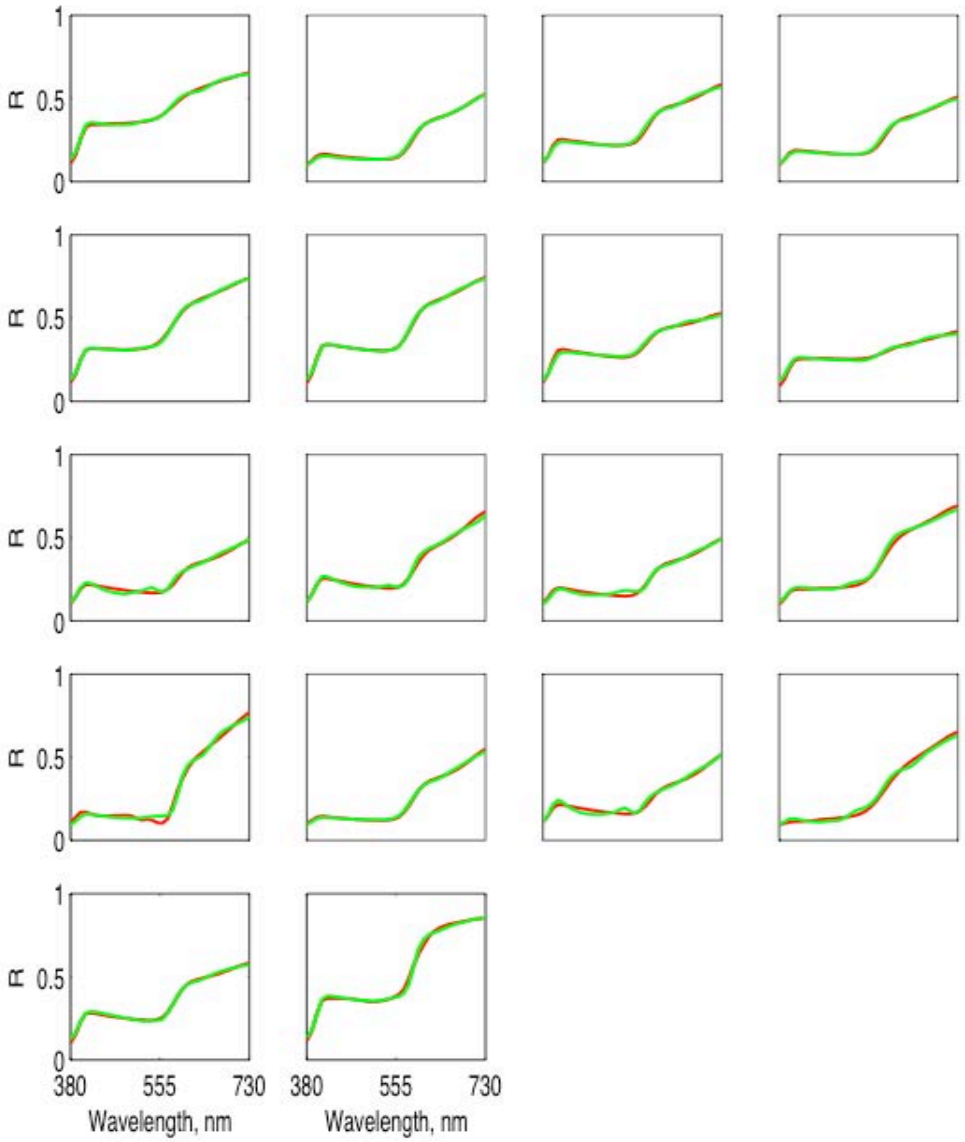


Figure 30. *Estimated spectral reflectance factors using set B compared with the measurement of red earth verification targets. Red lines indicate measurement and green lines indicate prediction.*

