xDNA™

Introduction to xDNA

x-rite

xDNA™

Background

There are two unique properties of light's interaction with material that can be exploited in the measurement process to learn and understand more about the structure and makeup of a material or coating. The first property that we can consider is the fact that all materials are dispersive. By this we mean that the ability of a material to bend light (its refractive index) is different for blue light (400nm) than it is for red light (700nm). This change in bending power exists regardless the apparent color (absorptive property) of the material. Even a material that appears black or shiny (like a mirror) exhibits dispersion due to the fact that light does not interact simply at the surface, but rather penetrates below the surface while being reflected or absorbed. [1] The second property that we can consider is the scatter of light within a material. The scatter of light within a material can be described in several different ways, but in all cases, the nature of scatter is also wavelength dependent. Blue light scatters differently than red light.

All materials will scatter light to some degree, even apparently clear glass. By performing sensitive spectrophotometric measurements of the light scattered by a material (or coating) and comparing the minute biases in where the blue light is scattered relative to the red light it is possible to determine the physical makeup and structure of the material. Energy must be conserved. So, by understanding the characteristics of the illumination energy and measuring the characteristics of the light returning from a material, we can solve increasingly complex models for determining the makeup and structure of materials and coatings. Light can only be reflected, refracted, scattered, or absorbed, and energy must be conserved.[2]

Perhaps the simplest model we can employ is called Effective Medium Theory, derived from electromagnetic theory. Effective Medium Theory simply states that no matter how complex the coating or material, we can treat it as a single homogeneous material. A coating with 3 layers and 9 ingredients is treated as if it is a single material that is a weighted average of the ingredients, weighted by their distribution through the layers, the thickness of the layers, and the structure of the boundary between two adjacent layers. A coating of a given formulation (recipe of ingredients and defined layer structure) will be characterized by its unique dispersive scattering properties. If anything changes in the formulation, those unique properties will change. Even if the distribution of mean particle size changes, the unique scatter properties will change.

1 Actually, what we are interested in is the dielectric constant of the material, which is dispersive. The complex refractive index (bending power + absorption) is proportional to the square root of the dielectric constant.

2 There are many other ways in which light can interact with material and other issues such as polarization which could be considered and discussed, but for simplicity sake we will forego those for this discussion. The special case of interference does arise and is considered later when addressing some special effects pigments.

Along with Effective Medium Theory, one of the simplest methods for characterizing the scattering behavior of the light is to measure in some coordinate system where the light is being scattered relative to where it is emerging from the sample. We can represent this as a bias, forward/backward and side to side with the magnitude corresponding to the light energy that is not absorbed. The more light that is scattered / reflected into a given direction, the greater the magnitude. If we then do this for each wavelength, we can then analyze the dispersive nature of the material or coating. Using this analogy, a material that is uniformly reflective at all wavelengths and uniformly scatters into all directions will exhibit no bias in any direction. A material which closely approximates this behavior is Spectralon™. Spectralon appears uniformly diffuse white under all illumination geometries and from all observation angles. There is no shine or gloss to well prepared Spectralon, even at very high grazing incidence angles. The easiest way to compute the bias of the energy is to represent each observation angle as a fixed vector, drawn from the center of the sample to the center of the spectrometer entrance pupil. One vector is created for each wavelength and each observation angle, with the magnitude being the amount of energy measured. The bias is then simply derived by a vector summation of all observation angles, wavelength by wavelength, which results in a single bias vector for each wavelength. This process of applying an Effective Medium Theory assumption together with a vector summation computation is what we call X-Rite Digital Numerical Analysis, or xDNA™ and is described in greater detail.

xDNA

xDNA is a method for summarizing multiangle spectral data into a two- or three-dimensional spectral representation. The xDNA is a weighted vector sum of the measurement directions, with the weights being the reflectance factors for each direction. The result of this sum is a spectrum of points in 2D or 3D space, one point for each measured wavelength.

The weighted vector sum is also scaled by the length of the vector sum of an ideal white Lambertian reflector in order to make the xDNA values reasonably comparable to typical reflectance values. The coordinate system for xDNA consists of the specular direction (z axis), the projection of the illumination direction orthogonal to specular (y axis), and the cross product of these two directions (x axis).

