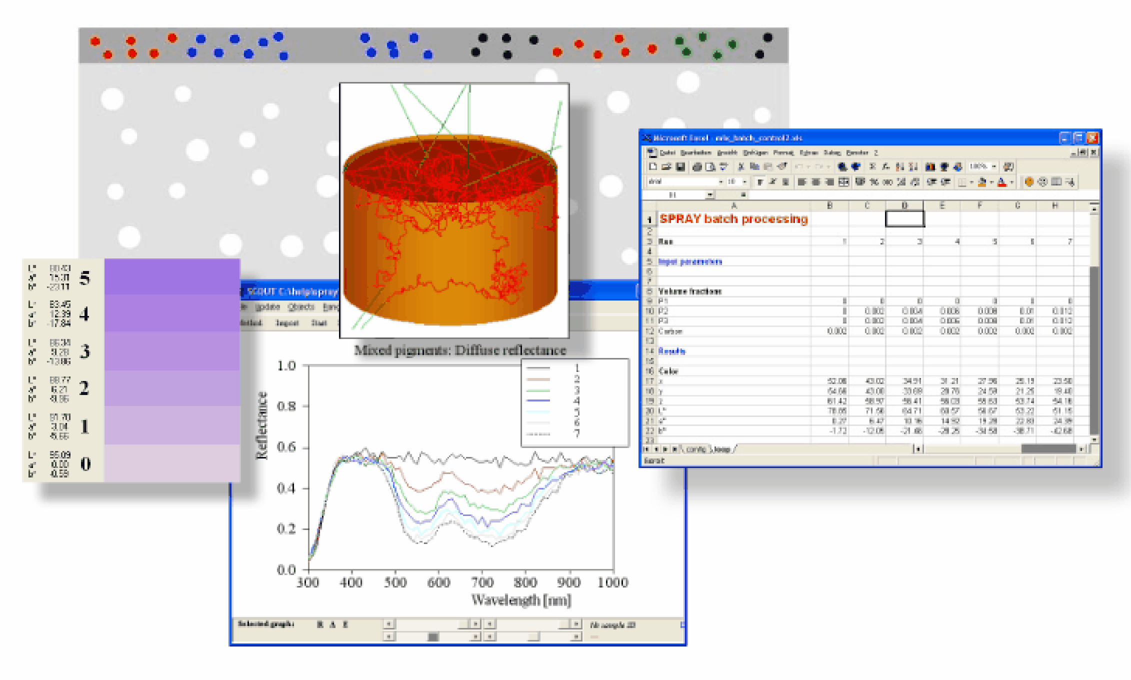
SPRAY



SPRAY special:

Physical models for color prediction

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SPRAY

Spectral ray-tracing simulations

by Wolfgang Theiss

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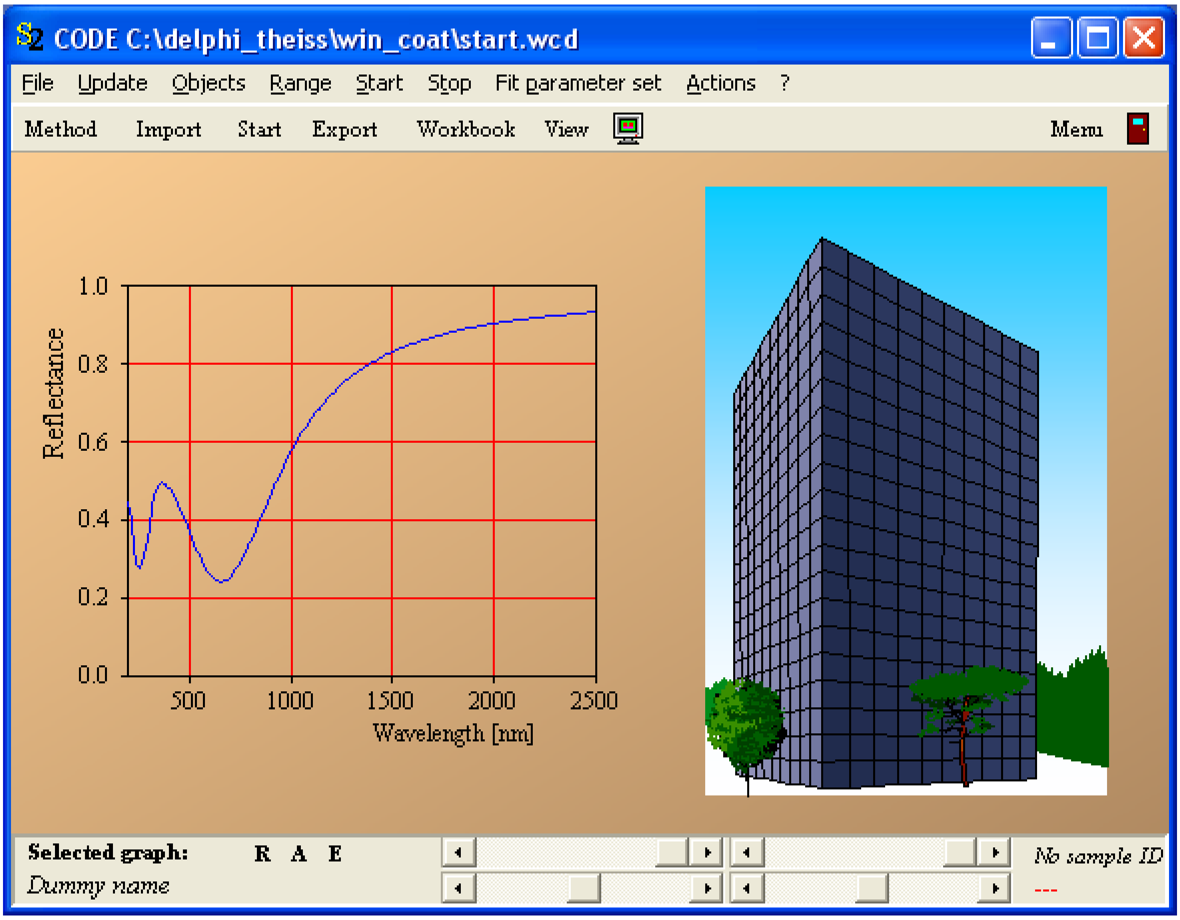
Foreword

Our company has specialized in software for the analysis and prediction of optical spectra. The specular reflectance and transmittance of almost arbitrary layer stacks can be treated with our main products SCOUT and CODE. These programs are widely used to analyze spectroscopic measurements (determine thicknesses, optical constants or compositional parameters) and to design layer stacks for optical applications, such as coatings for architectural glass or solar absorbers.



We now present our SPRAY ray-tracing software to people dealing with paints, digital prints or other imaging techniques.
SPRAY predicts the optical performance of systems based on physical models. This text should give you an impression on how you can solve problems with SPRAY. We are using quite simple models and fictional pigments. We hope, however, that it will be clear how the simple models could be extended in order to be prepared for realistic work.

Besides developing software we also offer our experience in optical problem solving. We determine optical constants, develop analytical methods, optimize products and train people in using our software products.

At the end of this text you'll find some information about other products of M.Theiss Hard- and Software.

Best regards
Wolfgang Theiss

1 Introduction

1.1 About this document

Spectral Ray-Tracing

Phyical models for color prediction

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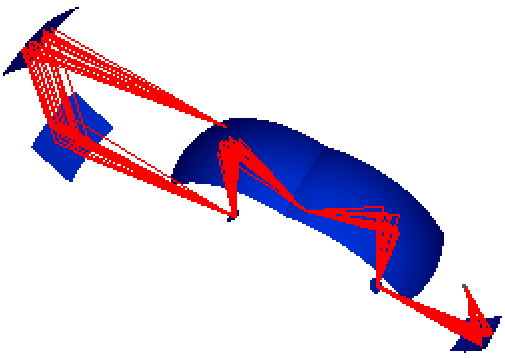
This text shows how our SPRAY ray-tracing software can be used to predict colors of paints, digital prints or similar imaging techniques. Other SPRAY applications are described in www.mtheiss.com/spray_ex/index.html. The SPRAY technical manual is available in www.mtheiss.com/docs/spray/index.html, a tutorial for beginners can be found in www.mtheiss.com/spraytl/index.html.

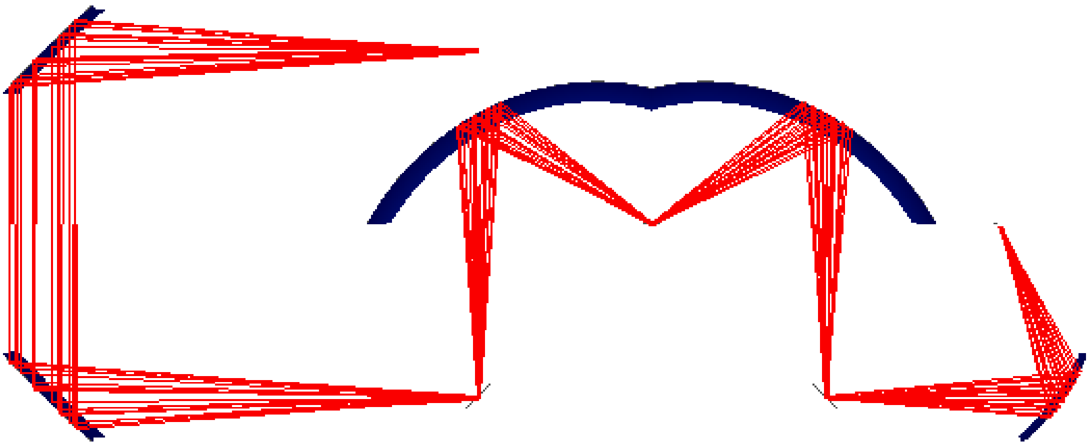
SPRAY history: Beyond Kubelka-Munk ...
In order to understand reflectance spectra of diffusely reflecting powders we started (many years ago) with the simple Kubelka-Munk two-flux concept. We computed the absorption and scattering coefficients from the optical constants and size parameters of our particles using the Mie theory (scattering of spherical particles). To be close to our experimental setup with a laser light source, we had to replace the diffuse illumination in the theory by a sharp illuminating beam. Then we wanted to describe the angle distribution of the emitted radiation for powders or arbibrary thickness. So we deleloped a multi-flux theory. Finally, in the attempt to analyze infrared diffuse reflectance spectra we found that we had to determine the intensity and angle distribution of the incoming radiation in our spectrometer. At this point we gave up extending the

Kubelka-Munk concept, and developed the SPRAY software that computes optical spectra by ray-tracing.

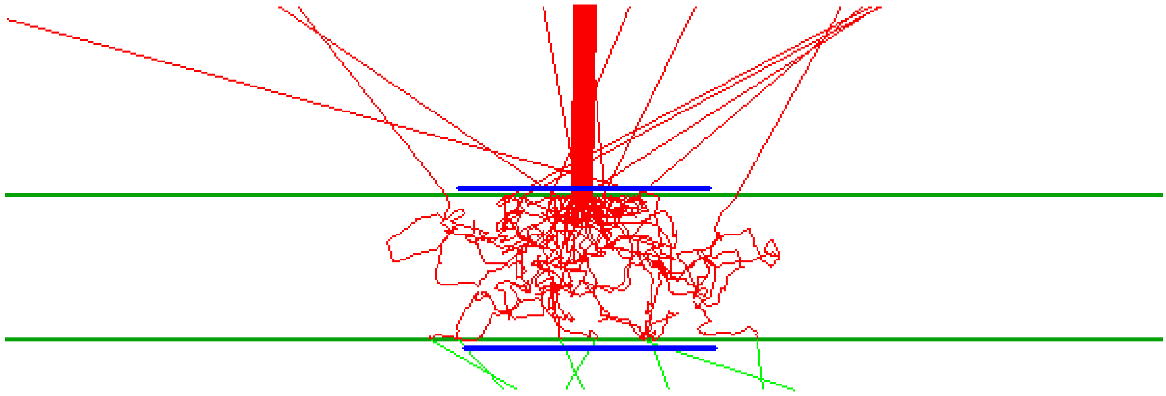
SPRAY features

Like many ray-tracing products, SPRAY has light sources, mirrors, lenses and various basic shapes which can be used to build up the scenery. Very powerful optical constant models and almost arbitrary layer stacks covering the surface of the various geometric objects are highlights of the software.





Meanwhile SPRAY has a number of features that turn it into an excellent tool for color prediction. Based on physical modeling, the transfer of light from the light source through light scattering, absorbing and fluorescent media and across partially reflecting interfaces is simulated. SPRAY performs fully three-dimensional ray-tracing with almost no compromises.



Color prediction demo systems
In order to show you the possibilities of SPRAY with respect to color prediction this text discusses some simple demo systems in the next section.

> **Warning: We are no experts in paints and digital prints (yet)! However, having studied some pieces of literature, we have the feeling that SPRAY could be a useful tool for people composing images. If you agree, feel free to suggest more advanced setups. We will be happy to learn how paints and prints really work.**

Paper: We discuss a simple model for paper based on scattering inclusions in a homogeneous host. You can tune the light propagation in the paper by the size distribution and the volume fraction of the inclusions, and the complex index of refraction of the host material.

Paints: Here we describe the optical performance of several pigment types in a homogeneous binder layer on paper. We show that SPRAY can be controlled as OLE automation server from Excel's VisualBasic (or any other OLE automation client) in order to create automatically charts of spectra and color coordinates vs. pigment volume fractions.

Prints: The setup of a simple test system is explained which can be used to simulate light propagation through ink dots on paper.

Pigment research: This section gives a few examples of pigment investigations you can do with SPRAY. Size variation and coatings with single and multiple layers are treated.

Background information
The following background information is given, just in case you want to know some details.

Optical constants: The heart of any physical model for color prediction are the optical constants of the materials in the system. SPRAY has very powerful optical constant models and a large database. The section about optical constants discusses some typical materials, and gives the optical constants of all materials used in the examples above.

Light scattering: SPRAY has an integrated Mie program that computes the scattering and absorption characteristics of spherical particles. You can define a size distribution, and the particles may be coated with a thin film layer stack. The properties of all light scatterers used in the examples of this text are discussed in this section.

SPRAY features not covered by this text:

- You can work with user-defined curved surfaces
- SPRAY can handle fluorescent materials
- Parallel computing: Lengthy computations can be distributed on several PCs
- In combination with OLE automation you can generate video sequences with SPRAY

2 Simple demo systems

2.1 A simple model of paper

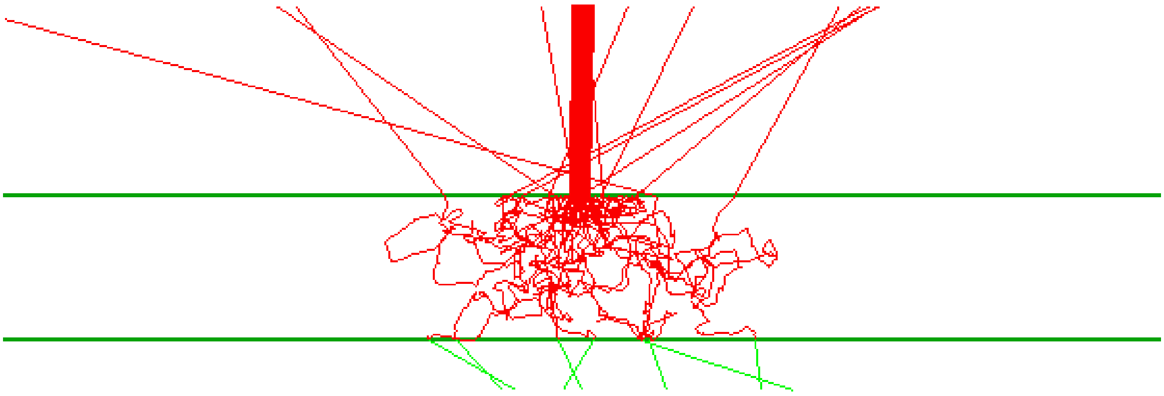
Paper is the basis of many prints. Its large diffuse reflectance is almost independent of wavelength. Hence it is used as a white background, onto which pigments with strongly wavelength-dependent absorption are deposited where color is wanted.
The propagation of light through paper is very important for the color of a printed area. For a successful color prediction a correct description of the underlying paper is required. A physical model should reproduce available measured optical properties of the relevant types of paper in a quantitative way.

In this SPRAY demo, we use a simple paper model which is able to reproduce some basic features of paper. Instead of taking into account all the specific paper ingredients and their microstructure, we describe paper as a two-phase composite: Spherical air inclusions are embedded in a host material with optical constants similar to those of glass (see details below in the section of optical constants). Here is a sketch of the setup:

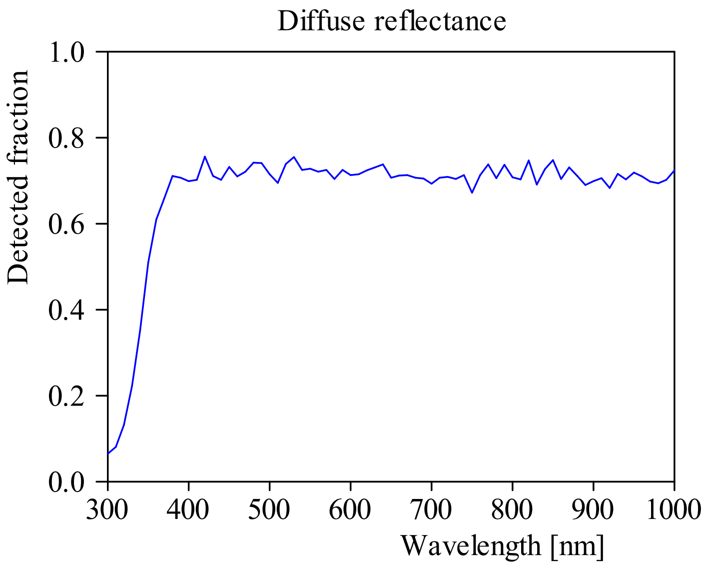
The size distribution of the voids determines the angle-dependence of the average single scattering event (which is computed by the Mie program integrated into SPRAY), whereas the volume fraction of the voids controls the strengths of the scattering, i.e. the scattering coefficient. The host material weakly absorbs in the UV which is controlled by an oscillator term in the optical constant model.