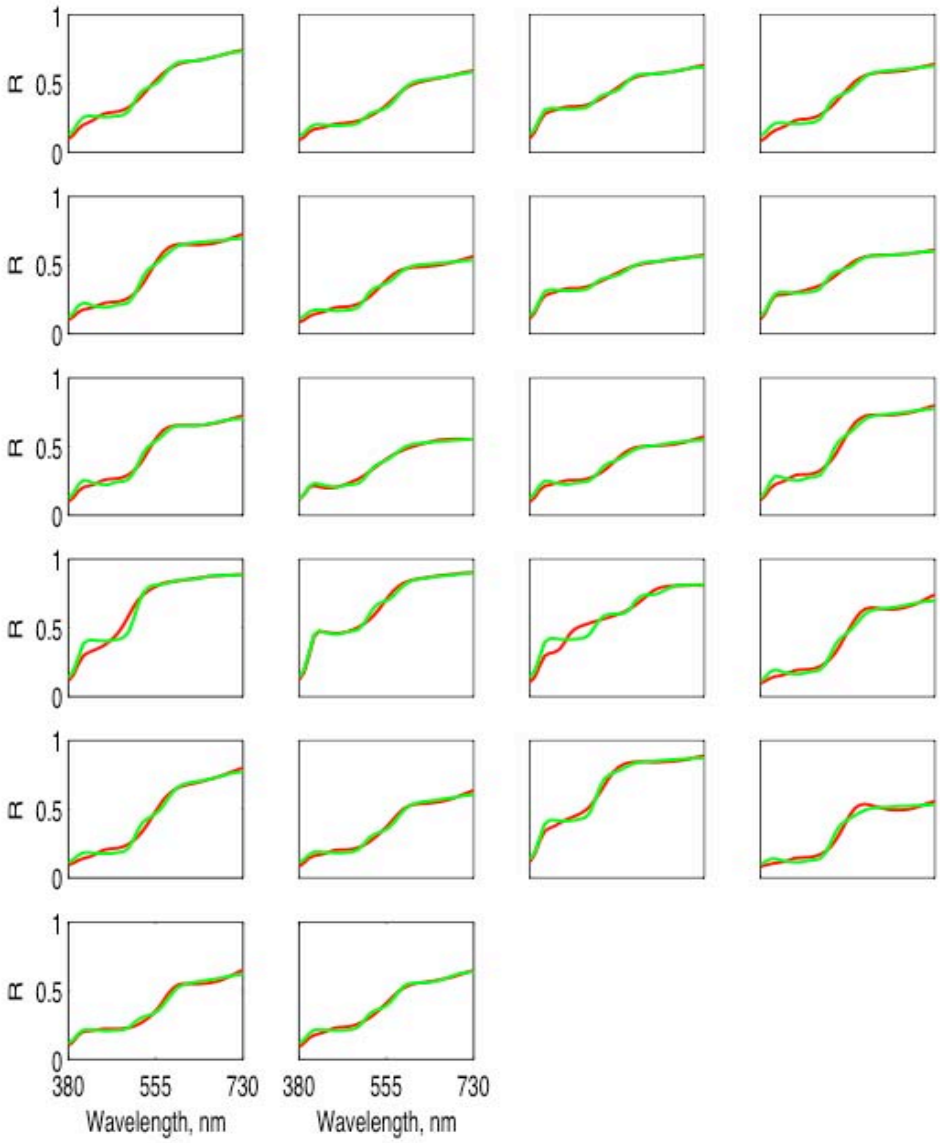


Figure 31. *Estimated spectral reflectance factors using set B compared with the measurement of yellow earth verification targets. Red lines indicate measurement and green lines indicate prediction.*