We describe a measurement direction using:

- The illumination angle from surface normal,
- The detection aspecular angle, and
- The detection azimuth angle from the illumination direction.

We separate the angles with the text 'as' and 'az'. As an example, the measurement with illumination direction 45°, detection aspecular angle 25°, and detection azimuth 90° is denoted 45as25az90. The (x,y,z) coordinates of the measurement direction □Ψas □Ψaz□ are then (sin(□)*sin(□), sin(□)*cos(□), cos(□)).

xDNA Example

Table 1 shows spectra and corresponding xDNA coordinates for a measured sample.

Table 1. Ten Angle Spectral Data And xDNA coordinates

WL	45as-15az0	45as15az0	45as25az-90	45as25az0	45as25az90	45as45az0	45as60az-54.7	45as60az54.7	45as75az0	45as110az0	x	y	z
400	34.1	98.5	8.1	43.2	6.9	4.8	1.5	1.4	1.3	1	-0.08	5.62	24.89
410	28.6	75.9	5.4	40.9	4.8	6.5	1.5	1.4	1.5	1	-0.04	5.09	20.55
420	33.4	49.6	4	30.9	3.5	7.2	1.3	1.3	1.7	1	-0.03	3.52	16.28
430	49.1	31.3	3.5	21	3.2	6.6	1.1	1.1	1.8	1	-0.02	1.70	14.56
440	75.5	21.4	4.2	13.9	3.7	5.2	0.9	0.9	1.7	1	-0.03	-0.13	15.82
450	112.6	18.1	5.8	9.8	5.1	3.8	0.8	0.8	1.5	1	-0.04	-1.94	19.91
460	153.6	21.1	8.5	8.3	7.4	2.9	0.8	0.8	1.3	0.9	-0.06	-3.46	25.94
470	184.9	29.8	12.1	9	10.4	2.3	0.8	0.8	1.1	0.9	-0.10	-4.29	31.95
480	197	44.7	16	11.9	13.6	2	0.9	0.9	1	0.9	-0.14	-4.06	36.64
490	185.2	67.3	19.2	17.5	16.4	2.1	1	1	1	0.9	-0.16	-2.52	39.47
500	158.4	93.6	20.4	25.9	17.4	2.4	1.1	1.1	1.1	0.9	-0.17	-0.15	40.74
510	127.5	117.8	19.4	36.2	16.5	3.1	1.3	1.2	1.1	0.9	-0.17	2.43	40.98
520	99.4	132.8	17.1	46.6	14.5	4.2	1.5	1.4	1.2	0.9	-0.16	4.66	40.15
530	77.6	131.3	14.3	53.1	12.1	5.7	1.6	1.5	1.4	0.9	-0.13	5.91	37.46
540	60.6	119.5	11.6	54.3	9.8	7.1	1.6	1.5	1.5	0.9	-0.11	6.31	33.40
550	46.8	101.1	9.3	50.7	7.9	8.3	1.6	1.5	1.7	0.9	-0.09	6.08	28.41
560	37.4	82.6	7.5	44.1	6.4	8.7	1.4	1.4	1.9	0.9	-0.06	5.44	23.62
570	31.2	67	6.1	37	5.2	8.5	1.3	1.2	1.9	0.9	-0.06	4.67	19.58
580	27.8	53.8	5.1	30.5	4.4	7.7	1.1	1.1	1.8	0.9	-0.04	3.85	16.32
590	27	43.1	4.3	24.8	3.7	6.7	1	1	1.7	0.9	-0.03	3.07	13.85
600	29.2	34.8	3.8	20.2	3.3	5.8	0.9	0.9	1.6	0.9	-0.03	2.33	12.29
610	35.2	28.3	3.7	16.5	3.2	4.9	0.8	0.8	1.4	0.8	-0.03	1.55	11.65
620	44.9	23.8	3.7	13.7	3.3	4.2	0.7	0.7	1.3	0.8	-0.02	0.81	11.91
630	58.6	20.7	4.1	11.6	3.6	3.6	0.7	0.7	1.1	0.8	-0.03	0.02	13.05
640	76.1	18.4	4.8	9.8	4.2	3.1	0.7	0.7	1	0.8	-0.03	-0.83	14.90
650	98.5	18.5	6	8.8	5.2	2.7	0.7	0.7	1	0.8	-0.05	-1.70	17.93
660	124.1	20.2	7.5	8.4	6.6	2.4	0.7	0.7	0.9	0.8	-0.05	-2.59	21.73
670	150.6	24	9.5	8.7	8.3	2.2	0.7	0.7	0.9	0.8	-0.07	-3.38	26.12
680	175.1	29.6	11.7	9.6	10.2	2.1	0.8	0.8	0.9	0.9	-0.08	-3.97	30.62
690	194.4	37.5	14.1	11.3	12.2	2	0.8	0.8	0.9	0.9	-0.11	-4.28	34.88
700	213	47.5	17	13.7	14.6	2.1	0.9	0.9	0.9	0.9	-0.14	-4.42	39.54

