Size determination via dynamic light scattering

Theory:

Light scattering
Colloidal particles when immersed in a fluid are able to scatter a beam of light (the Tyndall effect). The scattering pattern (i.e. the intensity of the scattered light as a function of $\theta$, the angle between the incident beam and the scattered beam) depends very strongly on the particle size and on the wavelength of the light. The spectral colours that are sometimes generated have fascinated investigators since before the end of the nineteenth century. It is only very recently, that the full potentialities of the study of light scattering have been realized, with the introduction of lasers to give coherent, monochromatic, intense and narrow incident beams, together with sensitive and stable photon-detection apparatus and rapid data analysis by computer.

Dynamic light scattering
This procedure depends on the fact that, if the scattering particle is moving when the light photon hits it then the re-radiated light will have a slightly different frequency when viewed by a stationary observer. This is why it is called quasi-elastic or dynamic light scattering. The frequency is slightly increased or decreased depending on whether the particle is moving towards or away from the observer. This is called Doppler broadening and if it can be measured accurately it provides a means of determining the diffusion coefficient of the particle.

The ZetaSizer can measure the size of particles with diameters from 3 to 1000 nm, using the method of photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS). Particles in this size range are called colloids. One of their characteristics is that they are in constant random thermal, or Brownian motion. This motion causes the intensity of light scattered from the particles to vary with time. Large particles move more slowly than small ones, so that the rate of fluctuation of the light scattered from them is also slower. Photon correlation spectroscopy uses the rate of change of these light fluctuations to determine the size distribution of the particles scattering light.

The movement of particles in suspensions can be characterised by a diffusion coefficient. This is a statistical quantity and quantifies how far from some arbitrary initial position the particle might be expected to be after a certain time. The diffusion
process is actually quantified by the first-order autocorrelation function which predicts the degree of correlation in the signal as a function of $\tau$ the correlation time.

$$g_2(\tau) = e^{-\tau/T} \quad (1)$$

For a monosized particle the translational diffusion coefficient can be related to particle diameter using Stokes’ diffusion law and the Einstein equation for Brownian motion [1].

$$D = kT/6\pi\eta R_h \quad (2)$$

t – absolute temperature, $k$ – Boltzmann’s constant, $\eta$ - solvent Viscosity, $R_h$ – hydrodynamic radius

**Static light scattering**

For particles much smaller than the wavelength of light (usually we take size < $\lambda/20$ at this criterion) a theory originally developed by Rayleigh is simple and applicable. In this model the main point is that the particle being so much smaller than the wavelength. All regions within the particle are subject to a similar electric field, so that the scattered waves produced by dipole oscillations of the electrons bound within the particle are in phase. The dipoles induced are also parallel with the plane of polarisation of the light, so if the scattered light is viewed in plane at right angles to this plane of polarisation, the scattered light will have no angular distribution, as it is simply the summation of all contributions from the individual dipoles adding constructively.
Consider light of wavelength $\lambda$ (in the medium), of intensity $I_0$ propagating in a medium of refractive index $n_0$, which encounters a particle of radius $R$ and refractive index $n_1$, the relative refractive indexes are then $n=n_1/n_0$. A detector some distance $r$ away from the scatterer, in the scattering plane will then receive an intensity $I$.

Rayleigh showed that:

$$I = I_0 \frac{\pi^4 R^6 ((n^2-1)/(n^2+2))^2 ((r^2 \lambda^4))}{r^2 \lambda^4}$$  \hspace{1cm} (3)

The reduced intensity of the scattered light, $R(\theta)$ at any angle $\theta$ to the incident beam of wavelength $\lambda$ can be related to the molar mass $M$, its concentration $c$, and the refractive increment $(dn/dc)$.

$$R(\theta) = \left[\frac{2\pi^2}{N_a \lambda^4}\right] \cdot (dn/dc)^2 \cdot (1+\cos^2 \theta) M c$$ \hspace{1cm} (4)

This equation applies when nonpolarized laser light is used, and the angular dependence is only due to the dipole characteristic in this case. That means, that no information about particle shape can be obtained from measuring the angular dependence $R(\theta)$ of the scattered light when the particles are small.

Debye used similar arguments in the '40s to describe the scattering of light from particles in solution based on the concentration, size, and shape of the polymer as well as the polymer-solvent interaction.

$$K c/R(\theta) = 1/M_w P(\theta) + 2 A_2 c + 3 A_3 c^2$$ \hspace{1cm} (5)

Here $A_i$ is the osmotic Virial Coefficient and $P(\theta)$ is the scattering function.

The argument centers around the fact that when a solute is dissolved in a liquid, scattering from a volume element arises from liquid inhomogenities, but now an additional contribution from fluctuations in the solvent are present. For polymer solution is to isolate and measure these additional effects [2].

References:

Experimental part:

**Chemicals:** 0.001 % polystyrene latex 1 (aqueous dispersion), 0.001 % polystyrene latex 2 (aqueous dispersion), colloidal gold dispersion, 0.01% aqueous dispersion of kaolin, 0.001% aqueous dispersion of TiO$_2$, 2 M NaCl-solution

Refractive indices: polystyrene, gold: 1.59
Kaolin: 1.55
TiO$_2$: 2.7

**Procedure:**
1) Measure the size of the aqueous latex dispersions 1 and 2.
2) Measure the size of the kaolin dispersion.
3) Measure the size of the TiO$_2$ – dispersion.
4) Measure the size of 1.5 ml colloidal gold dispersion.

**Topic 1-4:** All the measurements have to be done 5 times!

5) Measure the size of 1.5 ml colloidal gold dispersion (from topic 4) after adding 80 µl of a 2 M NaCl-solution.

**The measurements have to be done 5 times.**

**Discussion:**
1) The polystyrene latex was made by radical emulsion polymerisation by using potassium peroxidisulfate (KPS) as initiator and sodium dodecylsulfate (SDS) as surfactant.
   a) Explain how particle formation and particle growth take place in emulsion polymerisation!
   b) Discuss the particle size and particle size distribution with regard to the following recipes!

<table>
<thead>
<tr>
<th>KPS (in g)</th>
<th>SDS (in g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex 1</td>
<td>0.1</td>
</tr>
<tr>
<td>Latex 2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

2) and 3) Discuss the size and size distribution of the anorganic dispersions of kaolin and TiO$_2$ with regard to the particle morphology!

4) and 5) Discuss the differences in the size and size distribution of the two gold dispersions, give reasons! Explain the time dependence of the particle size in experiment 5)

(The colloidal gold was made from AuHCl$_4$·3H$_2$O in a reduction reaction by using Na-citrate.)