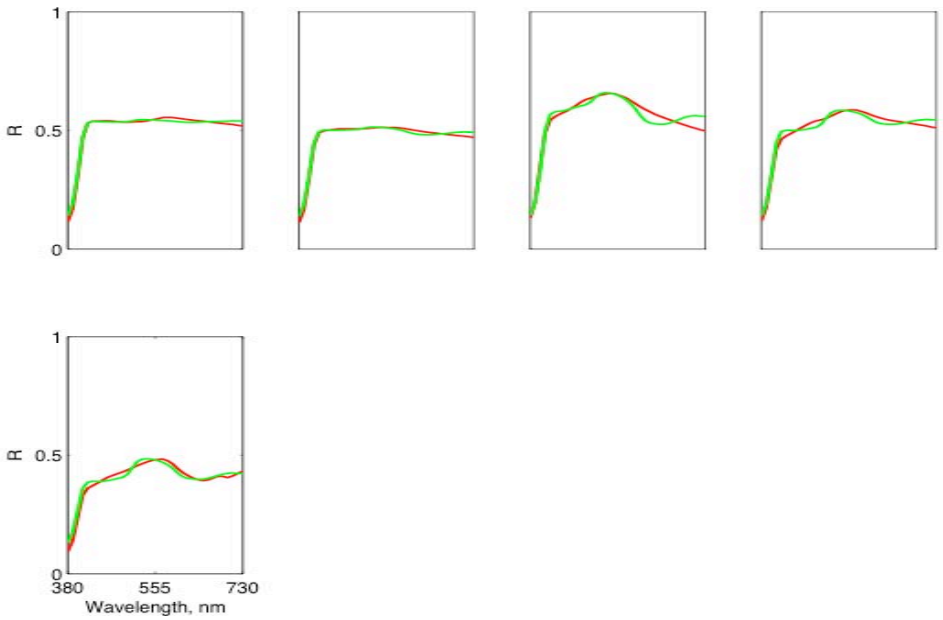


Figure 32. *Estimated spectral reflectance factors using set B compared with the measurement of green earth verification targets. Red lines indicate measurement and green lines indicate prediction.*

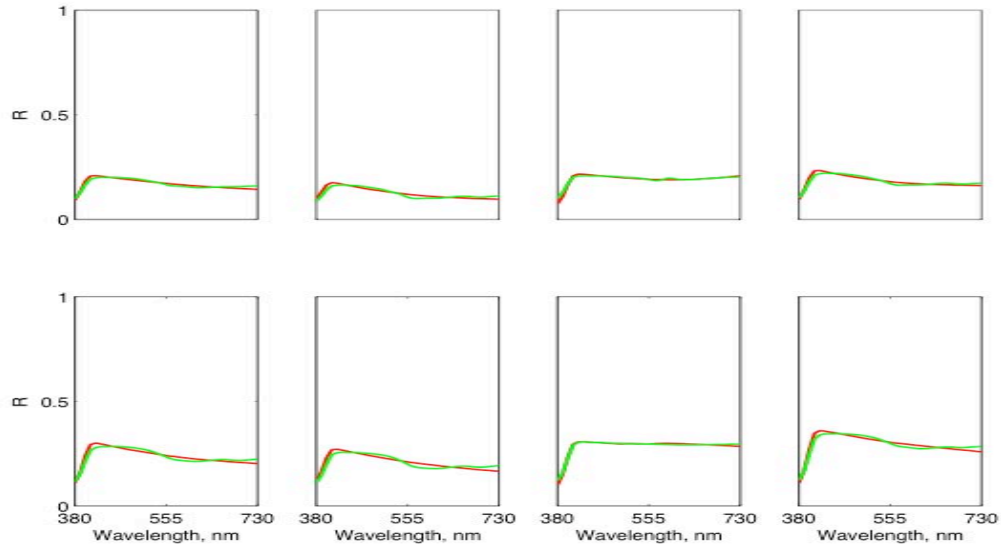


Figure 33. *Estimated spectral reflectance factors using set B compared with the measurement of black verification targets. Red lines indicate measurement and green lines indicate prediction.*

In comparison between the results of the three sets, set B was selected as the best set of pigments. The spectral plots of the pigments included in set B are shown in Figure 34. It should be noted that titanium dioxide and ivory black should always be included in the list of pigments.