xDNA Example

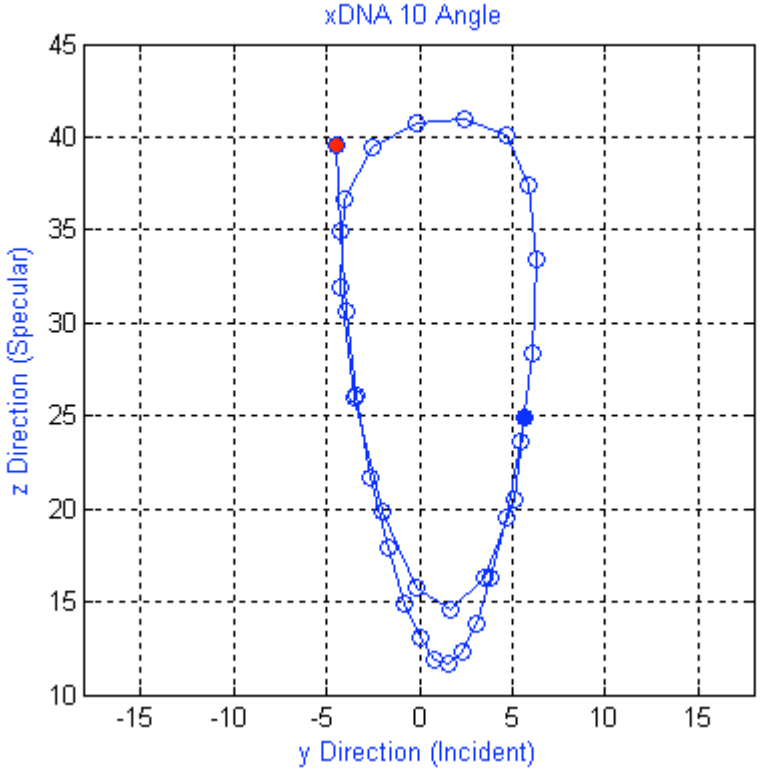
Table 2 shows the (x,y,z) coordinates of the measurement directions. Weighting these coordinates by the reflectances at 700 nm in the previous example gives x=17*(-0.42)+14.6*(0.42)+0.9*(-0.71)+0.9*(0.71)=-1.01, and similarly y=-32.94, and z=294.99; dividing by the length of the vector sum of the perfect white reflector (7.46) gives the values shown in Table 1.

Table 2. Measurement Direction (x,y,z) coordinates

	45as-15az0	45as15az0	45as25az-90	45as25az0	45as25az90	45as45az0	45as60az-54.7	45as60az54.7	45as75az0	45as110az0
x	0.00	0.00	-0.42	0.00	0.42	0.00	-0.71	0.71	0.00	0.00
y	-0.26	0.26	0.00	0.42	0.00	0.71	0.50	0.50	0.97	0.94
z	0.97	0.97	0.91	0.91	0.91	0.71	0.50	0.50	0.26	-0.34

Figure 1 is a plot of the (y, z) projection of the xDNA of the same sample.