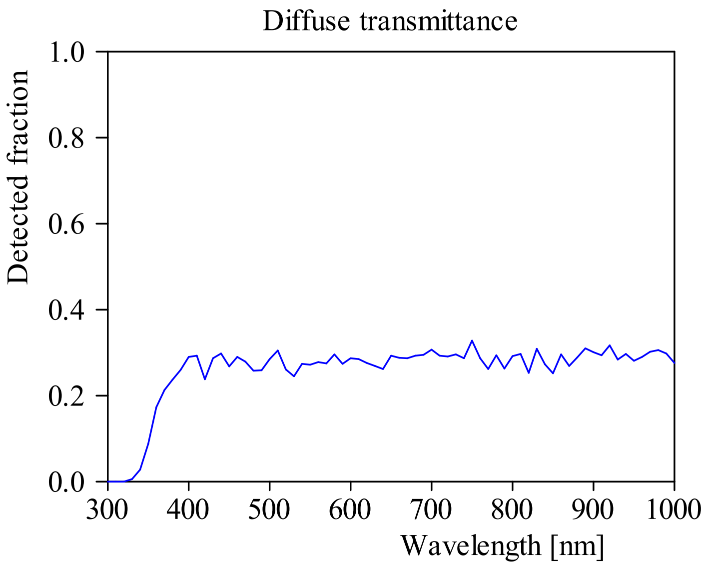
In the following the properties of two types of (model) paper are compared: One with large inclusions and another one with small ones.

The graph below shows a SPRAY visualization of some test rays for the case of large inclusions. A collimated incident beam is directed onto the paper from the top (normal incidence of light). The path of 20 test rays is displayed in the following graph for a volume fraction of 0.3:

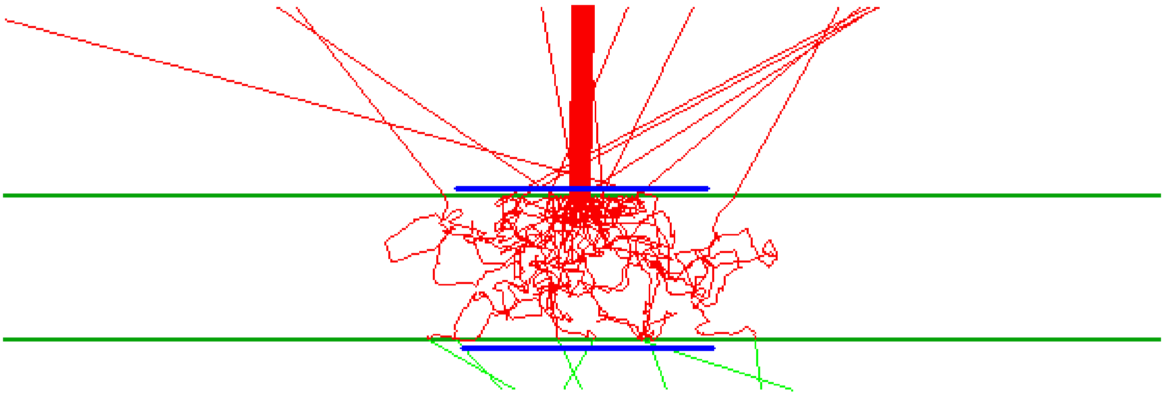


Starting many rays and placing large detectors above and below the paper one can compute the diffuse reflectance and transmittance of the model paper:

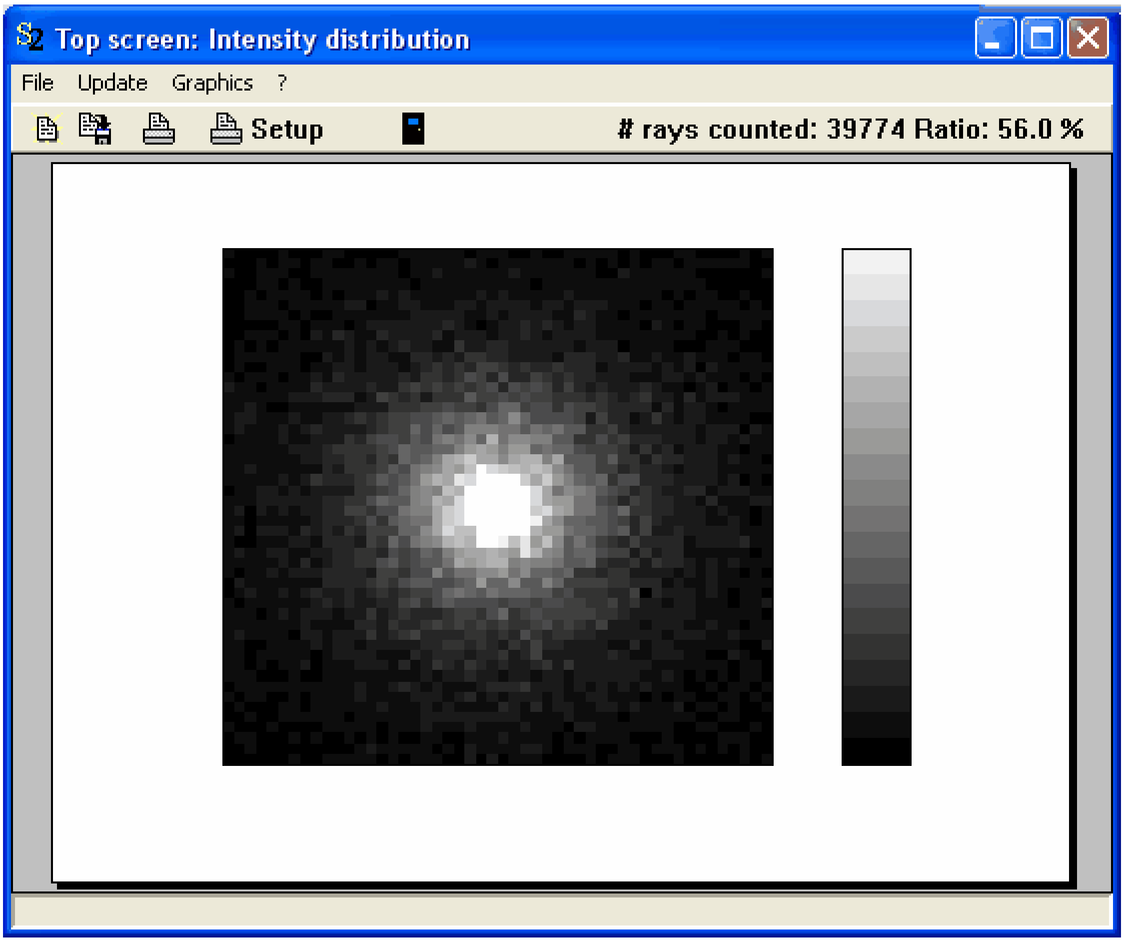




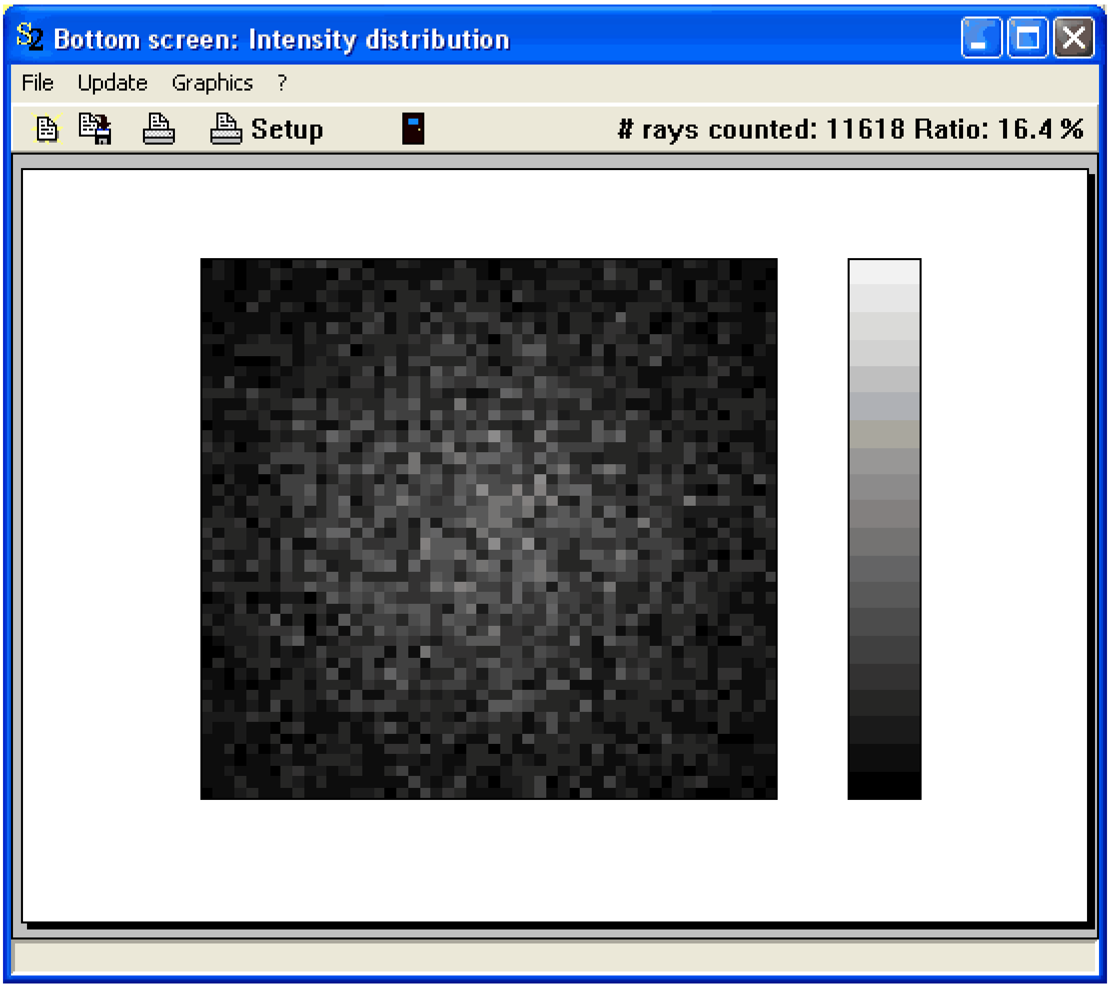
In order to visualize intensity distributions one can place screens (virtual CCD cameras, represented by the two blue bars in the sketch below) where detailed information is wanted:



The top screen looks like this

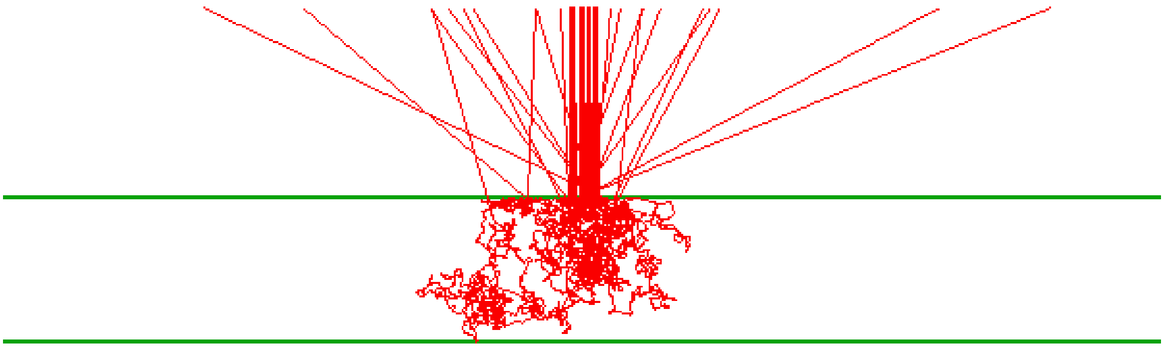


whereas the bottom screen shows a broader distribution:

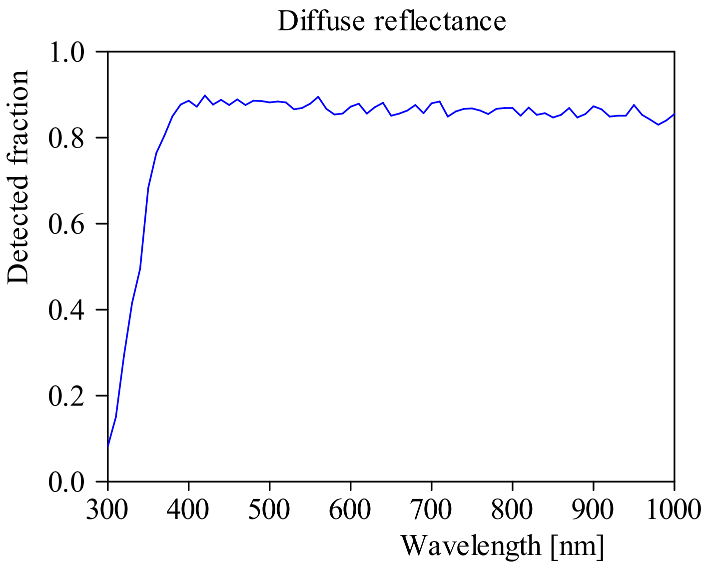


The intensity distributions as well as the diffuse reflectance and transmittance spectra could be compared to measured data in order to estimate how good the model describes the real paper.

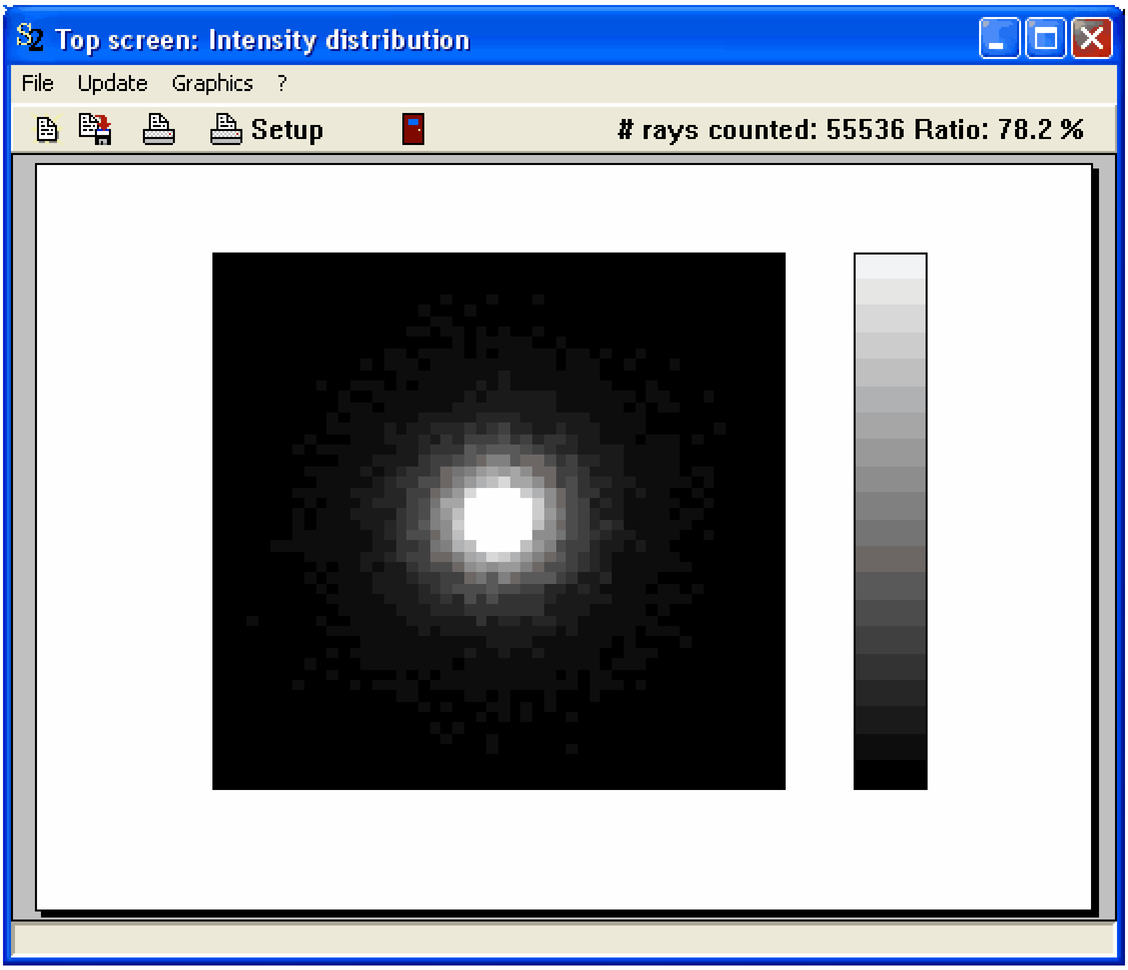
The smaller spheres with the same volume fraction have a larger scattering coefficient and a broader scattering distribution. This leads to a more concentrated radiation distribution:



The diffuse reflectance is significantly higher compared to that of the larger inclusions:



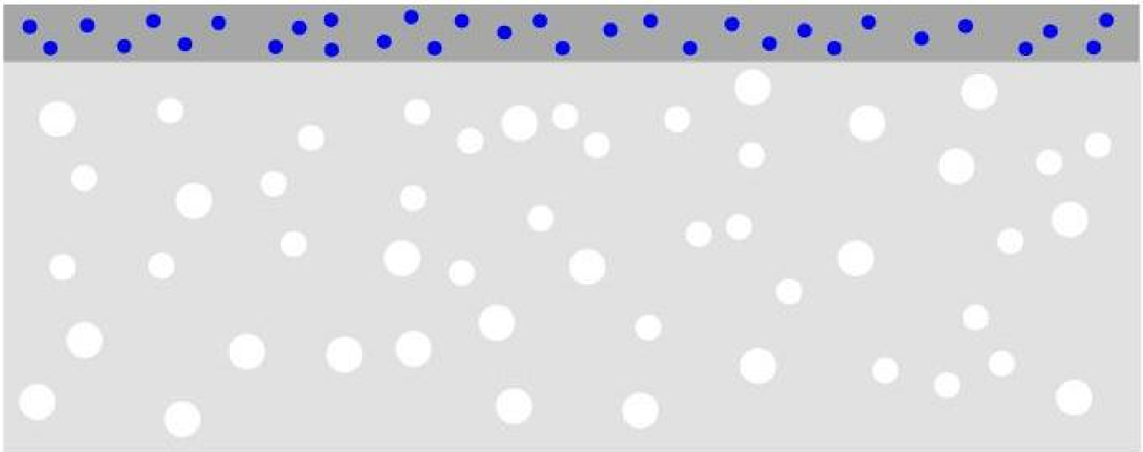
The distribution 'measured' with the top screen shows a more pronounced confinement of the rays:



This paper type (small inclusions) is used for the following simulations of paints and prints.