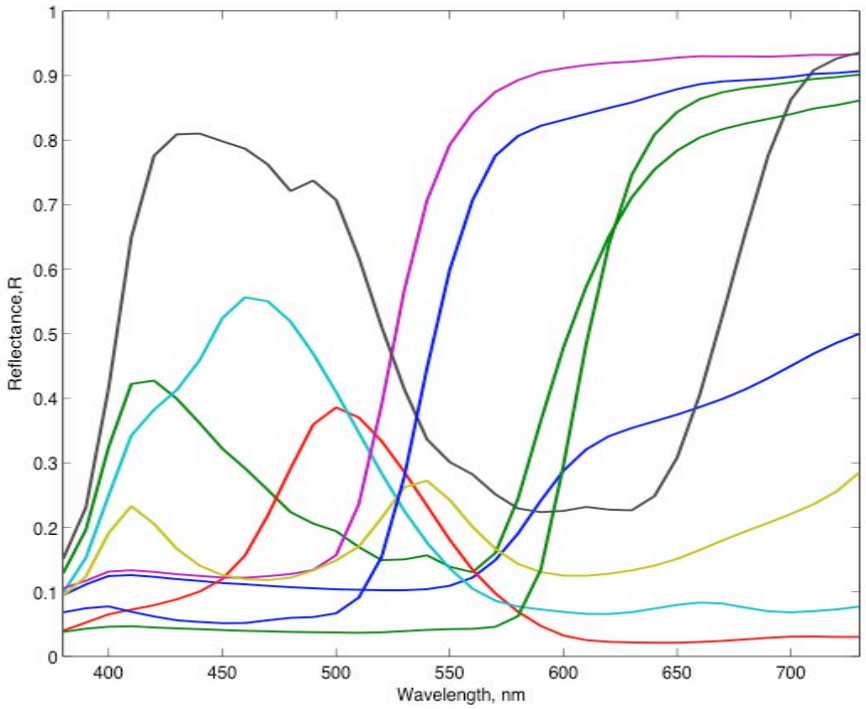


Figure 34. *Spectral reflectance of set B containing quinacridone red, venetian red, cadmium red medium, indian yellow, cadmium yellow medium, chromium oxide green, phthalocyanine green, cobalt blue, and phthalocyanine blue.*

The absolute values of the first derivative of reflectance curve of each selected pigments was calculated and plotted against wavelength; Figure 35 shows the scatter plot of the nine selected pigments. The marks on this plot are peak points of the absolute value of the first derivatives and show which wavelengths the maximum variation occurred.

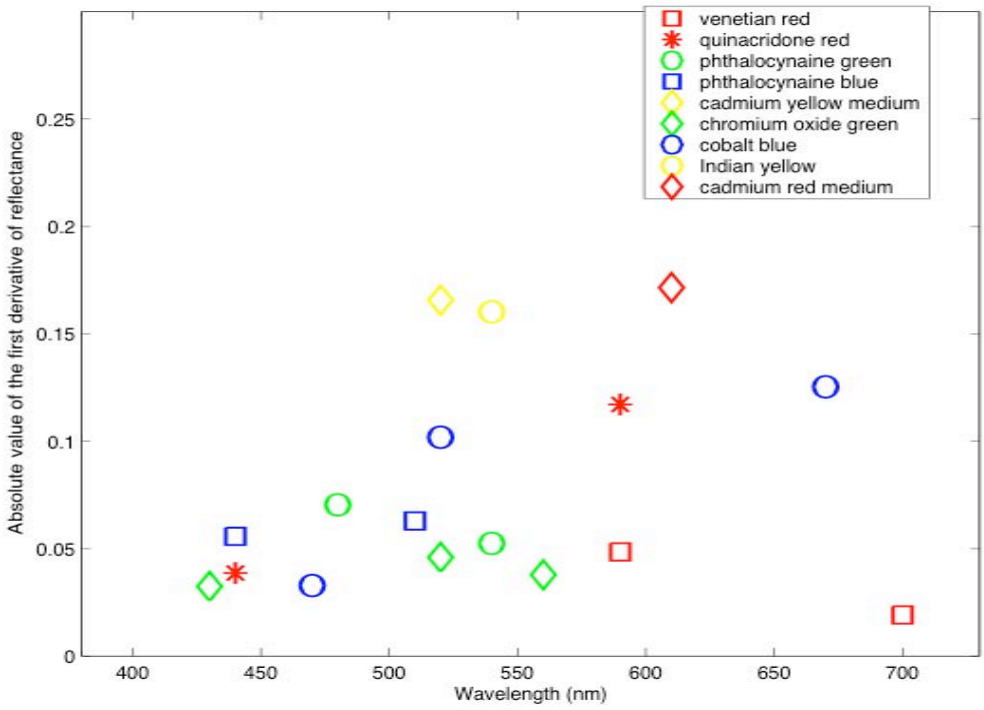


Figure 35. *Absolute values of the first derivative of reflectance curve of the selected pigments.*