Figure 1. xDNA Plot



Geometries

The xDNA methodology is applicable to any multiangle geometry. The geometry required for measuring a particular class of materials depends on the physical properties of the samples to be measured. For example, diffuse materials can be accurately characterized with a single angle measurement. Traditionally, three positive aspecular angles have been thought sufficient to characterize coatings with metallic pigments. Adequate measurement of coatings with pearlescent and special effect pigments requires additional angles beyond the traditional multiangle directions.

xDNA Principles

There are two main principles concerning the xDNA spectrum, a visual principle and a structural principle.

- Visual Principle: The xDNA spectrum represents the color appearance of the measured surface.
- Structural Principle: The shape of the xDNA spectrum represents the optical properties of the measured surface.

Another way of stating the structural principle is that the shape of the xDNA spectra represents formulation. According to these principles, two samples whose xDNA spectra have the same shape but a different position and orientation in space will have a different color appearance, with the difference in position and orientation of their xDNA spectra representing process differences.

xDNA Transformations

There are a number of goals in transforming xDNAspectra. The goals include:

- Distinguishing process differences from formulation differences
- Monitoring process stability
- Guiding process changes to compensate for normal variation in coating formulation.

The separation between process and formulation is not entirely sharp, and it is important to keep in mind that what is being measured is the end result of the relationship between process, and formulation. For example, changes in mean flake or particle size will alter a process even if the machine settings do not change. Also, some additives to an automotive paint coating such as fumed silica may make it more difficult to distinguish between formulation and process changes. Fumed silica is used to control metallic flake orientation in the coating. The additive is intended to be invisible and as such, the index of refraction of fumed silica closely matches the index of refraction of common solvents. Its impact on the measurement is invisible except in its effect on flake orientation. So personnel who are comparing the xDNA profiles of two samples of a certain paint may need to perform further investigation as to whether measured differences were a result of process variables such flow rate and atomization or the presence of fumed silica.

The effect of application equipment settings is, of course, specific to the particular application equipment. Thus, while two samples may have xDNA spectra with the same shape, and therefore be classified as process differences, there is no purely optical criterion that can classify whether the difference is due to different settings on the same equipment, different application equipment, flake orientation control additives, humidity differences, or other conditions that affect the application process.

Translation, Rotation and Scaling

To determine the equivalence of shapes of xDNA spectra, X-Rite uses the linear operations of translation, rotation, and scaling. All transformation operations are performed relative to a standard. The translation vector, rotation matrix, and scale factor are computed together, using a Procrustes algorithm to compute a least squares fit of the transformed sample xDNA spectrum to the standard xDNA spectrum. For purposes of comparison to the standard, the intermediate results of the translation and rotation operations are additionally translated to be centered at the standard's center.

The translation of an xDNA spectrum is the average 3D offset from the standard over all wavelengths. The magnitude of translation is denoted xT, and the individual components are denoted xTx, xTy, and xTz. The translation of an xDNA spectrum to be centered at the standard's center is denoted xDNAt. The dominate contributor to translational differences between two samples of equivalent recipe indicates a process difference. For instance, changes in flow and atomization in a painting process will change the size and kinetic energy of the droplets that adhere to the sample, and how they adhere.

The rotation of the translated spectrum xDNAt with the first two rotations is denoted xDNAa. Rotation is typically a characteristic that is coupled both to changes in process and recipe distribution. For example, personnel may observe a difference in a painting process rotation that is due to a change in process that results either in a distribution change in the size of particles in a recipe, or a change in size and / or orientation of particles that adhere to the sample due to these changes.

The rotation is reported by its decomposition into three rotations performed in the following order:

1. A rotation in the xy plane (xR azimuth)
2. A rotation in the xz plane (xR colatitude)
3. A rotation in the yz plane (xA alignment)

The result of scaling the spectrum xDNAa is denoted xDNAs.

It is not always obvious which of the aligned spectrum xDNAa or the scaled spectrum xDNAs values better detects formulation differences. In some situations, two samples that differ only in process conditions have significant differences in their aligned spectra xDNAa, so examining the scaled spectra xDNAs is needed to determine that the difference between samples is in fact a process difference, not a formulation difference. On the other hand, it is not too hard to come up with cases in which xDNAs could be very small for samples with noticeable formulation differences, such as different diffuse grays.