2.2 A paint model

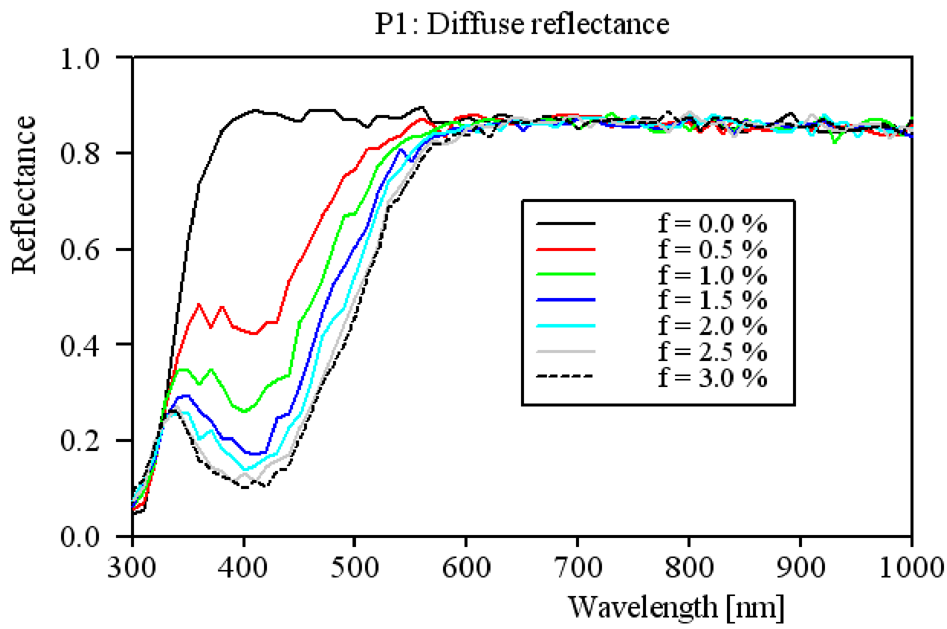
The most simple model of a paint is probably given by a binder layer with embedded pigments deposited on the simple paper model discussed above:



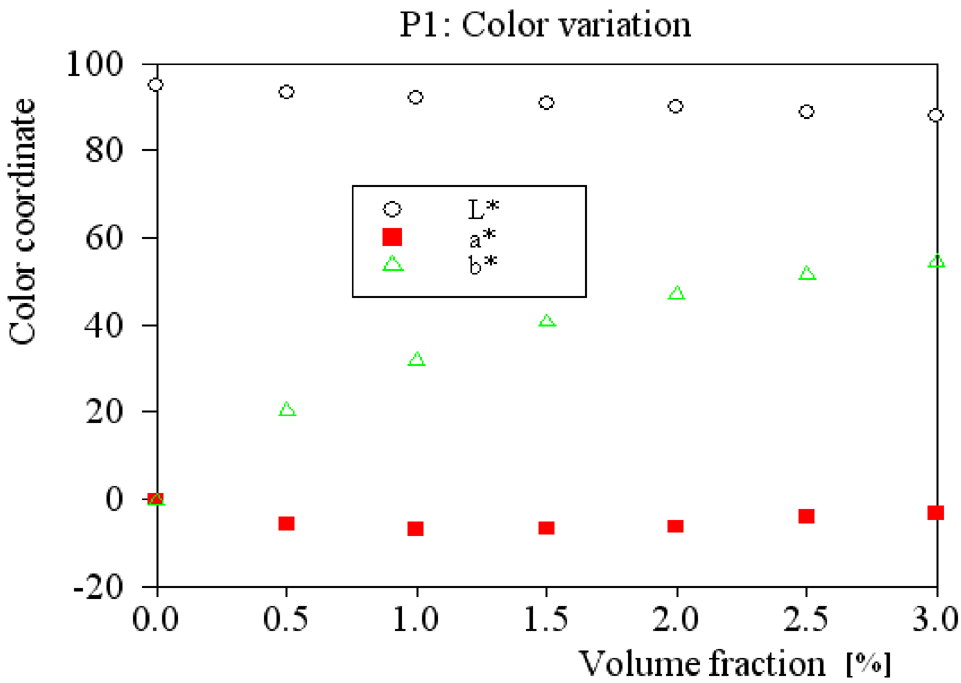
For simplicity we use for the binder the same optical constants as for the host material of the paper model. Four types of absorbing and scattering pigments are used: Three fictional ones absorbing in the blue (named P1), green (P2) and red (P3) part of the spectrum, and carbon particles which have a broad absorption over the whole visible spectrum. All particles are assumed to be spheres which makes it possible to compute their scattering and absorption features using the Mie program integrated in SPRAY.

Performance of the individual pigments

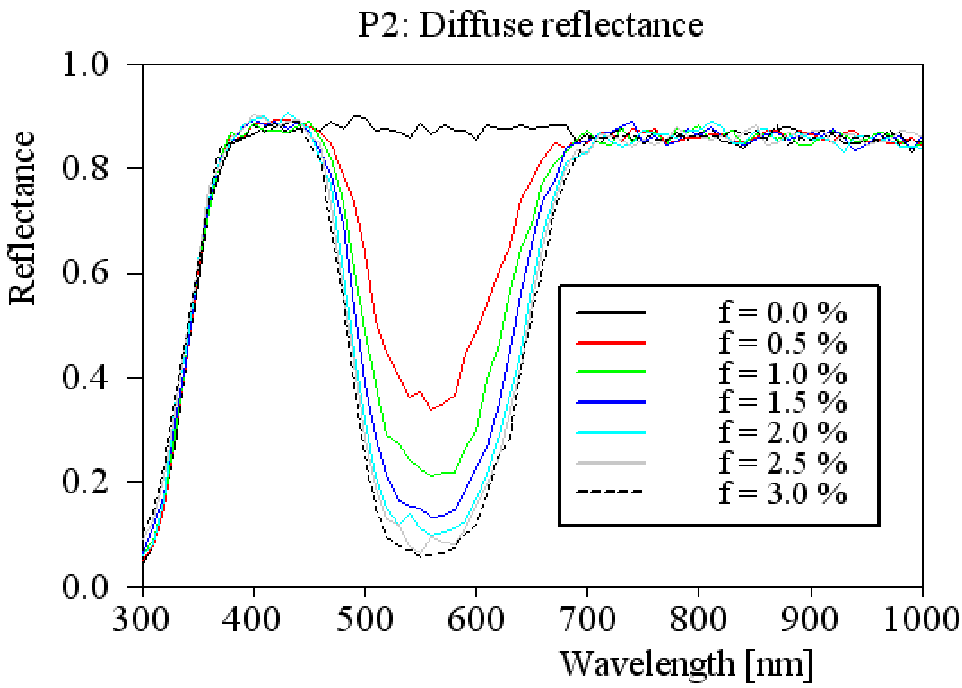
For each pigment type we have computed the diffuse reflectance of the paint, varying the volume fraction f of the pigments in the binder. Pigment P1 absorbs in the blue:

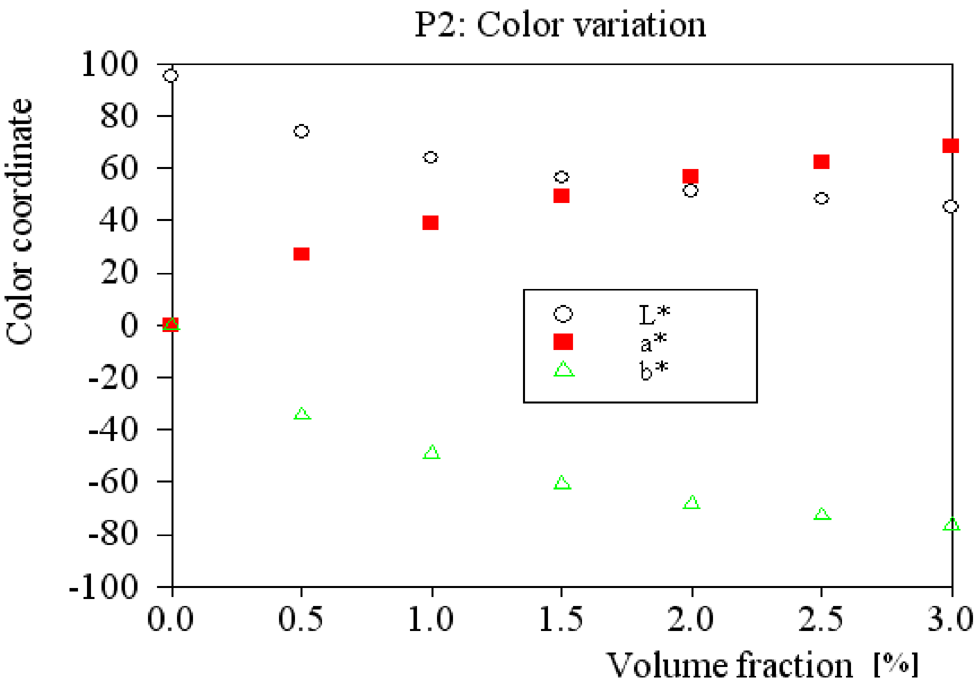


The corresponding color coordinates are theses:

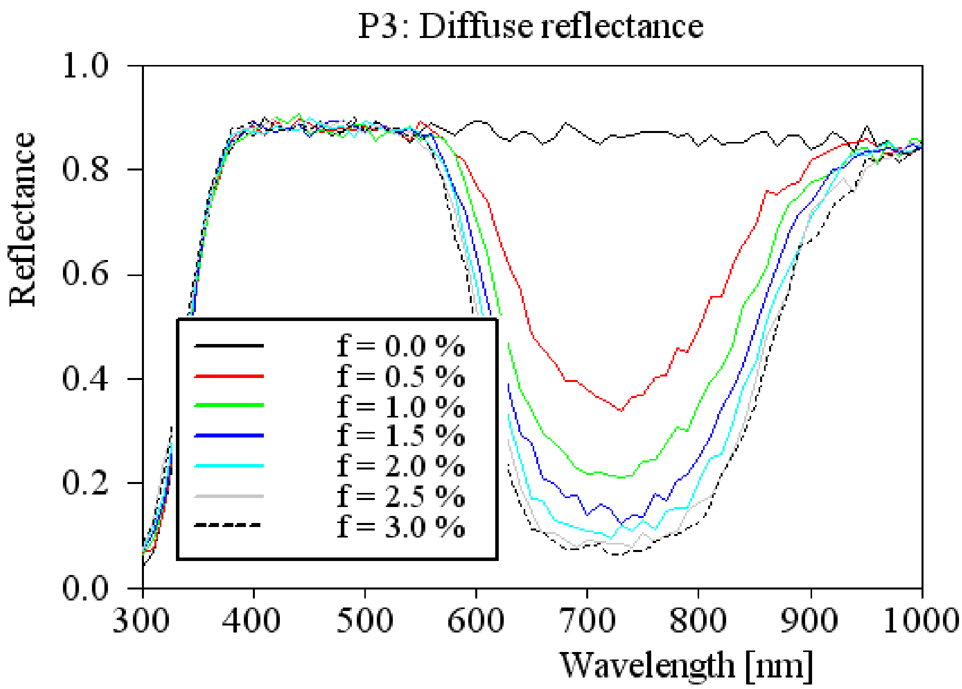


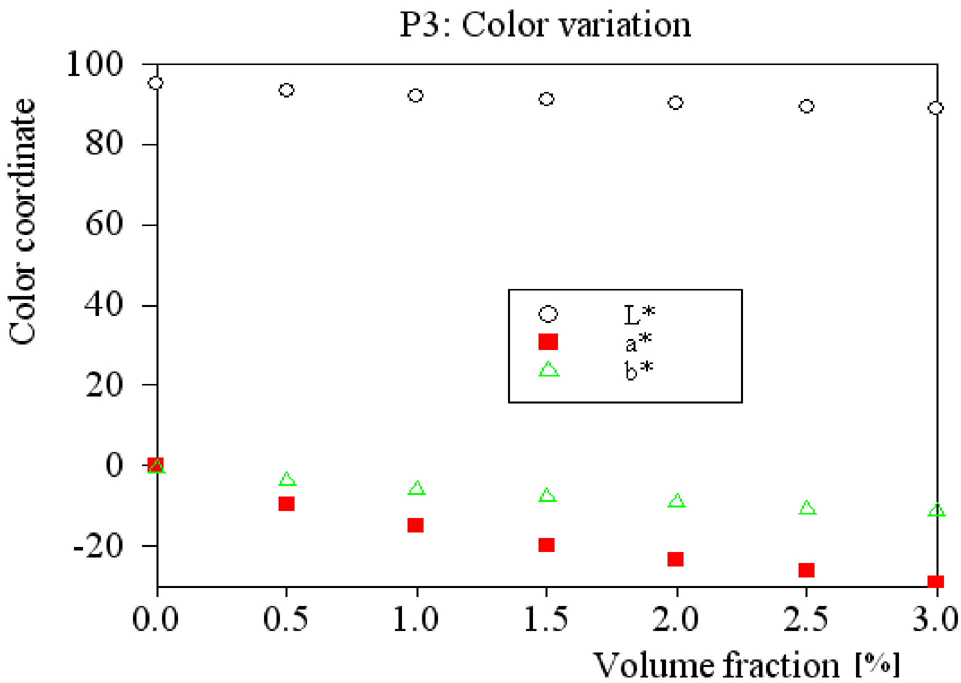
For the P2 pigment the following spectra and colors are obtained:



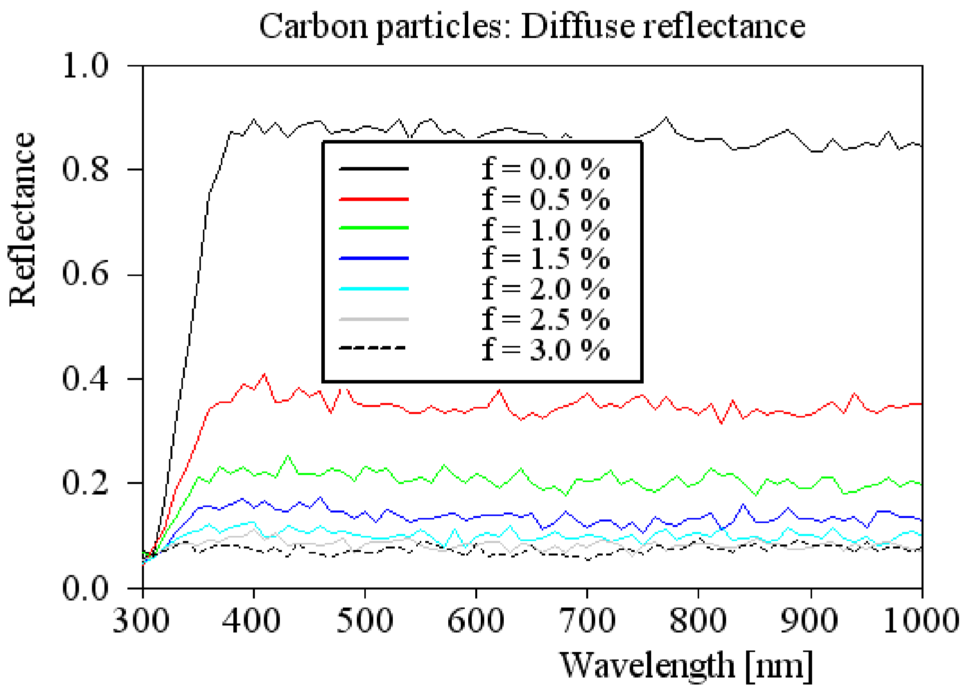


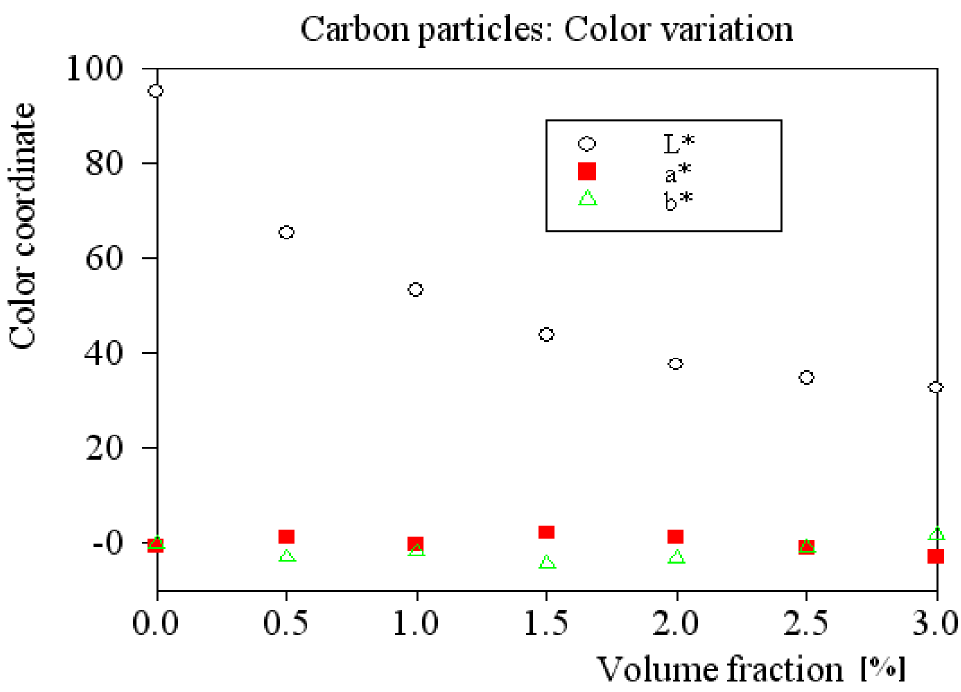
Here are spectra and color coordinates of P3 absorbing in the red:





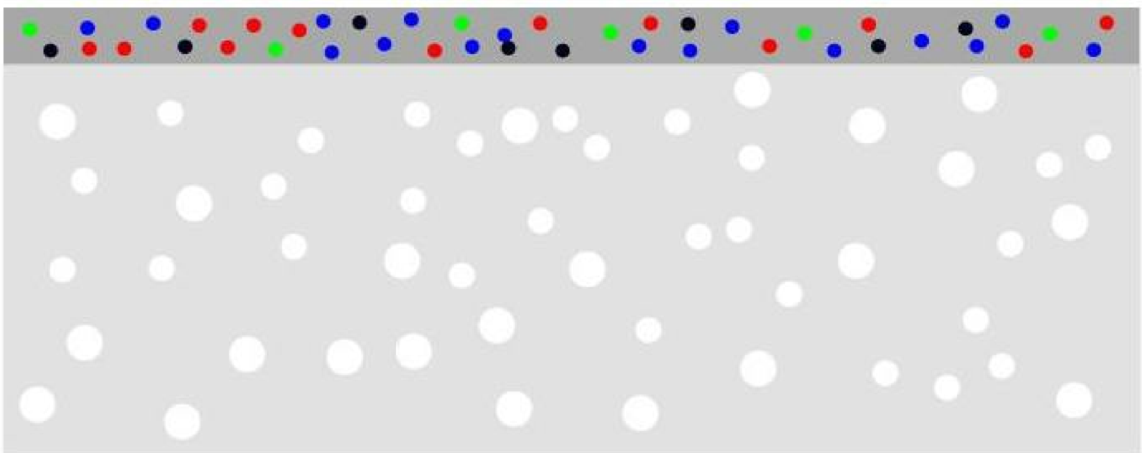
Finally the carbon particles can be used to realize different gray scales:



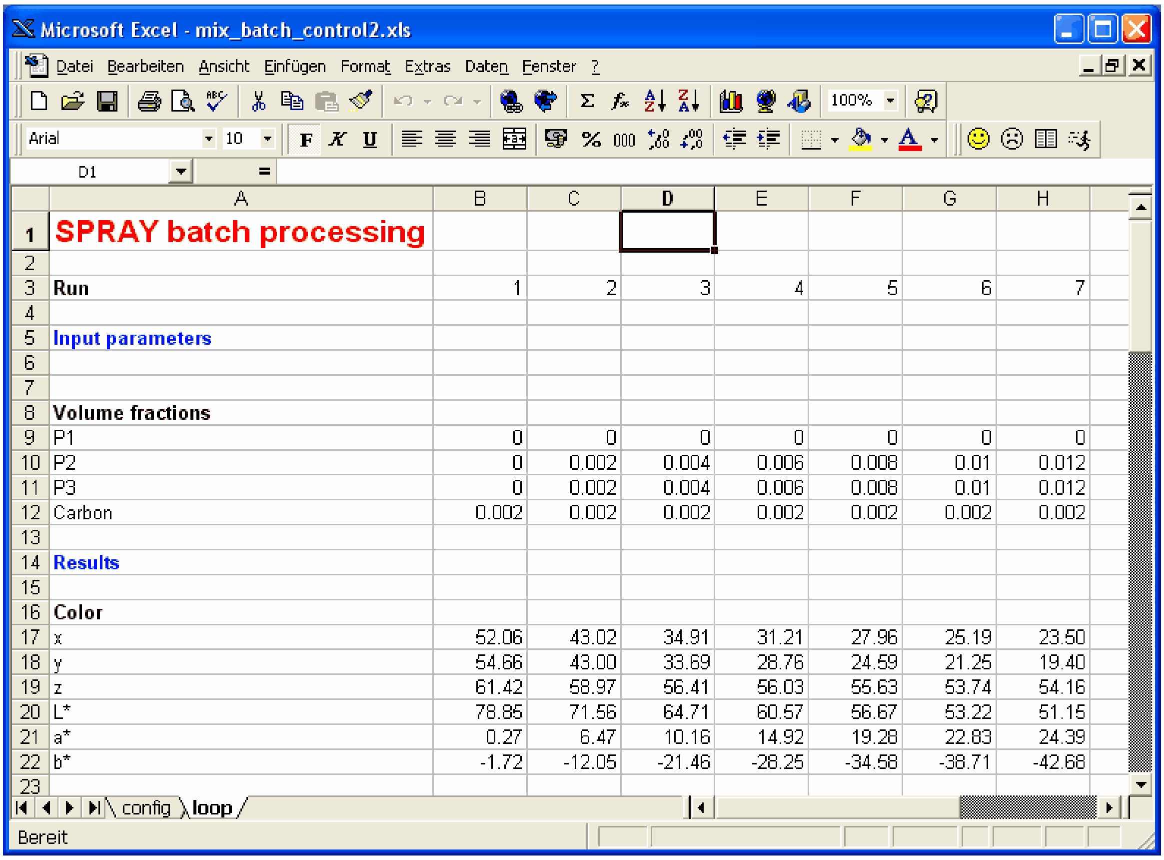


Mixing pigments

A scattering medium in SPRAY may contain several types of pigments. In that case the individual probabilities for absorption and scattering events are summed up. The angle distribution used for the re-direction of scattered rays is computed as an average of the scattering patterns of the constituents - weighted with the corresponding volume fractions.

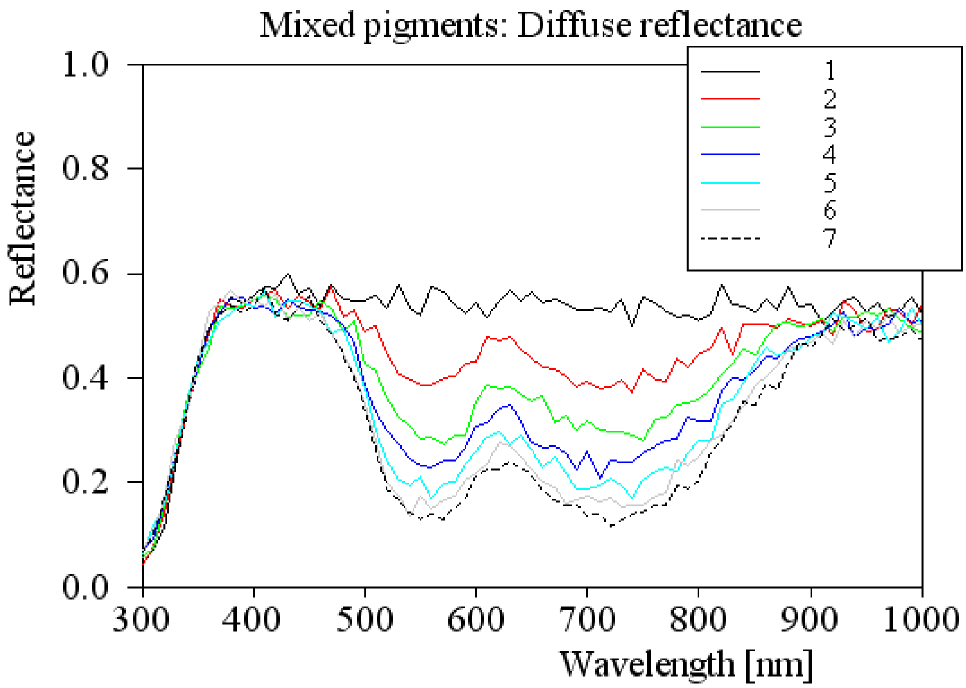


The following screenshot shows an Excel solution for color prediction of mixed pigment systems. You type in the volume fraction of the individual pigments and a small VisualBasic macro computes the color of the mixture. SPRAY works as OLE server in the background and delivers optical spectra and color coordinates.

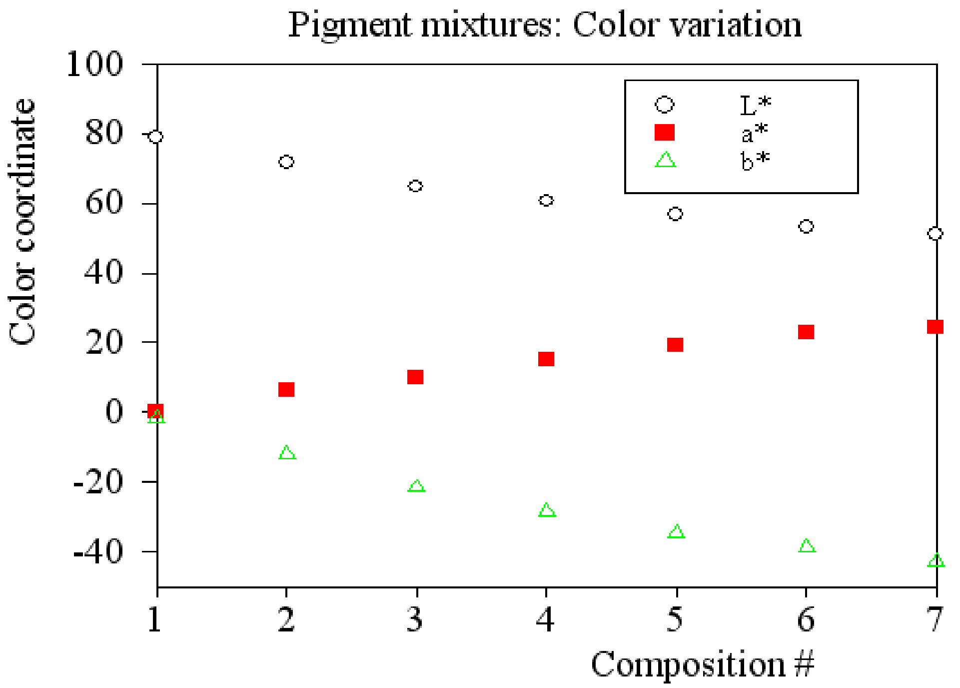


	A	B	C	D	E	F	G	H
1	SPRAY batch processing							
2								
3	Run	1	2	3	4	5	6	7
4								
5	Input parameters							
6								
7								
8	Volume fractions							
9	P1	0	0	0	0	0	0	0
10	P2	0	0.002	0.004	0.006	0.008	0.01	0.012
11	P3	0	0.002	0.004	0.006	0.008	0.01	0.012
12	Carbon	0.002	0.002	0.002	0.002	0.002	0.002	0.002
13								
14	Results							
15								
16	Color							
17	x	52.06	43.02	34.91	31.21	27.96	25.19	23.50
18	y	54.66	43.00	33.69	28.76	24.59	21.25	19.40
19	z	61.42	58.97	56.41	56.03	55.63	53.74	54.16
20	L*	78.85	71.56	64.71	60.57	56.67	53.22	51.15
21	a*	0.27	6.47	10.16	14.92	19.28	22.83	24.39
22	b*	-1.72	-12.05	-21.46	-28.25	-34.58	-38.71	-42.68
23								

The spectra computed for the 7 pigment compositions are these:

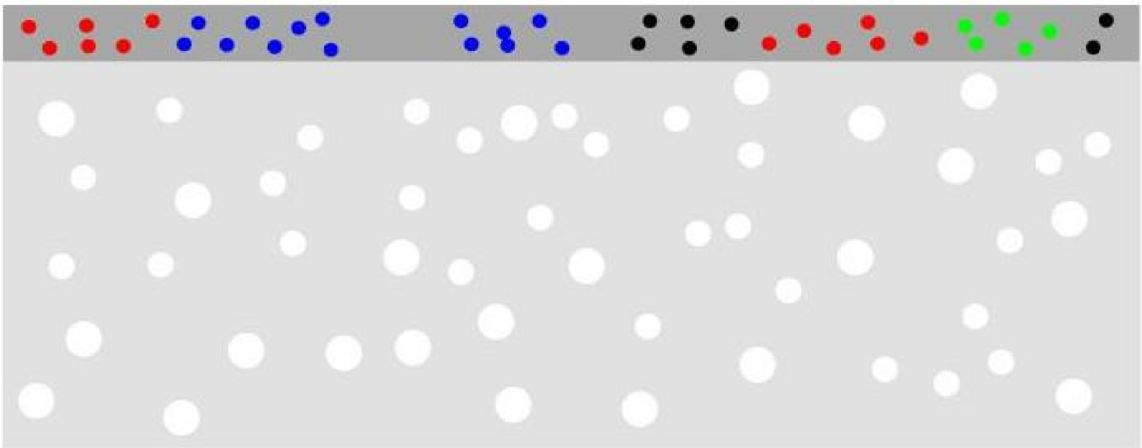


The corresponding colors are:



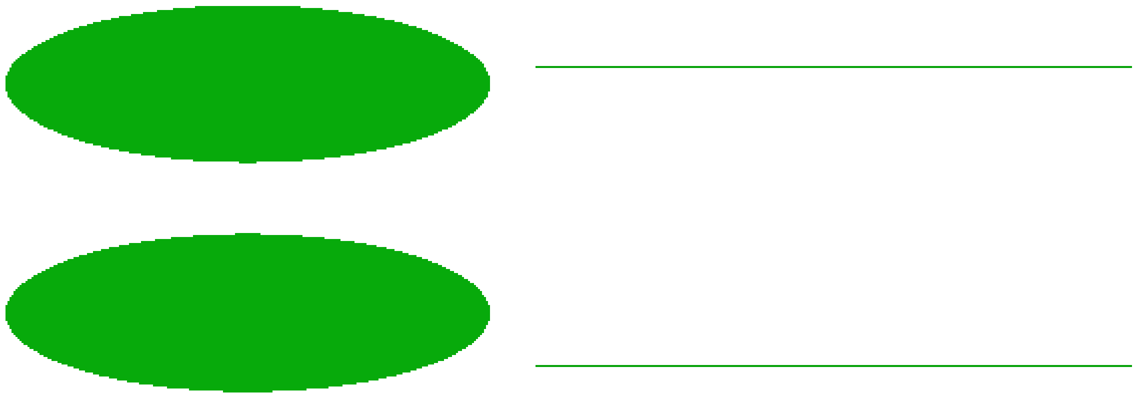
2.3 A model of digital prints

Colors in digital prints are made by placing dots of the available pigment types close to each other. Viewing the image from the distance with a spatial resolution that does not resolve the individual dots, the color impression is given by averaging the diffuse reflectance of several dots.

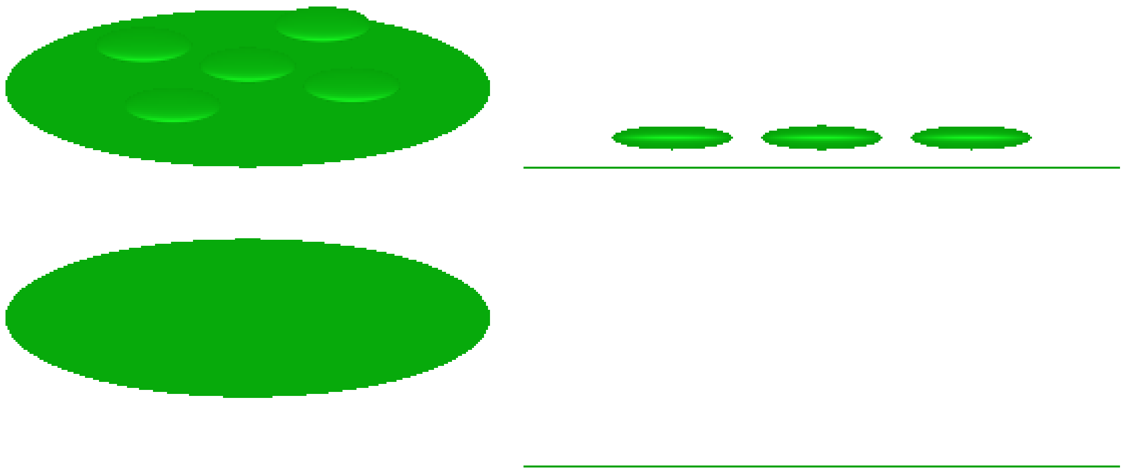


The following steps show how a simple SPRAY model for the simulation of digital prints on paper can be developed. We will consider a circular area of 100 µm radius, fill in some printed dots and compute the total diffuse reflectanc of the system.

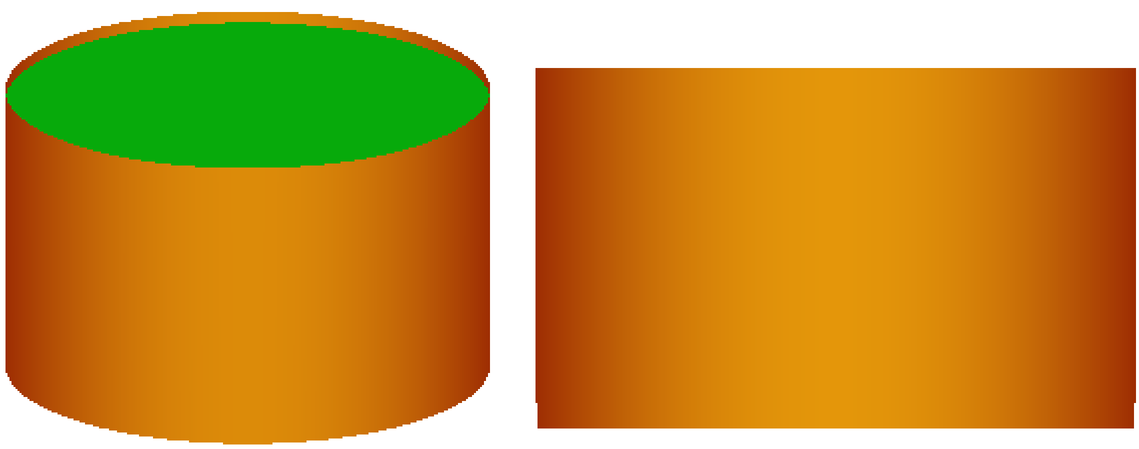
We start with two circles of 100 µm radius that define bottom and top of the underlying paper. On the left picture below you see the scenery from a raised observation point whereas the right image shows a side view:



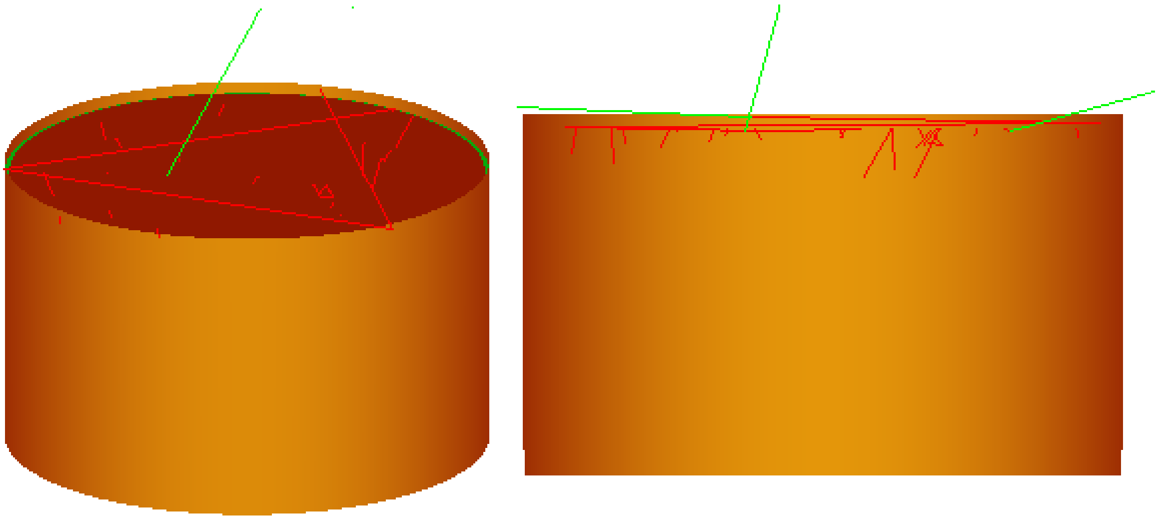
The dots are modeled by flat ellipsoids which are filled with pigments. The volume fraction of the pigments inside the dots is 5%, the dot diameter and height are 40 µm and 8 µm, respectively:



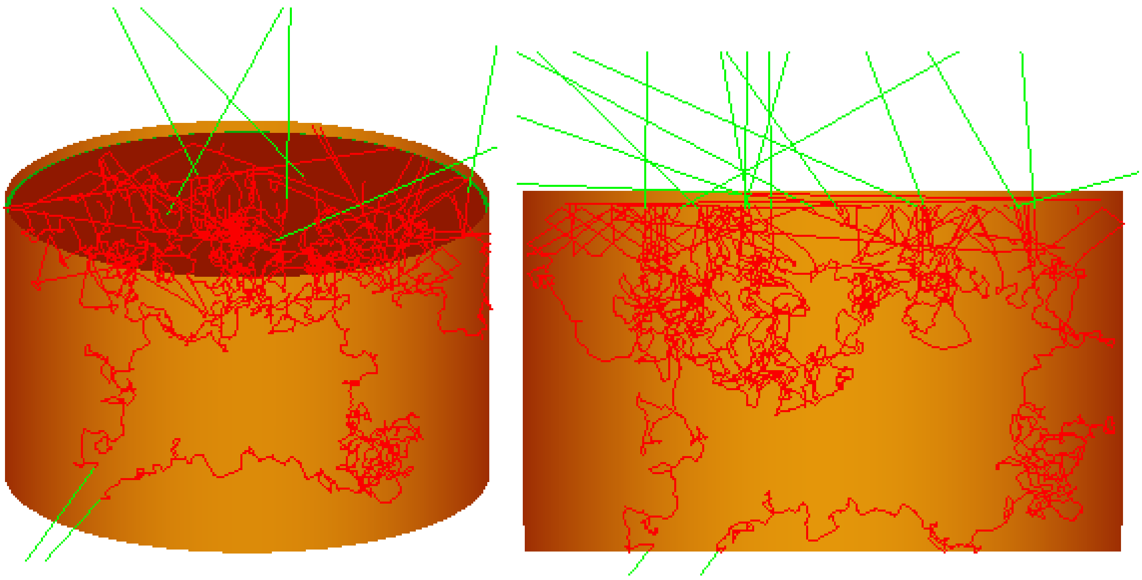
The dots are embedded in a homogeneous layer with a thickness of 15 µm. A circular transparent light source is set directly above the top surface. It illuminates the sample from the top with Lambertian characteristics. Around the scenery we have placed a cylindrical ideal mirror which introduces reflecting boundary conditions:



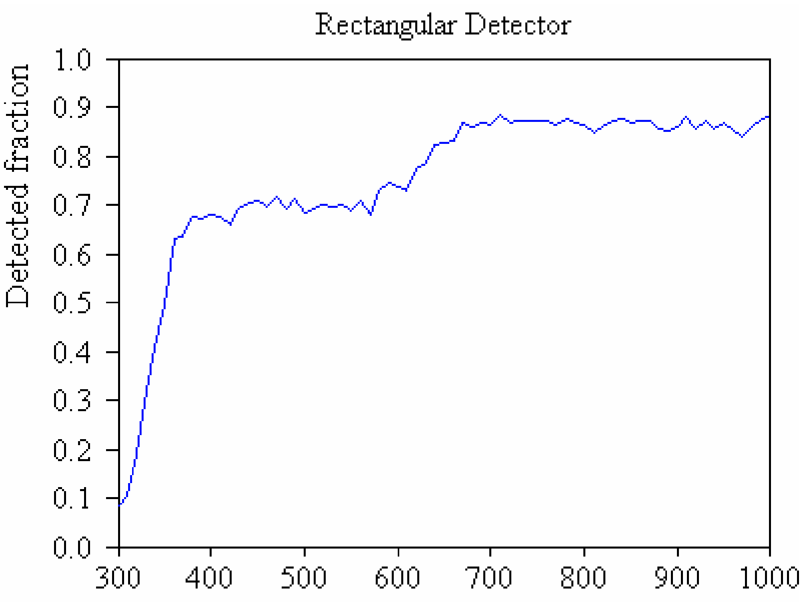
Now it's time for light. In the UV at 300 nm wavelength the penetration depth of the radiation in the paper is very short. Here are some test rays:



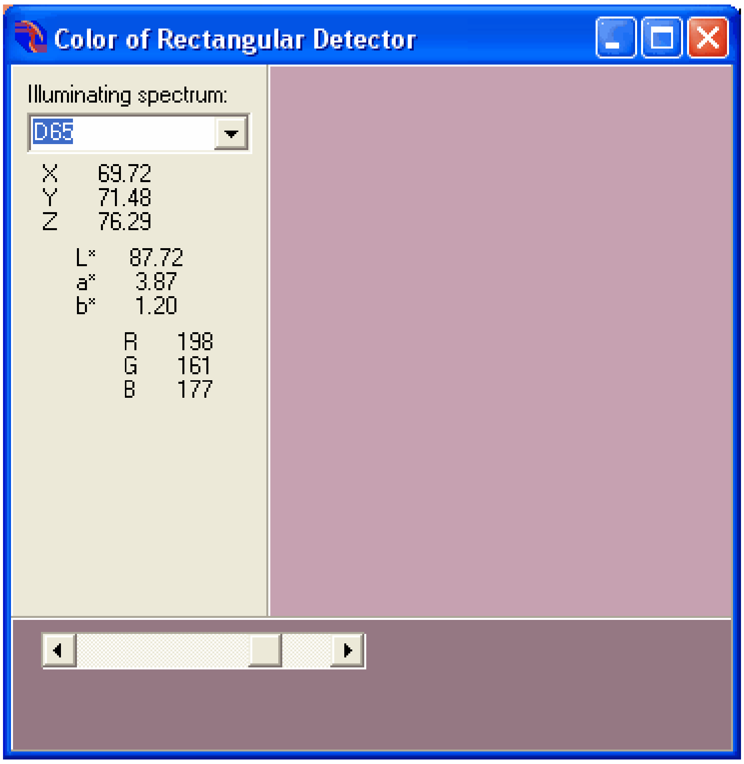
At 600 nm wavelength the rays travel much longer distances before they are emitted or absorbed:



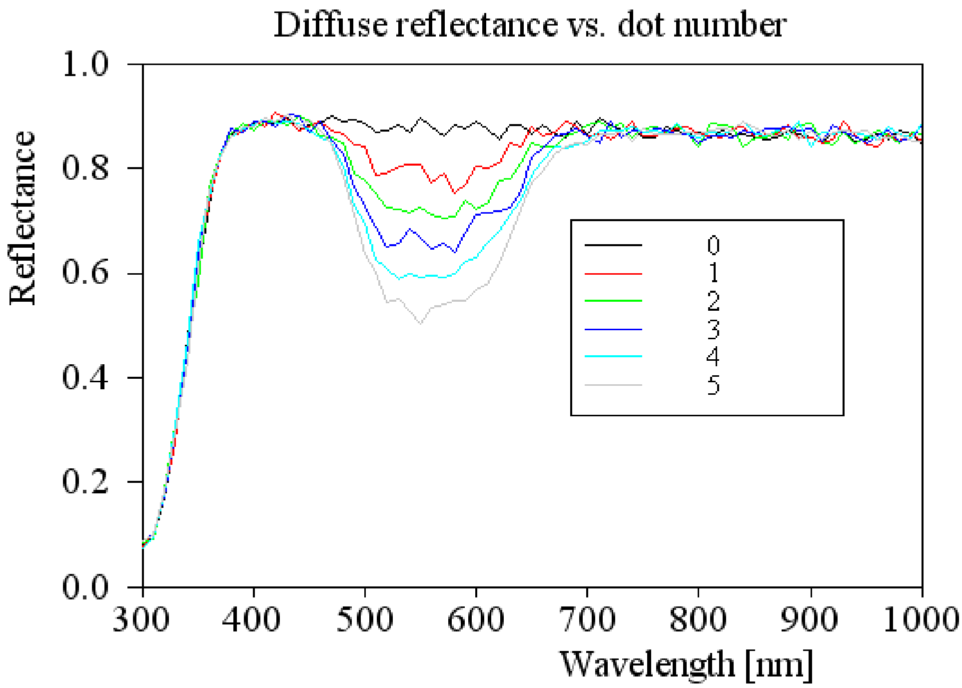
The next graph shows the spectrum for 3 dots with pigment P1 and 2 dots with pigment P2:

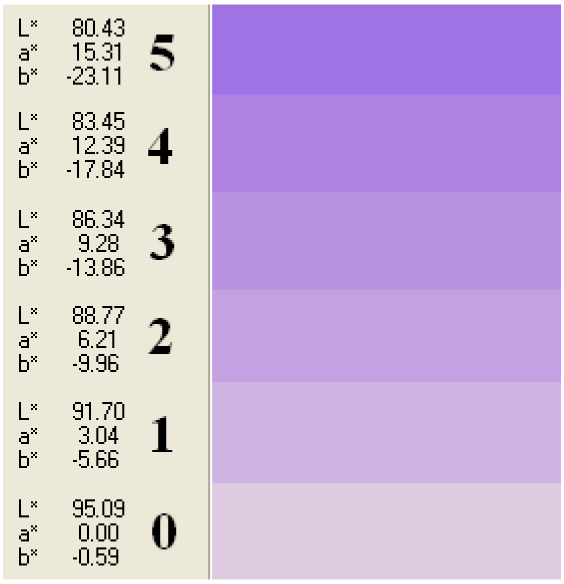


The corresponding coordinates and a rough impression of the color are given below:



Taking 0 to 5 dots of pigment tpye P2 gives the following spectra and color coordinates:





2.4 Investigating pigment properties

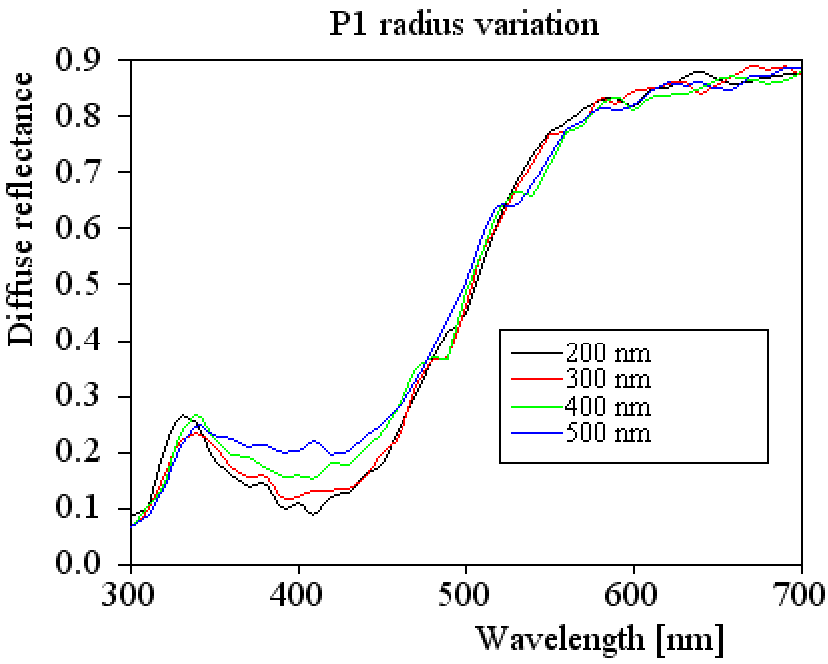
This section shows how pigment research can be assisted by SPRAY. Knowing the optical constants of the involved pigment materials can save a lot of experiments and time. Instead of realizing many samples and doing many measurements you can predict the optical performance of a system with SPRAY. You should, of course, check the established relations and numbers with selected real cases.

Here we investigate the following questions:

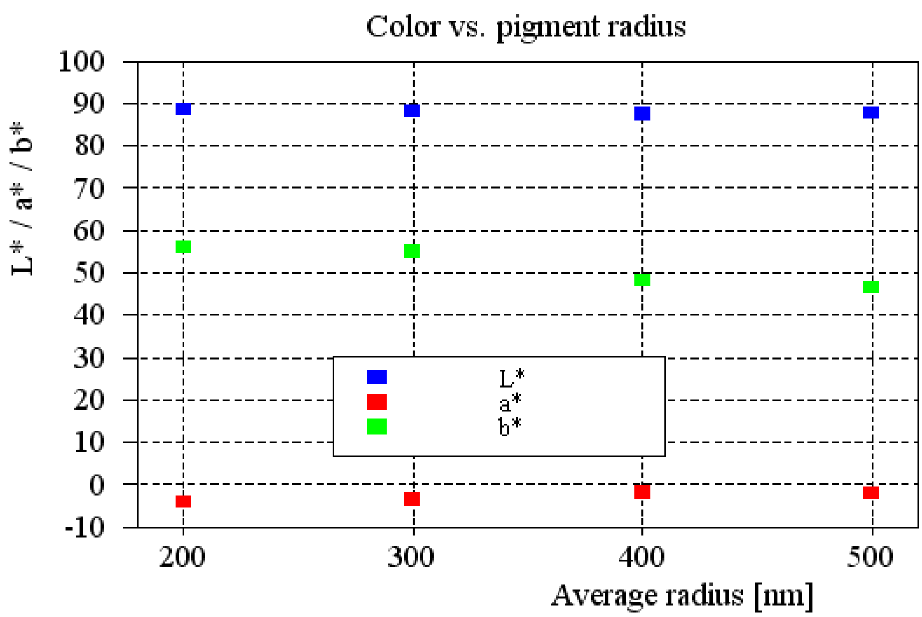
- Does the color of a paint change with pigment size?
- How thick must the coating of a particle be in order to hide the interior completely?

- How depends the reflectance spectrum of a multiply coated plate on the viewing angle?

Pigment size variation
What happens to the color of a paint if you change the particle size? Here we show how the predicted color of the 'P1 paint' (see above) depends on the size of the pigment particles. Increasing the size from 200 to 500 nm (average radius) leads to a noticeable change in visual appearance:

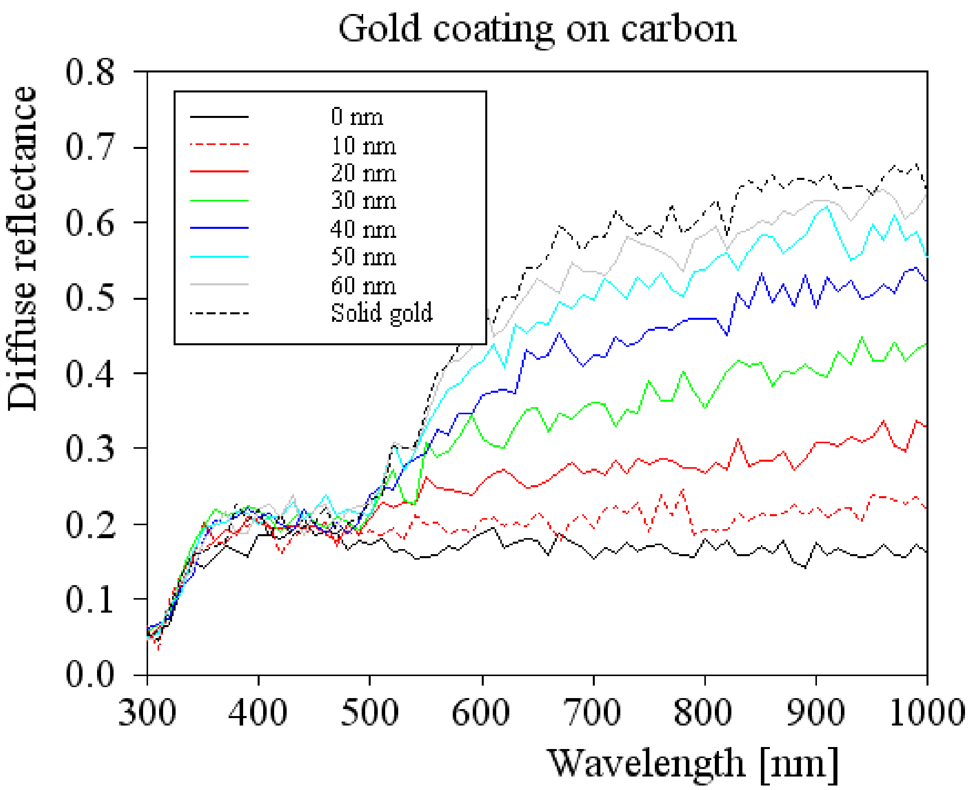


The corresponding color changes are significant:

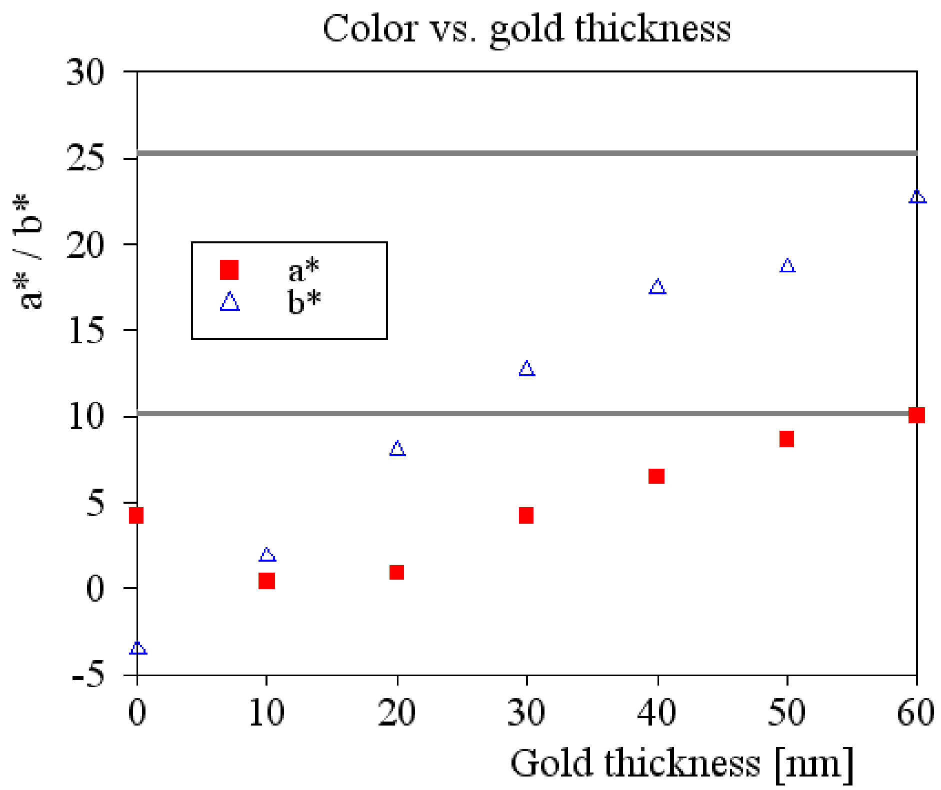


Turning carbon into gold ...
With SPRAY you can investigate single and multiple coatings of spherical particles. Sometimes pigments are coated on purpose in order to achieve a certain appearance or other function,

sometimes 'natural' coatings like surface oxides exist and have to be taken into account.
The demo question for coated spheres is this: How thick must a gold layer be on carbon particles (average size about 2 µm) in order to make the pigments look like solid gold nuggets of the same size?
Well, with SPRAY you can just try. The next graphs show the reflectance spectra (for the simple paint model discussed above) of various test 'samples' including pure carbon and pure gold. The thickness of the gold coating is indicated in the legend:



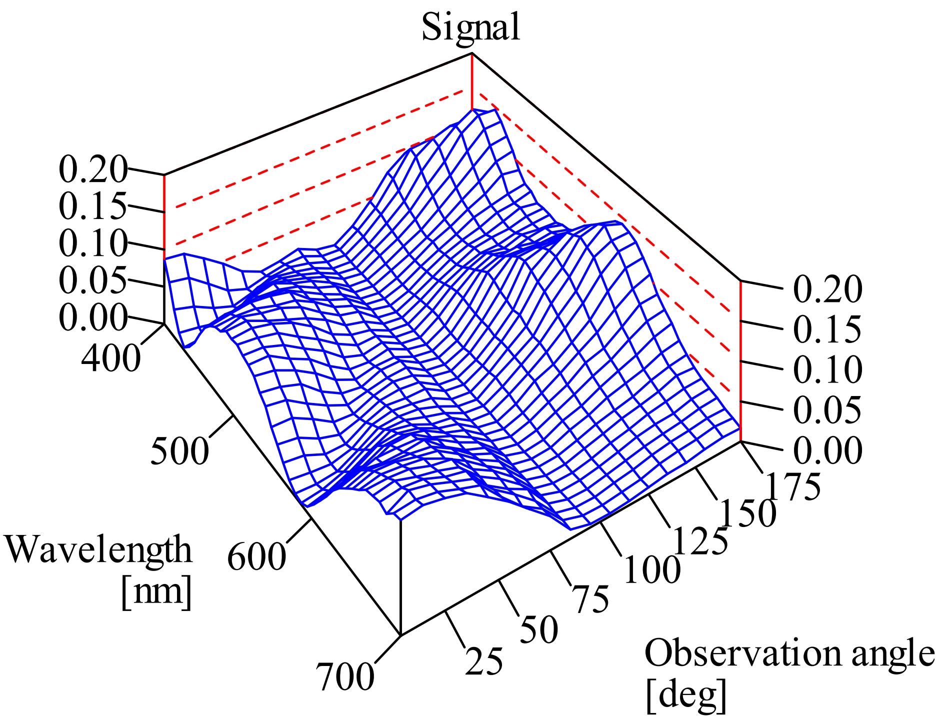
The coating should have a thickness of at least 50 nm. But even at 60 nm thickness the color coordinates are still different from those of a 'solid gold paint'. The latter are indicated by the gray lines in the graph below:



Inspecting advanced coatings

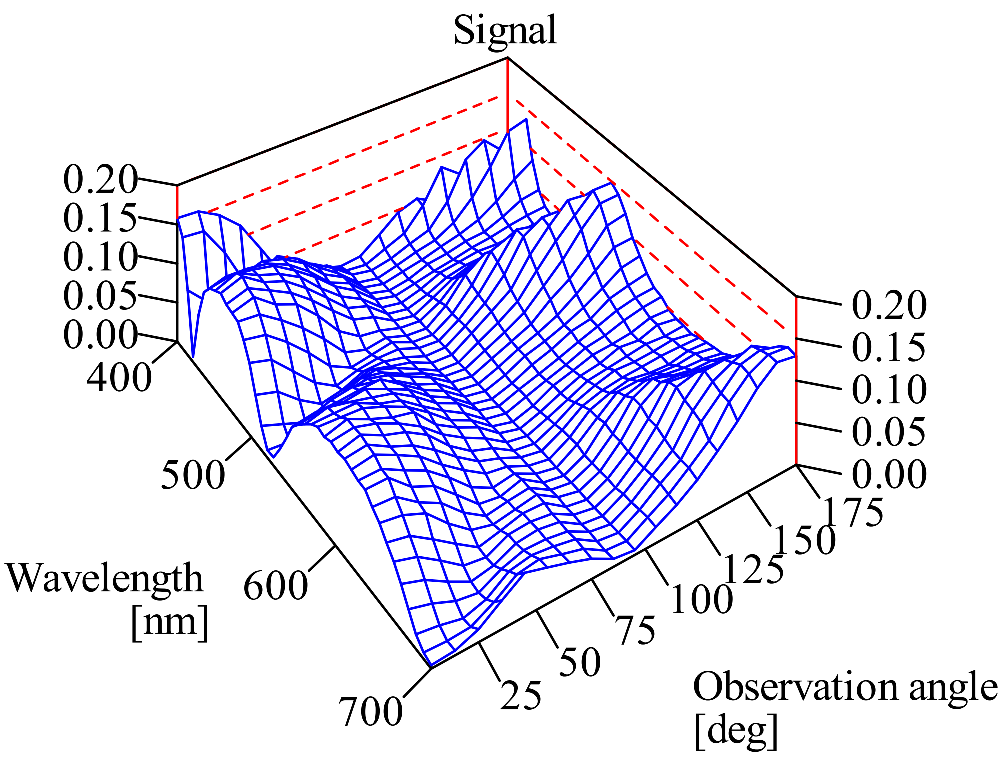
Finally we show an example of complex coatings. Any object in SPRAY may be covered with an almost arbitrary layer stack. Here a glass plate is covered with a 12 layer coating. The coating is made repeating the basic stack [TiO_2 (10 nm) / SiO_2 (50 nm) / Ag (10 nm)] 4 times:

The plate has been illuminated by diffuse radiation. A special detector (with multiple angle segments) records how many rays are leaving the plate in which direction. The following plot summarizes the results: From 0 to 90 degrees the reflected radiation is displayed (0 degree is the surface normal), the range 90 ... 180 deg covers the transmitted rays:



The observed features are interference effects which depend on the angle of observation, of course.

Changing the basic stack to [TiO_2 (20 nm) / SiO_2 (50 nm) / Ag (10 nm)], i.e. doubling the TiO_2 thickness, leads to a significant shift of the spectra:



3 Optical constants

3.1 Overview

The term 'Optical constants' is used for the so-called dielectric function ε = ε1+ i ε2 or its square root, the complex refractive index n + i k. The dielectric function represents a material in Maxwell's equations and determines the solutions for electromagnetic waves.
Light propagation through any system depends on the optical constants of all involved materials and geometry (shapes, sizes, distances). Hence optical constants must be the basis of any physical model. SPRAY is equipped with a large database of optical constants. There are fixed data sets taken from literature sources, and flexible models that can be adapted to individual cases.

If you are not familiar with optical constants, the next section about typical materials could be useful for you.

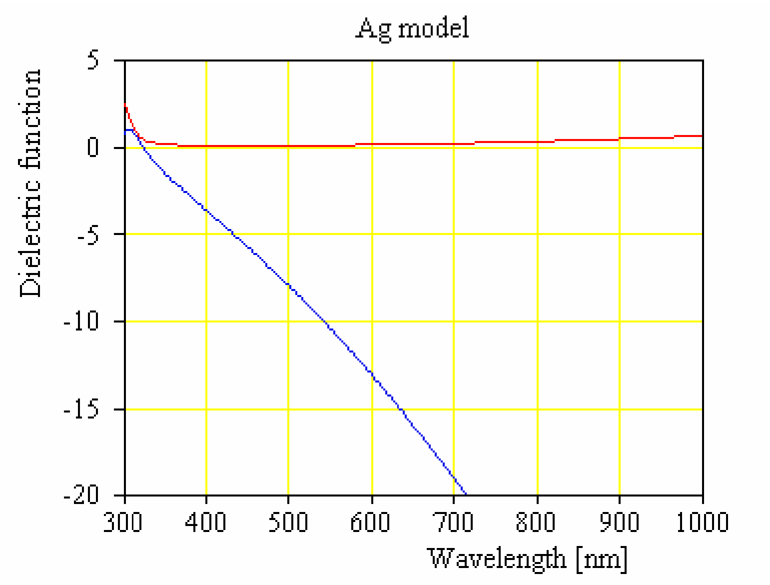
The optical constants of the demo pigments used in this text are given in separate sections below.

3.2 Optical constants of typical materials

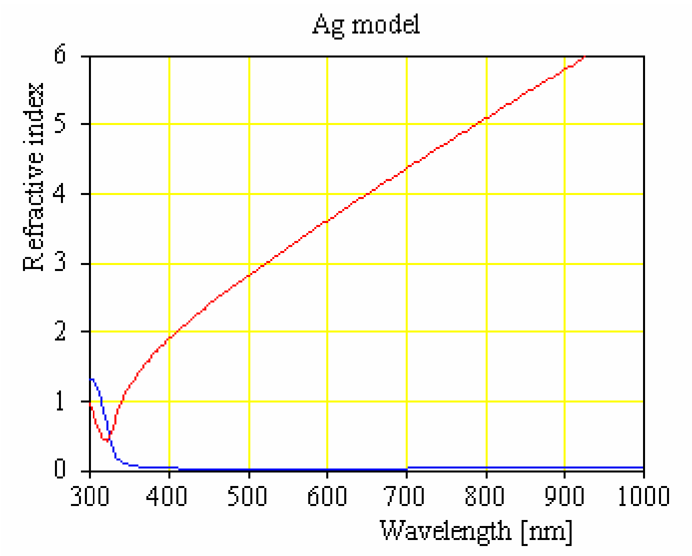
Here are optical constants of some typical materials. All graphs show the real part in blue and the imaginary part in red.

Noble metals

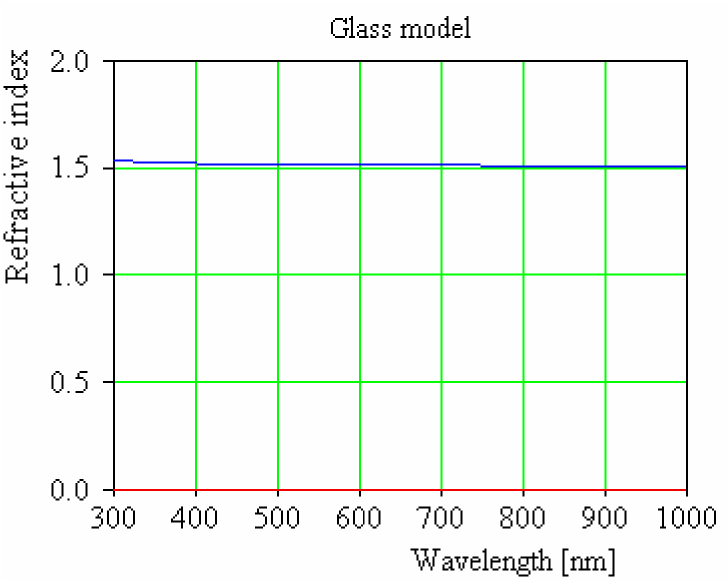
A noble metal like silver is characterized by a large negative real part of the dielectric function and an imaginary part which increases towards large wavelengths:



The complex square root of the dielectric function, the refractive index, has an almost vanishing real part and a much larger imaginary part in the case of metals:



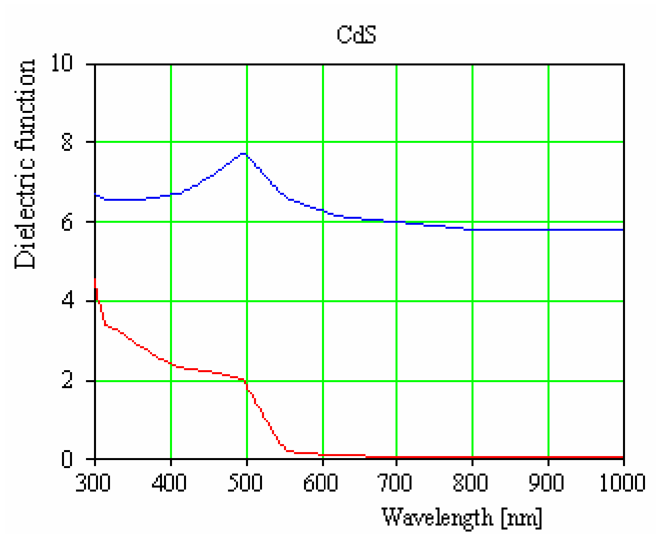
Dielectrics
Insulators like glass have optical constants which are very different from those of metals. The imaginary part is almost zero, the real part almost constant. In most cases the refractive index in the blue is a little larger than in the red - this effect is called 'normal dispersion'. Here is the refractive index of a typical glass:

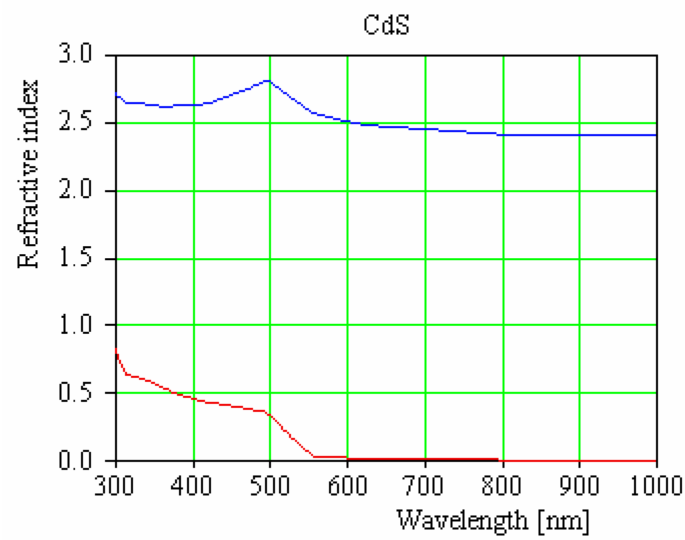


In glasses significant absorption occurs in the mid infrared region (by vibrational modes) and in the far UV (by optical interband transitions). Due to the large electronic bandgap in these types of material the visible spectral range is almost absorption-free.

Semiconductors

Semiconductors have smaller separations of energy bands (band gap) than insulators. In many cases visible light has enough energy to excite electronic interband transitions which leads to large absorption above the bandgap like in the case of CdS shown here:





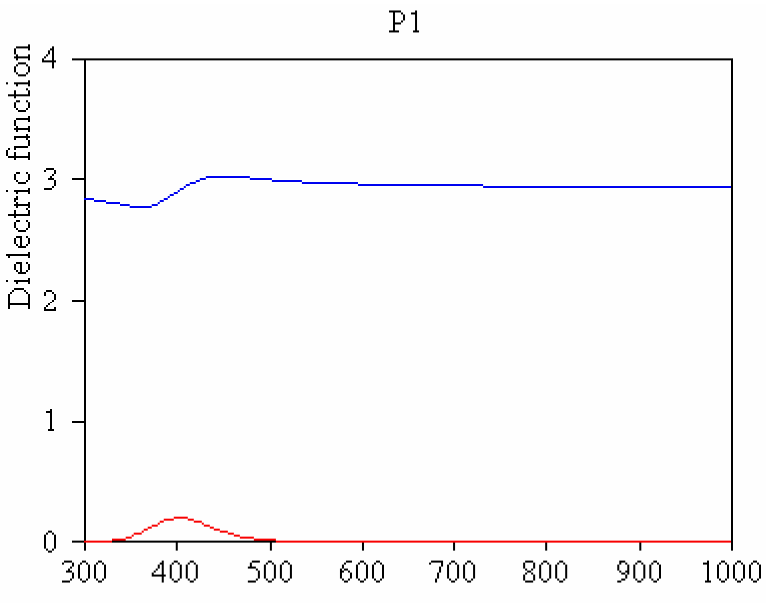
Since CdS absorbs in the blue, CdS particles appear to be yellow if illuminated with white light.

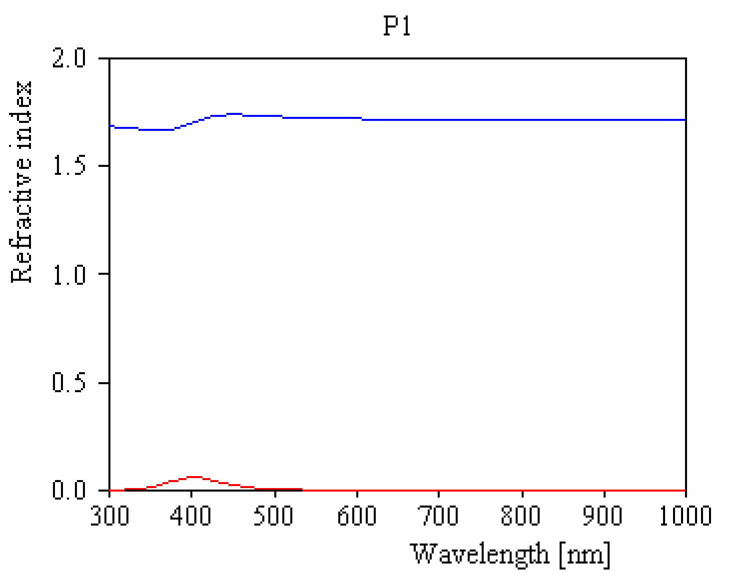
There are almost no homogeneous, crystalline materials which have sharp, isolated absorption bands in the visible spectral range. If you need absorption in the green or yellow you have to make use of electronic transitions in organic molecules (assisted by some incorporated metal atoms). The demo pigments P1, P2 and P3 (shown in the following) are fictional examples with more or less typical optical constants.