The three properties required of a pigment for artist's color are adequate lightfastness, chromatic properties, and toxicity. The selected pigments almost cover these requirements. Venetian red as an iron oxide is a dull red pigment that possesses excellent properties such as lightfastness. Venetian red as a synthetic iron oxide has a superior tinting strength and it has an excellent toxicity rating [10]. Indian yellow yields a beautiful clear color. It has fluorescence effect in the visible range. Indian yellow is included in the lightfast artist's pigments. Little has been written about the toxicity of this material [9]. Chromium oxide green is a dull olive green. The pigment has a low overall spectral reflectance. The pair of absorption bands is characteristic. The reflectance characteristic at short- and long-wavelengths would be noted. This pigment is described as a non-toxic pigment [10]. Quinacridone red is especially useful in tints. It has two or more distinctive absorption bands. Quinacridone red is characterized by good lightfastness [8].

Summary and Conclusions

The problem of selecting a best set of pigments out of a thirty-pigment database for predicting a series of known and unknown targets were studied. Spectral matching, the practical method for pigment selection and color matching, were employed. The

simplicity of single Kubelka-Munk theory and non-negative least square technique were of benefit to direct the purpose of the research. The SpectraEye 45/0 and Matlab software facilities were used for measurement and programming, respectively. Unit $(k/s)_{\square}$ as a signature of the pigments were calculated using spectral reflection factors of the mixture of each pigment with white pigment (TiO_2). All three, four, and five combinations of thirty pigments of Gamblin colors were employed for spectral matching of the same pigment database. Chromatic and earth pigments were predicted separately using all pigment in the database. The $(K/S)_{mixture}$ was minimized for prediction of Gamblin samples using the large set of pigments and NNLS technique. It was assumed that total material was $1+\sum_{1}^{n} C_i$, one designated for white concentration. The spectral matching results were reported as spectral RMS, $\square E_{oo}$, GFC, and metamerism index. The first sorted thirty top set of pigments for predicting the Gamblin samples at each error criterion were selected for further analysis. Volume of Convexhull of generated color solid by each set of pigments was calculated and a set with maximum volume was selected for each criteria. The average of 10.6% spectral RMS and 11.2 $\square E_{oo}$ of three-pigment set shows that the existence of only three pigments in a set was not sufficient for predicting the chromatic targets but it is 1.3 % spectral RMS and 2.3 $\square E_{oo}$ for predicting the earth pigments that is acceptable. Therefore a set of eight pigments containing five chromatic pigments and three earth pigments were selected based on RMS criteria for the first selected set of pigments. Fifteen samples of Matisse's Pot of Geraniums were predicted with all three combinations of the eight selected pigments and also with all three combinations of 28 Gamblin pigments (white and blacks were excluded) plus white and black. The difference of average 1.3 $\square E_{oo}$ and 0.4% spectral RMS between the prediction of the painting using two groups of database (eight and twenty eight pigment databases) demonstrates that a group containing 8 pigments would be a reasonable number of pigments.

Reflectance and absorption characteristic of pigments along with the knowledge of reputation of pigments among artists made us to have a slight change to the computational selected pigments. Therefore the new selected set was quinacridone red (PV 19), venetian red (PR 101), cadmium red medium (PR 108), cadmium yellow medium (PY 37), indian yellow (PY 83), phthalocyanine green (PG 7), phthalocyanine blue (PB 15:2), and cobalt blue (PB 28). The effect of chromium oxide green and phthalocyanine green were compared. Three sets included phthalocyanine green, both greens, and chromium oxide green, respectively based on the new selected set were used for matching a series of oil verification paints. In this part of study it was assumed that the total amount of material was $\sum_{i=1}^{n} C_i = 1$. Again three combinations of eight- and nine-pigment sets plus white and black were used. The performance for predicting the blue, yellow, orange, green, red, and violet pigments using a group contain both greens were 3.2% RMS and 1 $\square E_{oo}$, 4.4% RMS and 2.6 $\square E_{oo}$, 5.1% RMS and 3 $\square E_{oo}$, 3.4% RMS and 0.6 $\square E_{oo}$, 3.1% RMS and 0.2 $\square E_{oo}$, and 4.6% RMS and 1.3 $\square E_{oo}$. It should be noted that RMS error is spectral RMS and $\square E_{oo}$ is converged $\square E_{oo}$. The accuracy of prediction of yellow is not as good as the other pigments and consequently orange, which needs