Continuing along the biological analogy, we can consider the relationship between the untransformed xDNA spectrum and the scaled xDNAs spectrum to be somewhat like the relationship between the phenotype and genotype of a living being. Just as the phenotype of a living organism results not just from its genetic makeup, but also from its interaction with its environment, the xDNA of a surface results from both the underlying material, characterized by xDNAs, and its interaction with its environment, represented by application process conditions.

continues ...

Translation, Rotation and Scaling
continued

In considering xDNA transformations, we want to keep in mind both the transformed spectra, as well as the transformation parameters. Current colorimetric values in use with multiangle measurements include L*a*b* values per angle, and Flop Index, which is a measure of relative lightness change between near specular and near retro angles. The parameters xT, xA, and xS all are related to the difference in reflectance at the various angles, but they provide different views of the situation than Flop Index.

In a hypothetical situation, one could reduce the Flop Index of a coating containing metallic flake either by applying it under dryer conditions, or by using a finer flake in the coating. These different changes would be more likely to be detected monitoring xT, xA, and xS than by just Flop Index.

That doesn't mean that Flop Index is not useful. Multiangle measurements are useful when observing materials whose multiangle reflectances have multiple dimensions. No single number can capture all of the information of interest in these situations. Keep in mind that the reason to use indices or other single values such as color difference formula is that their simplicity and the amount of information they do provide makes up for the information that is lost when going to a single value.

Difference Formulas
We describe difference formulas that generalize colorimetric functions and difference formulas to xDNA coordinate data. Also considered are formulas that use reflectance data directly, and applications of all these formula to spatially transformed xDNA data.

The DF Formula
Just as one derives colorimetric data from spectral data using illuminant and observer weighting functions, CIELAB functions, and DE, DE94, DE2000, and other weighting functions, one can derive colorimetric data from 3D xDNA spectra. Among the possible approaches to generalizing color difference formulas to higher dimensional spectra are these:

1. Compute colorimetric data such as XYZ, L*a*b*, and difference formulas on each of x, y, and z planes. Combine difference formulas computed on the different planes as the square root of the sum of the squares of the single plane difference formulas.

2. Compute XYZ data on each of x, y, and z planes. Use these values as the x,y,z components of vector valued X, Y, and Z data, then compute the magnitude of the three dimensional X, Y, and Z vectors. Now compute L*a*b* and color difference data using the one dimensional X, Y, and Z magnitudes.