3.3 Demo pigments

3.3.1 P1

The optical constants of the demo pigments P1, P2 and P3 are composed of a constant and an oscillator contribution. The latter creates the absorption band responsible for the pigment's color. The optical constants of real pigments may be obtained by a fitting procedure which adjusts the parameters of a suitable dielectric function model. Realistic models sometimes require several oscillator terms or interband transition models.
The dielectric function and the refractive index of the demo pigment P1 are the following:

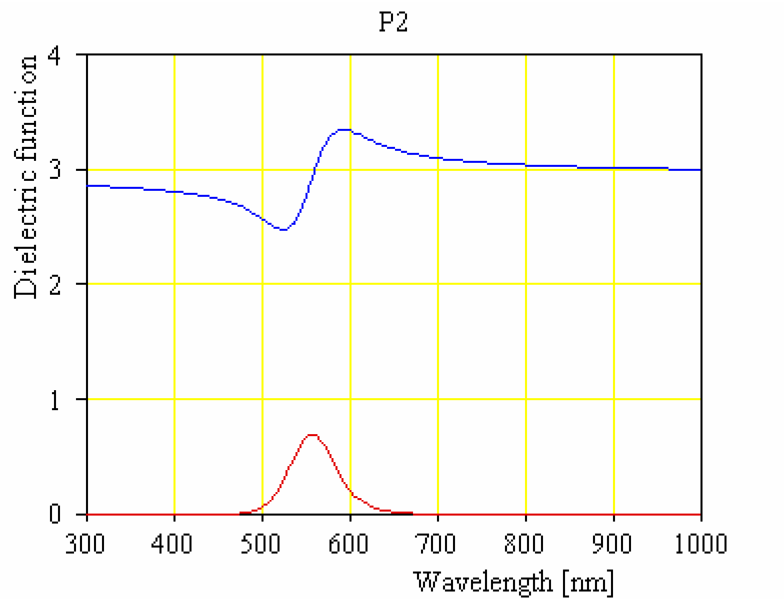


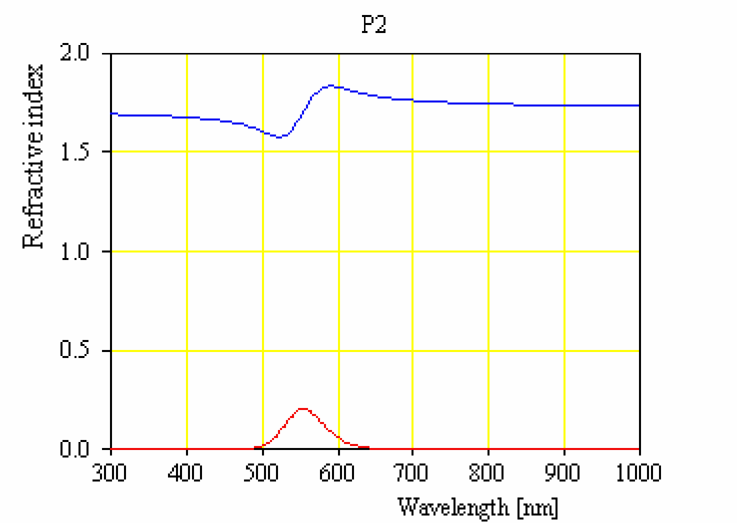


P1 absorbs in the blue part of the visible spectrum.

3.3.2 P2

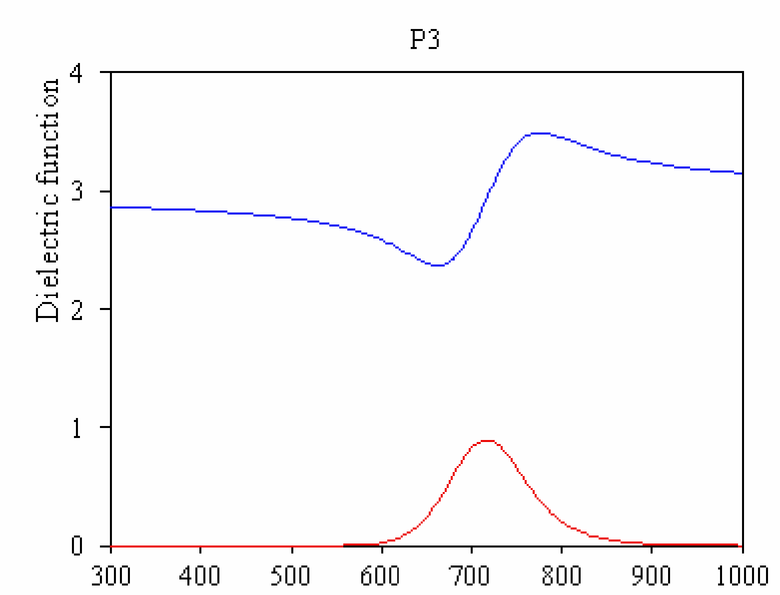
Demo pigment P2 absorbs in the center of the visible spectral range. Here are its optical constants:

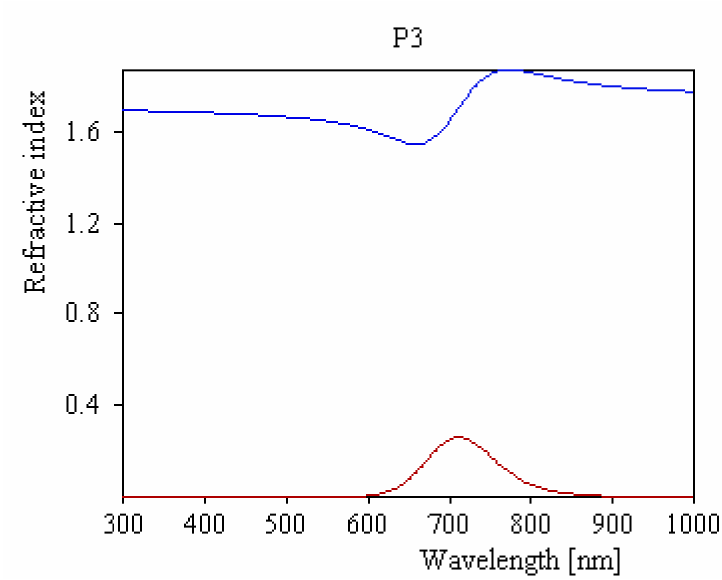

P2
Dielectric function
4
3
2
1
0
300
400
500
600
700
800
900
1000
Wavelength [nm]


P2
Refractive index
2.0
1.5
1.0
0.5
0.0
300
400
500
600
700
800
900
1000
Wavelength [nm]

3.3.3 P3

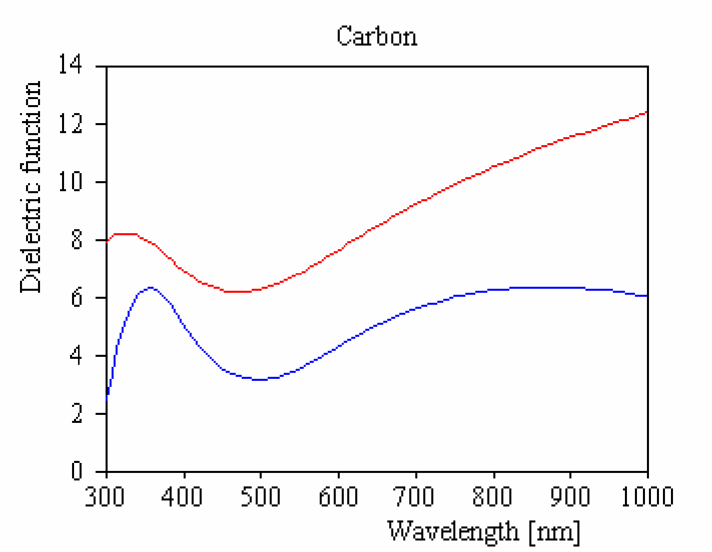
P3 absorbs in the red:

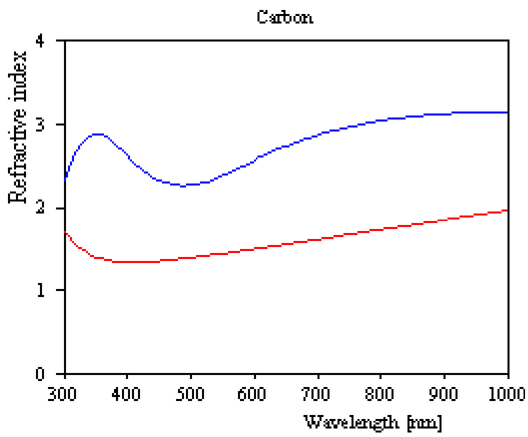




3.3.4 Carbon particles

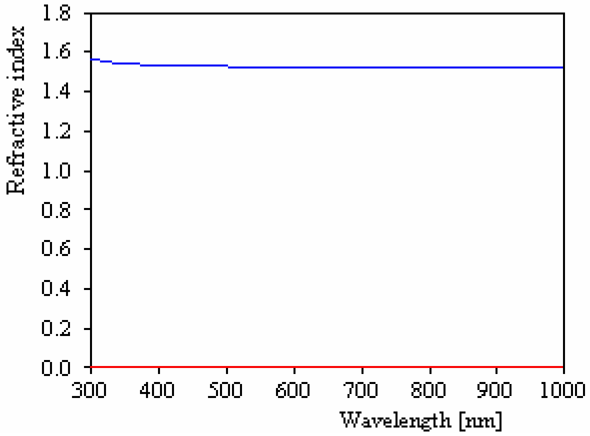
Carbon particles absorb in a broad spectral range. They can be used as 'black pigments'. The optical constants of carbon have been taken from the SPRAY database. The dielectric function and the refractive index are these:

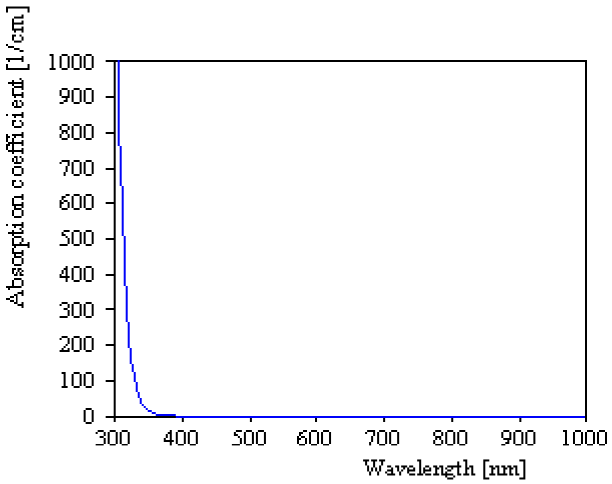




3.4 Host material of paper model

The host material used in the simple paper model has optical constants similar to glass. The real part of the refractive index shows a weak dispersion, the absorption increases towards the UV. The following graphs show the complex refractive index and the absorption coefficient:





4 Light scattering and absorption

4.1 Overview

If the optical constants of embedded pigments and host material differ from each other, light waves travelling through the medium are scattered and absorbed. In order to perform ray-tracing computations one must know the probability/distance for scattering and absorption events. In addition, the angle distribution of the scattered light must be taken into account when the new direction of a scattered ray is computed.
In the case of spheres embedded in a homogeneous host material the problem is solved by the so-called Mie theory. The SPRAY software contains a module that performs Mie computations for user-defined size distributions of spheres. The spheres may have multiple coatings.
In the following the scattering and absorption properties of the demo pigments are given:

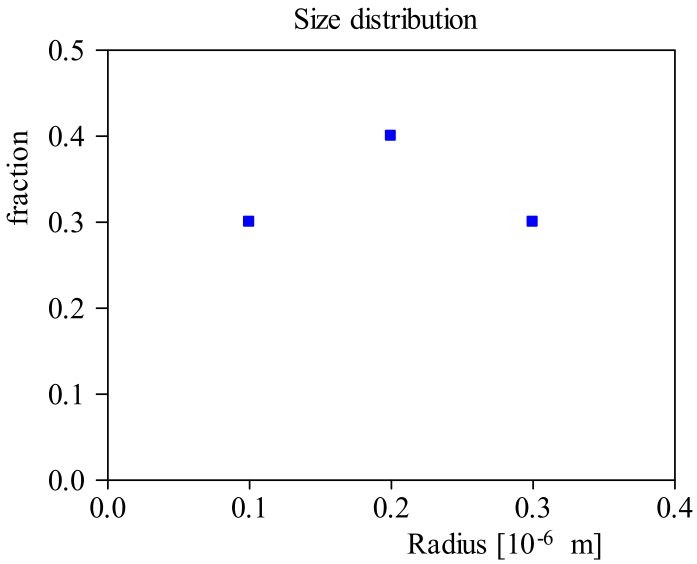
- P1

- P2
- P3
- Carbon
- Scattering voids in paper

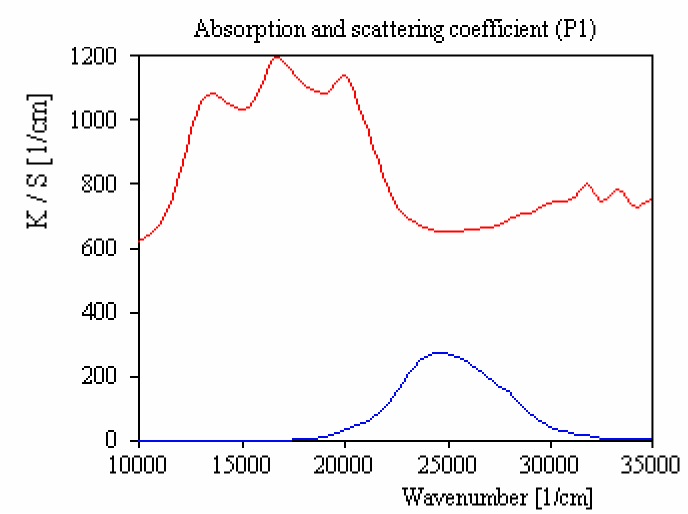
4.2 Demo pigments

4.2.1 P1

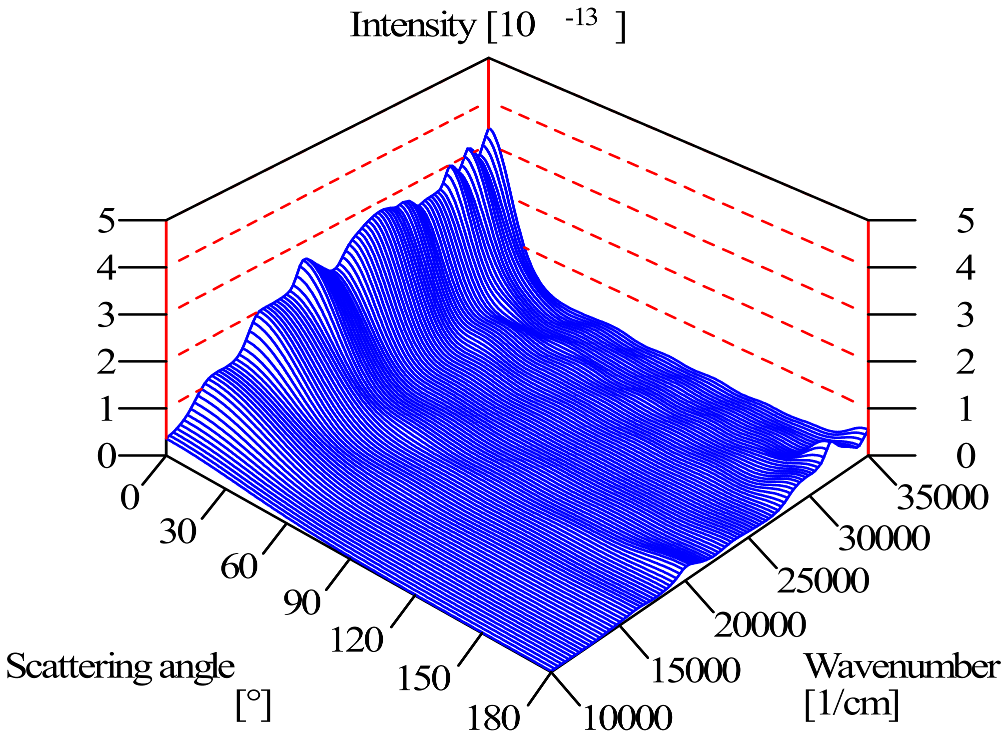
The optical constants of pigment P1 have been given above. The following radius distribution with 3 size classes has been assumed:



The Mie program computes the scattering and absorption data in a way such that the volume fraction of the pigments can be varied afterwards without repeating the calculation again. For a volume fraction of 1% the following absorption (blue) and scattering (red) probabilities are found:



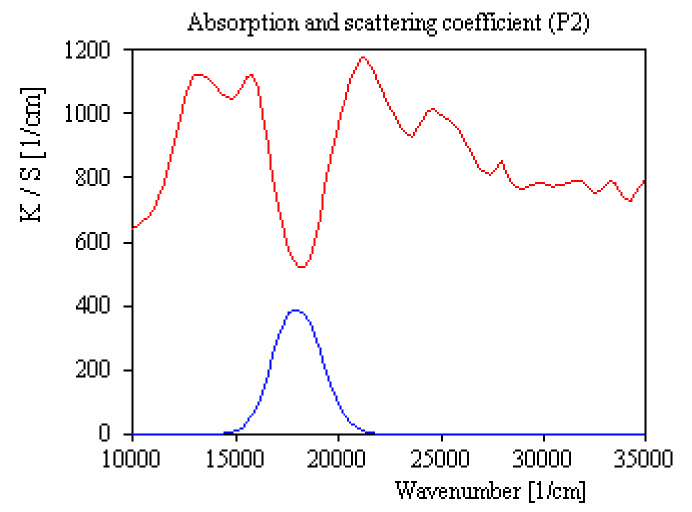
Sorry, all scattering properties are displayed in SPRAY using wavenumbers. Wavenumbers are inverse wavelengths measured in cm (i.e. 1/cm). 10000 1/cm correspond to 1000 nm wavelength (near infrared), 25000 1/cm are 400 nm (blue end of the visible).
Note the rich structure in the scattering probability which depends on the sphere size distribution. The rays scattered by pigment P1 get new directions according to this distribution:

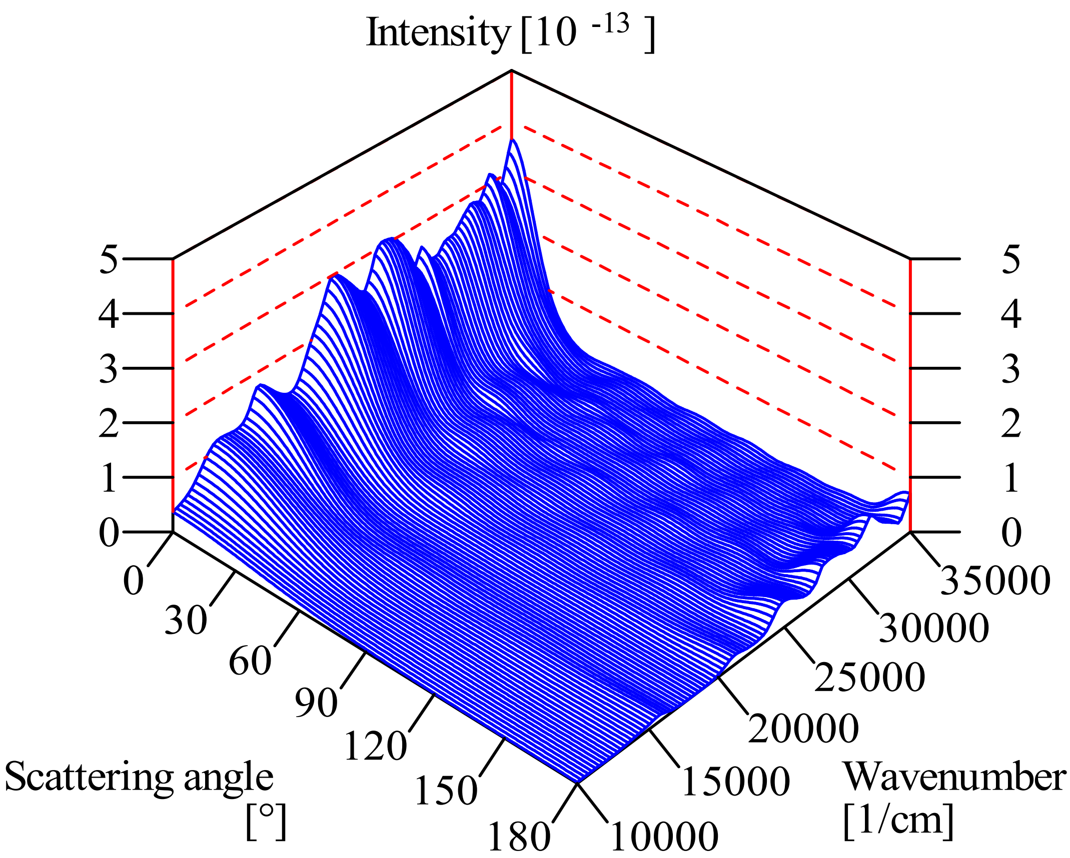


The scattering distribution depends very much on the ratio of the light wavelength and the particle radius. In the infrared (below 15000 1/cm) the ratio is large which leads to a broad angle distribution. In the UV (above 25000 1/cm) the ratio is smaller. Here the distribution is dominated by a strong and sharp forward peak and (weak) backward scattering.
Note that in the whole spectral range from the near infrared to the near UV the distribution is very different from isotropic scattering. Isotropic scattering (which is often used as a first guess) hardly occurs in real systems.