yellow pigment to make it. This might be due to the selected yellow pigments in the using database. Earth pigments included black, brown, red earths, yellow earths, and green earths were predicted with higher accuracy than chromatic pigments. The performance of predicting these pigments are 1% RMS and 0.1 ΔE_{oo}, 0.7% RMS and 0 ΔE_{oo}, 1.1% RMS and 0.4ΔE_{oo}, 2.3% RMS and 0 ΔE_{oo}, 1.7% RMS and 0 ΔE_{oo}, respectively.

The results of volume of the generated color solids by different set of pigments demonstrate that phthalocyanine green has the significant impact on making a bigger color gamut. On the other hand, due to the double reflectance characteristic bands of chromium oxide green and its tails at short- and long-wavelengths we opted to select both greens in the set of pigments. The characteristic of tails of chromium oxide green in the absence of pigments with absorption characteristic in these regions should be noted for predicting this part of spectrum.

The selected pigments with special absorption characteristic, toxicity and lightfastness properties are a reasonable selection for prediction a range of color applied in the artist's palettes.

Further consideration for selecting yellow pigments is suggested for future study.

References

1. Berns, R.S., *Billmeyer and Saltzman's Principle of Color Technology*, 3rd edition, John Wiley & Sons, New York (2000).
2. Kubelka P., and Munk F., 'Ein Beitrag zur Optik der Farbanstriche', *Zeitschrift für technische Physik* **12** (1931) 593-601.
3. Berns, R.S., J. Krueger and M. Swicklik, 'Multiple pigment selection for inpainting using visible reflectance spectrophotometry, *Studies in Conservation*, **47** (2002) 46-61.
4. Johnson R.A, Wichern D.W., Applied *Multivariate Statistical Analysis*, 5th edition, Prentice Hall, New Jersey (2002).
5. J.Hernandez-Andres and J. Romero, Colorimetric and spectroradiometric characteristics of narrow-field-of-view clear skylight in Granada, Spain, *JOSA **A*** **18** (2001) 412-420.
6. Francisco H. Imai, Mitchell R. Rosen and Roy S. Berns, Comparative study of metrics for spectral match quality, *CGIV* 2002, 492-496.
7. M. Ronnier Luo, M.Chun Lo, W. Guey Kuo, 'The LLAB(l:c) color model', *Color research and application,* (1996) **21** 412-429.
8. Johnston-Feller, R, *Color Science in the examination of Museum Objects*, (2001).
9. Feller Robert L., *Artists' Pigments, Vol. I.* Oxford university press (1986)
10. Patton Temple C., *Pigment Handbook,* Vol. I-III, John Wiley & Sons, New York (1973).
11. Allen E.*, Optical Radiation Measurements, Vol. 2,* 1966.
12. M. R. Luo, G. Cui, B. Rigg, The Development of the CIE2000 color-difference Formula: CIEDE2000*, Color research and application, Vol. 26, Number 5, October 2001.*

Appendix A

A.1.Root Mean Square Error (RMS)

Spectral difference metrics is a common error metric for evaluating the accuracy of spectral matching. The error between the estimated spectral and the original at all wavelengths were calculated and squared. The root value of the mean value of the squared errors is known as root mean square error or in the abstract form RMS (A.2.1).

$$\left[\frac{\sum_{\lambda}\left(\hat{R}_{\lambda}-R_{\lambda}\right)^{2}}{n}\right]^{1/2} \qquad \text{(A.2.1)}$$

Where R_{λ} and $\hat{R}_{\lambda}$ are the original and estimated spectral reflectance at wavelength λ and n is the number of samples.
Target and estimated in equation (A.2.1) can be any properties of a pigment eg., spectral reflectance or (K/S) values.