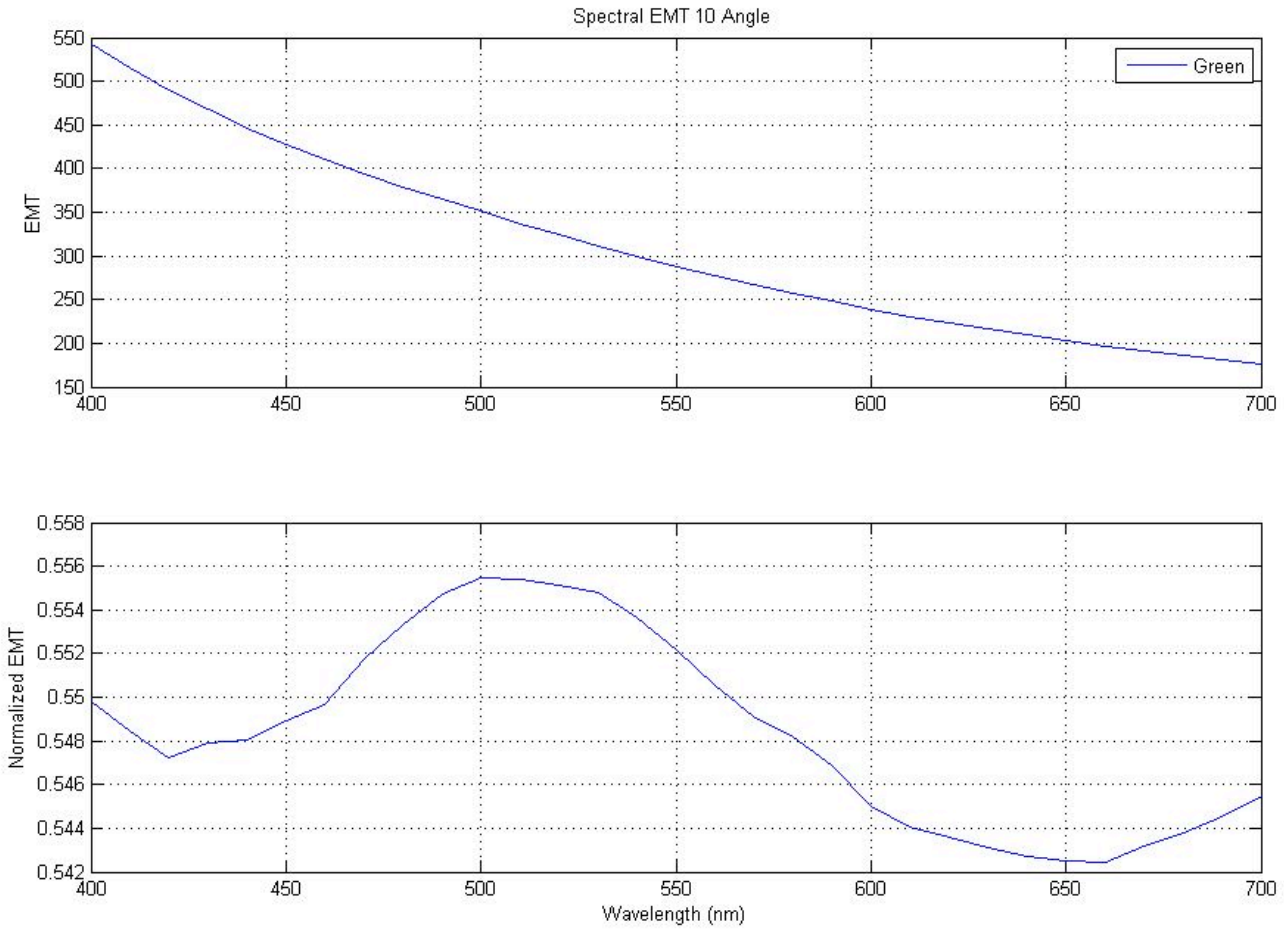
We use the notation DF for the color difference formula computed by generalizing ordinary Delta E with approach 1.

As colorimetric functions were constructed to approximate human perceptual differences, they are likely not the best measure to apply to transformed xDNA spectra such as xDNAt, xDNAa, and xDNAs. Still, the above approaches to generalizing difference formula work just as well on transformed spectra as on untransformed xDNA.

The application of Delta E to the various transformed spectra is denoted DFt, DFa, and DFs, corresponding to the spectra designation.