4.2.2 P2

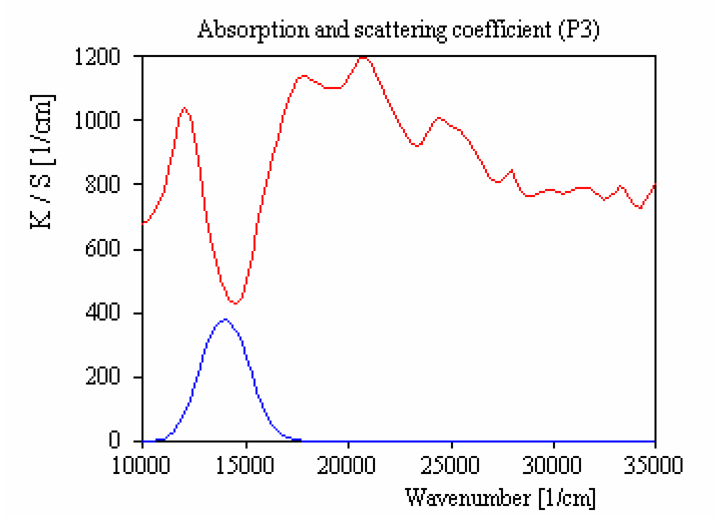
The same radius distribution as for P1 was used here. The optical constants of pigment type P2 were given above.
The Mie results for the probabilities and the scattering distribution are shown in the graphs below:

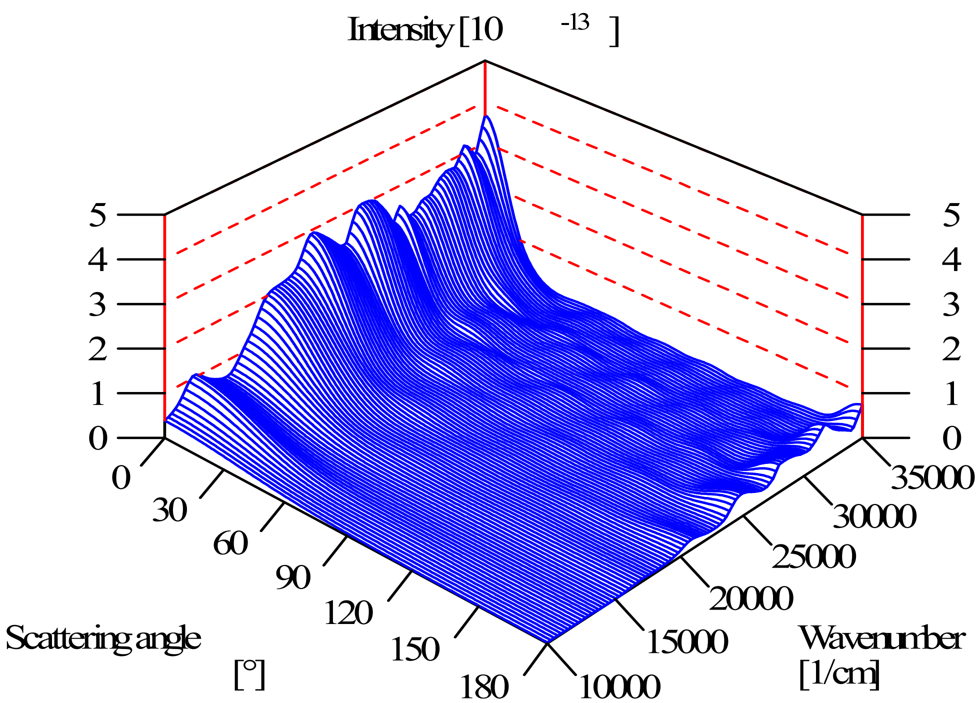

Absorption and scattering coefficient (P2)
K / S [1/cm]
1200
1000
800
600
400
200
0
10000
15000
20000
25000
30000
35000
Wavenumber [1/cm]


Intensity [10 -13]
5
4
3
2
1
0
0
30
60
90
120
150
180
Scattering angle [°]
10000
15000
20000
25000
30000
35000
Wavenumber [1/cm]

4.2.3 P3

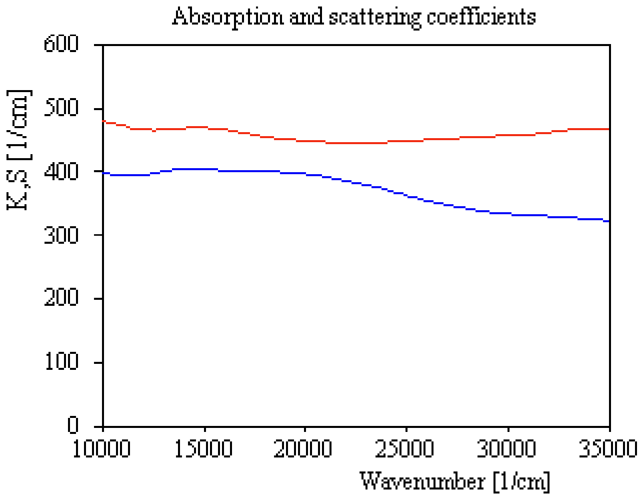
Working again with the radius distribution already used for pigment P1 and the optical constants with absorption in the red one obtains the following scattering characteristics for pigment P3:



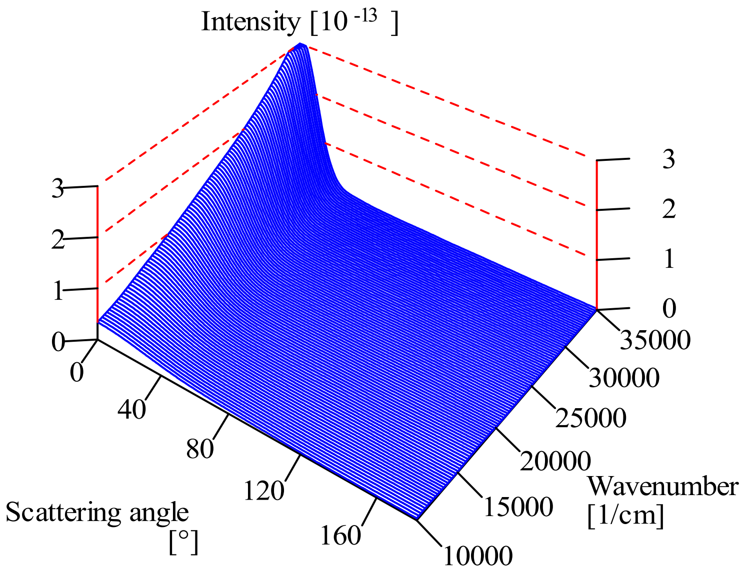


4.2.4 Carbon particles

For the carbon particles the probabilities for absorption and scattering have similar values over the whole visible spectral range:

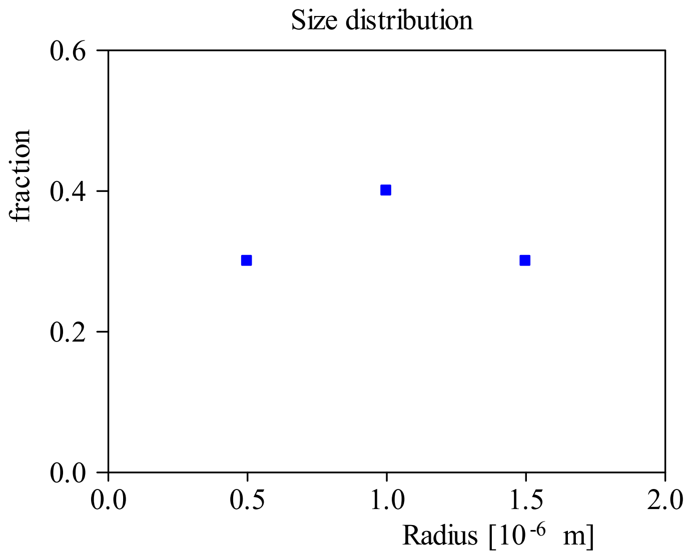


The scattering characteristics does not show any backward contribution:

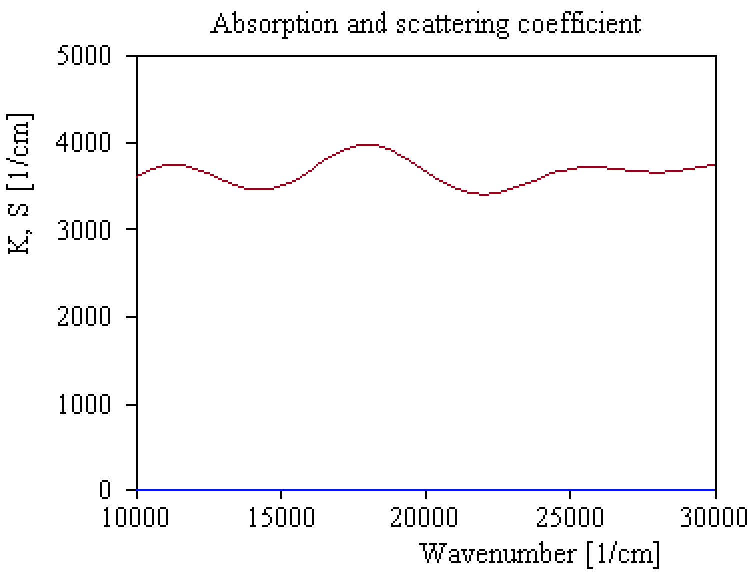


4.3 Light scattering in paper

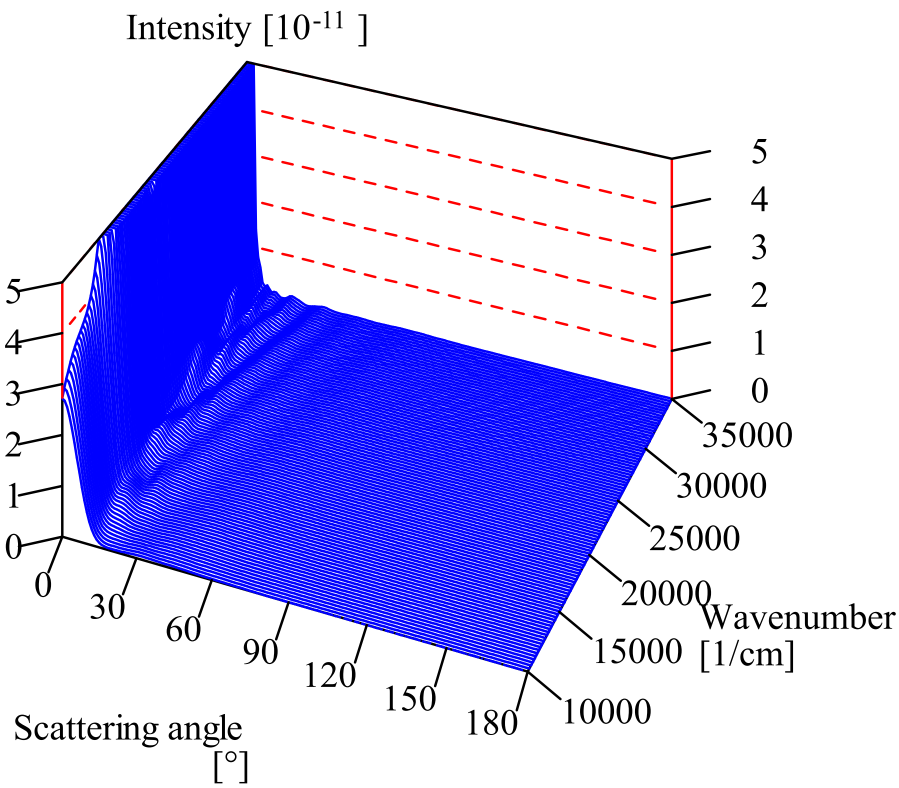
The simple paper model discussed above is based on spherical voids embedded in a homogeneous host material. The optical constants of the host material have been shown above. Two different size distributions of the spherical voids are considered. The first one is centered around 1 µm radius:



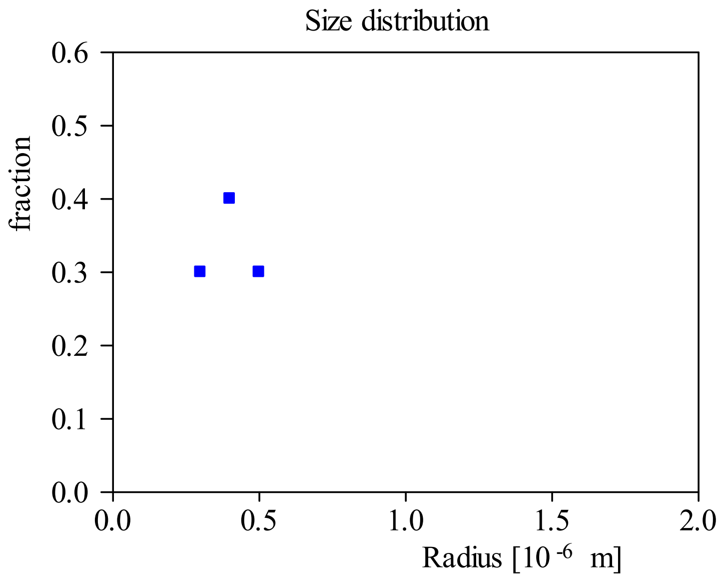
The voids do not absorb, of course, and have a more or less constant scattering coefficient, given by the red curve in the graph below for a volume fraction of 0.3:



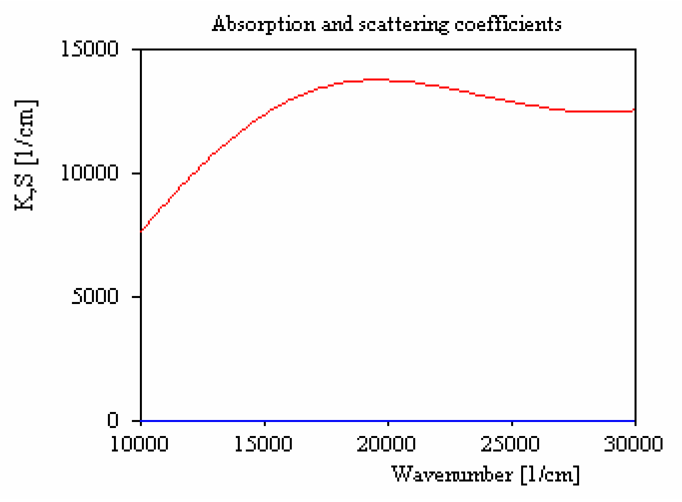
The angle dependence of the average scattering event is - due to the quite large size of the voids - forward oriented:



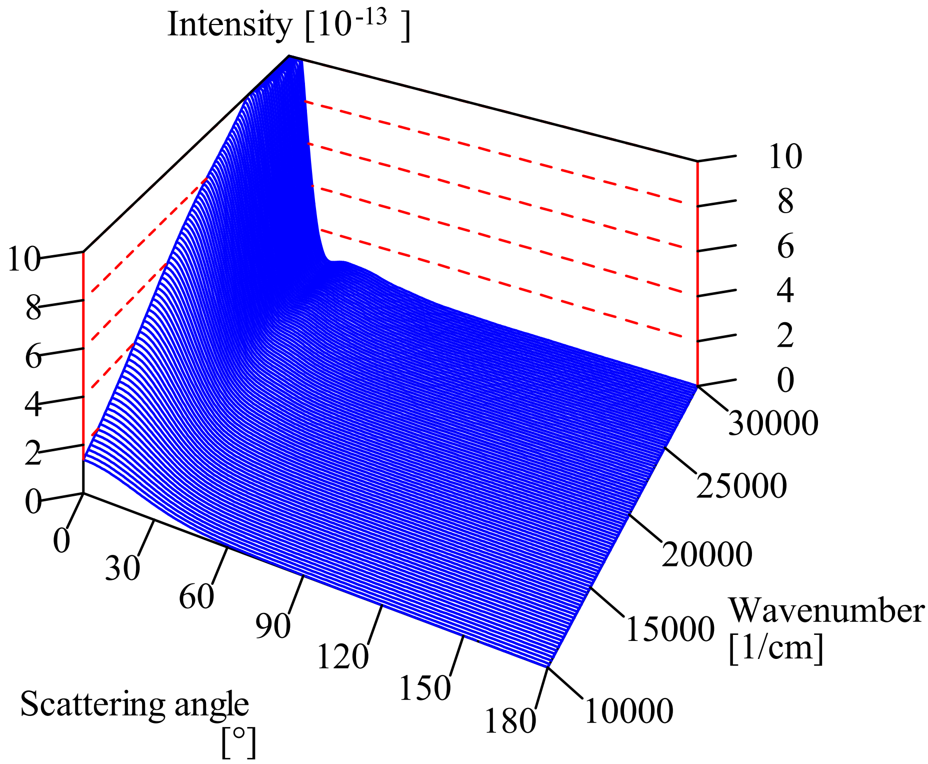
Reducing the size of the spherical inclusions to this distribution



leads to larger scattering coefficients (for the same volume fraction)



and a broader angle distribution of the single scattering event:



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