A.2. GFC metric

Hernandez – Anders *et al.* have suggested a goodness of –fit coefficient (GFC) to test reconstructed daylight spectra [5, 6]. The GFC is described by the equation (A.2.2)

$$GFC = \frac{\left|\sum_{j} R_m(\lambda_j)R_e(\lambda_j)\right|}{\sqrt{\left|\sum_{j}\left[R_m(\lambda_j)\right]^2\right|}\sqrt{\left|\sum_{j}\left[R_e(\lambda_j)\right]^2\right|}} \qquad \text{(A.2.2)}$$

where $R_m(\lambda_j)$ is the measured original spectral data at the wavelength λ_j and $R_e(\lambda_j)$ is the estimated spectral data at wavelength λ_j . GFC ≥ 0.999 and GFC ≥ 0.9999 are required for respectively good and excellent spectral matches.

A.3. Color- difference, $\Delta E_{00}(D_{65},2^o)$

CIEDE 2000, designated as ΔE_{00}, is a color-difference equation based on *CIELAB*. It includes not only lightness, chroma, and hue weighting functions, but also an interactive

term between chroma and hue differences for improving the performance for blue colors and a scaling factor for CIELAB a* scale for improving the performance for gray colors [11].

Step 1. Calculate the CIELAB L^*, a^*, b^*, and C^*_{ab}

$$L^* = 116 f(Y/Y_n) - 16$$
$$a^* = 500\left[f(X/X_n) - f(Y/Y_n) \right]$$
$$b^* = 200\left[f(Y/Y_n) - f(Z/Z_n) \right]$$
$$C^*_{ab} = \sqrt{a^{*2} + b^{*2}}$$

where

$$f(I) = \begin{cases} I^{1/3} & for\ I > 0.008856 \\ 7.7871 + 16/116 & otherwise \end{cases}$$

Step 2. Calculate a', C' and h'

$$L' = L^*$$
$$a' = (1 + G) a^*$$
$$b' = b^*$$
$$C' = \sqrt{a'^2 + b'^2}$$
$$h' = \tan^{-1}(b'/a')$$

where

$$G = 0.5\left(1 - \sqrt{\frac{\overline{C^*_{ab}}^7}{25^7 + \overline{C^*_{ab}}^7}}\right)$$

where $\overline{C^*_{ab}}$ is the arithmetic mean of the C^*_{ab} values for a pair of samples.

Step 3. Calculate $\Delta L'$, $\Delta C'$ and $\Delta H'$

$$\Delta L' = L'_b - L'_s$$
$$\Delta C' = C'_b - C'_s$$
$$\Delta H' = 2\sqrt{C'_b C'_s}\sin\left(\frac{\Delta h'}{2}\right)$$

where

$$\Delta h' = h'_b - h'_s$$

Step 4. Calculate CIEDE2000 ΔE_{00}

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_c S_c}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_c S_c}\right)\left(\frac{\Delta H'}{k_H S_H}\right)}$$

where

$$S_L = 1 + \frac{0.015\left(\bar{L}' - 50\right)^2}{\sqrt{20 + \left(\bar{L}' - 50\right)^2}}$$

and

$$S_c = 1 + 0.045\bar{C}'$$

and

$$S_H = 1 + 0.015\bar{C}'T,$$

where

$$T = 1 - 0.17\cos\left(\bar{h}' - 30^o\right) + 0.24\cos\left(2\bar{h}'\right) + 0.32\cos\left(3\bar{h}' + 6^o\right) - 0.2\cos\left(4\bar{h}' - 63^o\right)$$

and

$$R_T = -\sin(2\Delta\theta)R_c$$

where

$$\Delta\theta = 30\exp\left\{-\left[\left(\bar{h}' - 275^o\right)/25\right]^2\right\}$$

and

$$R_C = 2\sqrt{\frac{\bar{C}'^7}{\bar{C}'^7 + 25^7}}$$

A.3. Non-negative least square (NNLS)

Non-negative least square optimization was used to derive a matrix with all positive values. In this experiment calculation of unit (k/s) values of the pigments and all optimization for prediction the Gamblin targets in order to calculate the concentrations were performed using NNLS technique. It could be a valid mathematical method to generate unit (k/s) of a pigments that could correlate with physical properties of the pigment.