EMT

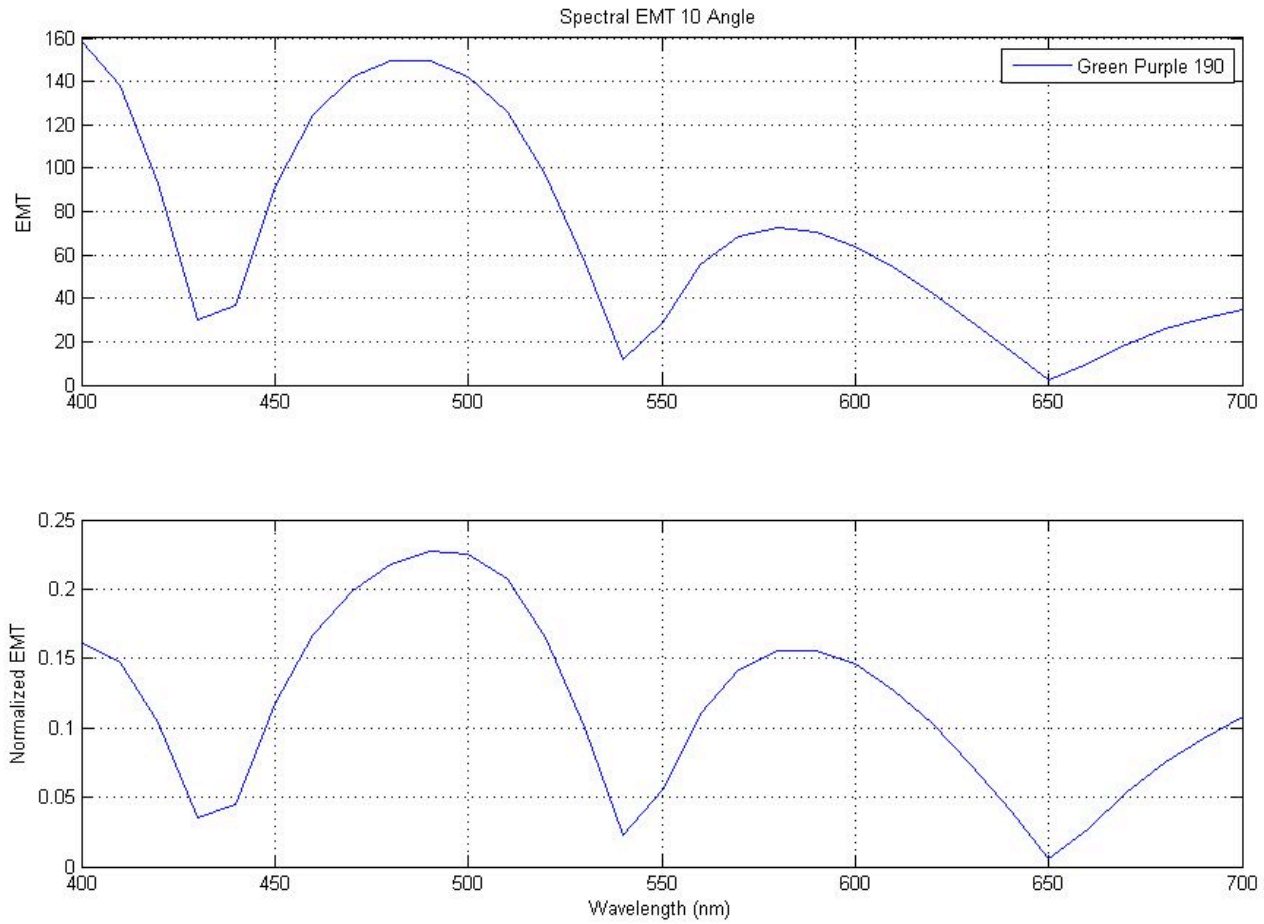
In the absence of an opacity constraint and by using Effective Medium Theory principles, it is possible to represent a complex coating or material as a single homogeneous material with a distinct dielectric constant which has unique dispersive characteristics. Since the complex optical refractive index (bending power + absorption) is proportional to the dielectric constant, it is possible to cast the results in a form proportional to the refractive index and generate a dispersion curve. A simple homogeneous absorptive coating is shown below.



