[correction] Exercice 7.1: Reflectance properties of different crystal sizes

1) For weakly absorbing media, like copper sulfate or a glass marble, the depth of light penetration and therefore the absorbance depends on the particle size: Smaller particles will scatter more and cause a smaller depth of light penetration. The diffuse reflectance is higher than for larger particles. At the same time, specular reflectance is low in the case of weakly absorbing media. In fact, the specular component of reflectance can even be neglected for weakly absorbing particles of sizes < 100 µm. This explains why these systems look colored in big pieces (copper sulfate is blue in big crystals) and appear substantially white in a finely powdered form.

2) For a highly absorbing medium, as stated by Fresnel's equations, specular reflectance is very important. Furthermore, the depth of light penetration is so small for strong absorbers that diffuse reflectance becomes almost independent of the particle size (for particles in the micrometer range – for nanoparticles the size could matter). A decrease in particle size will significantly lower specular reflectance, while having little effect on diffuse reflectance, therefore the material will appear more colored. As a result, the net effect of grinding potassium permanganate is just the opposite as grinding copper sulfate: it becomes more colored for smaller particle sizes. On analyzing potassium permanganate behavior at two particle sizes, it is important to realize that for the spectral region of low absorption (< 450 nm) it behaves like copper sulfate.

[correction] Exercice 7.2: Kubelka-Munk function

We assume that the grinded glass is homogeneously dispersed in the matrix. Therefore, we can apply the following Kubelka-Munk function to fit the curve:

$$F(R_\infty) = \frac{k_s}{s} = \frac{\ln 10 \cdot \varepsilon \cdot c}{s}$$

So, the slope is given by

$$M = \frac{\varepsilon \cdot \ln 10}{s}$$

Here from Figure 3, $M \simeq 8{,}5 \cdot 10^3$, one finds a molar decadic extinction coefficient of $\varepsilon = 370\ \mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$.

[correction] Exercise 7.3: Ellipsometry

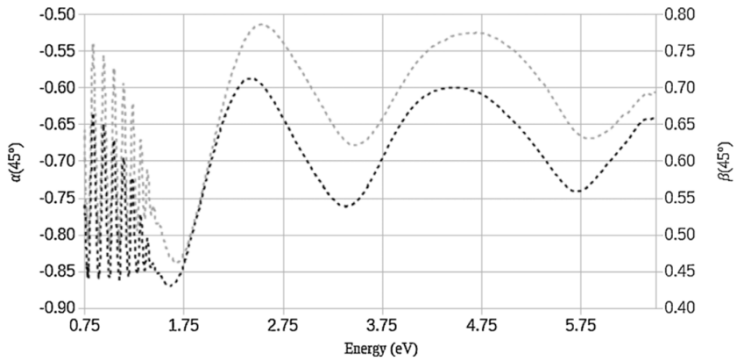
Quick reminder on ellipsometry: the polarization state of light is changed with reflection on an interface, because transverse electric (s) and transverse magnetic (p) contributions of the incident light will experience a phase change for complex optical constants. The way how the polarization state changes is directly related to the properties of the material. This is how, by probing the output polarization state, one can characterize some material properties. Spectroscopic ellipsometry is used for many different absorbing film/substrate applications.

1. If absorption of the sample is weak, the specular reflection might not be intense enough for detection or analysis.

2. The sample should not be too rough: roughness can scramble the polarization of light, by randomizing the polarization output (depolarization). This depolarization effect would be stronger if the structure size is > 0.1 λ. Note that ellipsometry can be used to measure the roughness of a sample.

3. For investigating the intrinsic properties of a material, the sample should preferably not be composed of multiple layers, because the reflected light's polarization state is more complex to model. But it is still possible, if an appropriate optical model is used for data fitting. Note that the layers thicknesses and the order of each layer need to be known for such a model. Besides, multiple-angle incidence is generally used for more complex multilayers, to ensure that the used model is unique. If the sample can be fabricated in a layer-by-layer process, a very good way of establishing a robust model is to analyze the ellipsometric data after each added stack, starting from the bare substrate.

4. In principle, the ellipsometry measurement provide the two parameters Ψ and Δ which allow to mathematically solve for two unknowns. So, if either *n* or *k* are known, the thickness can be determined by ellipsometry. The most common case is a very weakly absorbing film (*k*=0), where it is possible to deduce *n* and the thickness d. The thickness can be extracted from the interference fringes due to the multiple reflections occurring at the sample's interfaces. The graph here below shows an example interference fringes in the range from ~0.75 to ~1.75 eV:



Determining the thickness is straightforward for large enough thicknesses (allowing for clear interference fringes) but becomes tricky for very thin layers (a few nm). This also implies that it will be more difficult to determine the thickness for very absorbing materials, where the light penetration depth is short. In that case, one may use the fact that interference fringes shift to longer wavelengths with increasing wavelength and build a calibration curve using samples of known thicknesses.

Note: Standard measurements of thickness and refractive index only require a single angle of incidence. As the sample complexity increases, there is more need for multiple angles of incidence. It is recommended to take 2 or 3 angles of incidence for very thick films (> 1 micron), anisotropic materials, and complex multilayers.