Appendix B

Table I. *All Recipe used to pigment characterization*

Pigment	Sample No	TiO_2(gr)	Pigment (gr)	% TiO_2	% Pigment
Viridian	1	1.00	0.80	55.6	44.4
	2	0.40	1.50	21.1	78.9
	3	0.88	0.64	57.9	42.1

Ultramarine Blue	3	0.88	0.64	57.9	42.1
Ultramarine Violet	5	0.88	0.70	55.7	44.3
Venetian Red	4	0.37	1.03	26.4	73.6
	6	0.31	0.99	23.8	76.2
Earth Yellow	7	0.96	0.73	56.8	43.2
	8	0.33	0.92	26.4	73.6
Trans Earth Red	9	0.96	0.74	56.5	43.5
	10	0.38	1.02	27.1	72.9
Raw Umber	11	0.96	0.70	57.8	42.2
	12	0.29	0.92	24.0	76.0
Yellow Ochre	13	0.92	0.70	56.8	43.2
	14	0.36	0.95	27.5	72.5
Quinacridone Red	15	0.74	0.93	44.3	55.7
	16	0.50	1.07	31.8	68.2
Prussian Blue	17	0.95	0.74	56.2	43.8
	18	0.36	0.90	28.6	71.4
Phatalocyanine Green	19	0.32	1.03	23.7	76.3
	20	1.02	0.83	55.1	44.9
Phatalocyanine Blue	21	0.96	0.75	56.1	43.9
	22	0.30	0.91	24.8	75.2
Dioxazine purple	23	0.96	0.73	56.8	43.2
	24	0.32	0.94	25.4	74.6
Hansa Yellow Medium	25	0.93	0.68	57.8	42.2
	26	0.38	0.96	28.4	71.6
Indian Red	27	0.28	1.14	19.7	80.3
	28	0.98	0.70	58.3	41.7
Cadmium Orange	29	0.39	1.00	28.1	71.9
	30	0.99	0.72	57.9	42.1
Ivory Black	31	1.02	0.74	58.0	42.0
	32	0.41	0.98	29.5	70.5
Manganese Blue Hue	33	1.10	0.77	58.8	41.2
	34	0.35	0.95	26.9	73.1
Cadmium Yellow Light	35	1.04	0.79	56.8	43.2
	36	0.40	1.05	27.6	72.4
Cadmium Yellow Medium	37	1.05	0.73	59.0	41.0
	38	0.41	1.05	28.1	71.9
Chromium Oxide Green	39	0.40	1.03	28.0	72.0
	40	1.10	0.84	56.7	43.3
	41	1.05	0.76	58.0	42.0
	42	0.43	1.05	29.1	70.9

Cobalt Green	43	0.98	0.73	57.3	42.7
	44	0.53	1.17	31.2	68.8
Cobalt Violet	45	0.44	1.03	29.9	70.1
	46	0.99	0.76	56.6	43.4
Black Spinel	47	0.42	1.01	29.4	70.6
	48	0.98	0.75	56.6	43.4
Burnt Sienna	49	0.45	1.05	30.0	70.0
	50	0.91	0.73	55.5	44.5
Burnt Umber	51	0.38	0.96	28.4	71.6
	52	1.01	0.76	57.1	42.9
Raw Sienna	53	0.45	1.07	29.6	70.4
	54	1.02	0.75	57.6	42.4
Indian Yellow	55	0.48	1.08	30.8	69.2
	56	1.09	0.79	58.0	42.0
Cadmium Red Light	57	0.95	0.74	56.2	43.8
	58	0.30	0.92	24.6	75.4
Cadmium Red Medium	59	0.35	0.97	26.5	73.5
	60	1.01	0.77	56.7	43.3