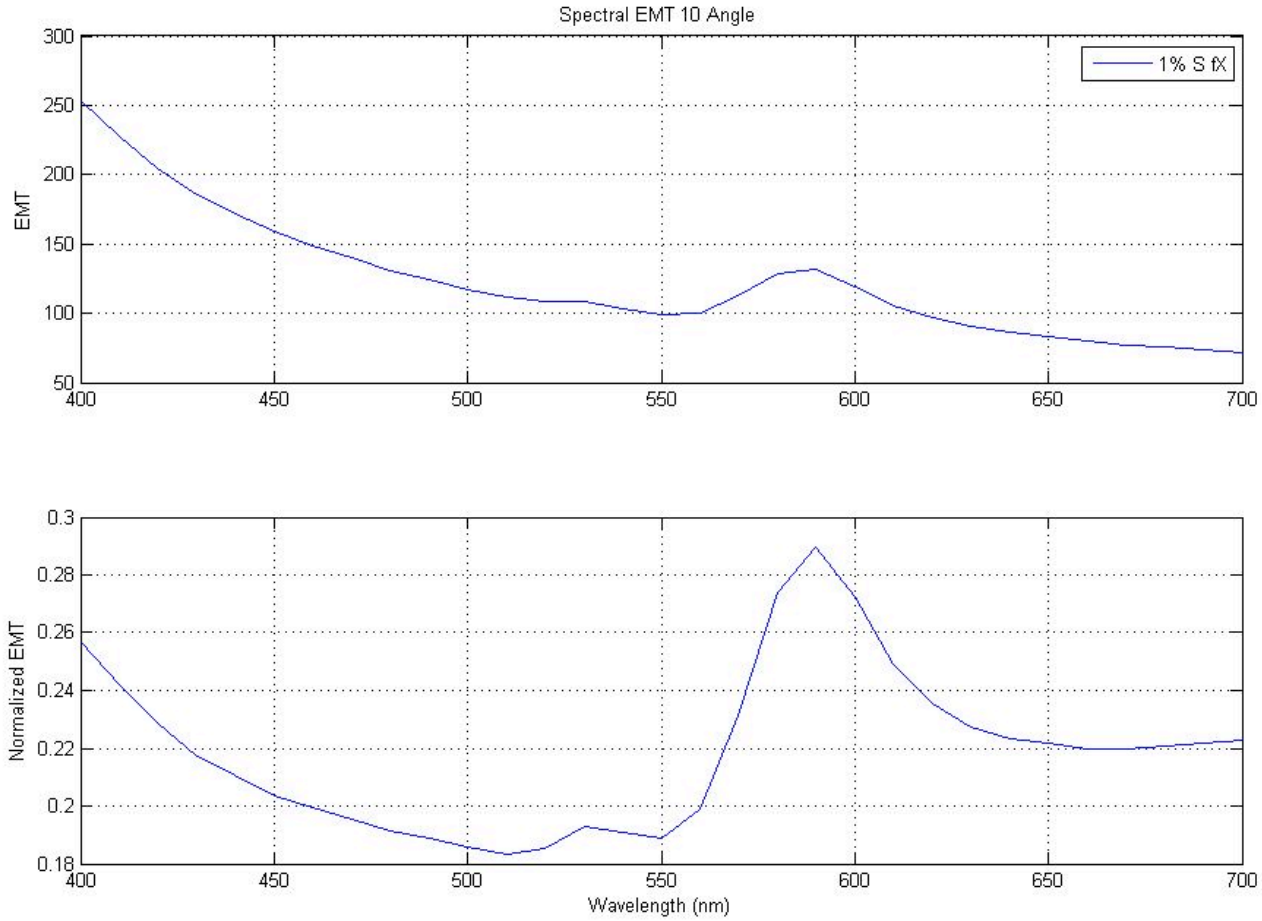
This is useful in the detection of certain pigments, and for changes in concentration of pigments or other additive materials. In the case of absorptive pigments, the "Optical Power" of the pigment can be directly related to the particle size as absorption can be directly related to the mean free path length of scatter interaction and total surface area, thus resulting in a more "dispersive" EMT model. The equation is computed as:

$$<EMT_{ba}>=(16\pi^2/\lambda^4)\cos^2\theta_i\Phi_{ba}(\varphi_s)R_a(\theta_i)$$

For more complex materials such as special effects pigments, there is an interefence of light which gives rise to an "impedence mismatch" and the dispersion curves look like below:



For a coating which contains a mixture of both absorptive and special effect, the EMT is a combination of the two whose shape is dependent on the weighting of the two materials:



Or in our case we first compute the projected magnitude in the x-y plane and the vector magnitude of the measured reflectance. We then compute the direction cosine in the z direction of the magnitude and in the x-y plane. The EMT is computed by multiplying the Direction Cosines by $\frac{16\varpi^2}{4}$ wavelength by wavelength.

Per-Angle Colorimetry

Just as in traditional colorimetry or with the original MA68 multiangle spectrophotometer, it sometimes useful to compare colorimetric values such as L*a*b* on a per angle basis.

In this case, comparison of out-of-plane angles can reveal issues associated with appearance differences under other potential illumination conditions.


x-rite