

## Sizing colloidal particles from their contribution to the effective refractive index: Experimental results

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**Abstract.** In this work we assess experimentally a new methodology for sizing non-absorbing colloidal particles *in situ*. It requires measuring the real and imaginary part of the effective refractive index per unit volume fraction occupied by the particles. The mean size and refractive index of the particles are determined from a suitable model for the effective refractive index of dilute colloids. We present results of experiments made with polystyrene and silica nano-particles and compare them with dynamic light scattering and electron microscopy measurements.

### 1. Introduction

In many industries as well as in many research laboratories it is critical to measure accurately the size of small dielectric particles in suspension. Size particle determination has been an interesting area for researchers where different techniques have been already proposed and commercially developed. Characterizing many types of particles is of great interest today. Ranging from biological particles in medical and pharmaceutical industries, to pigments in the form of inorganic particles used in the ink and paint industries; among many others that one can easily foresee. There are many techniques to size small particles, many of them developed since many years ago. In some cases it is possible to adsorb some of the particles on a flat surface, draw them outside the matrix, and prepare them for inspection under an electronic microscope. Actually this is done very often by research groups synthesizing nano-particles for different applications. This method, however, is expensive and time consuming, and it is not applicable to many types of particles because they change their composition and size when drawn out of the matrix where they were synthesized. Furthermore, the adsorbed particles tend to modify some of their properties over time, and therefore the output measurements would not necessarily match these values for suspended particles. There are several techniques used to infer the size of colloidal particles *in situ*; most are based on optical measurements. Optical techniques dedicated to measure accurately the size of small colloidal particles fall within the three following types: Spectroturbidimetry (ST) [1], Static Light Scattering (SLS) and Dynamic Light Scattering (DLS) [2].

In ST techniques a spectrum of the extinction coefficient is measured, and from it, the particle size distribution is obtained. In SLS techniques, features from the scattering pattern of isolated particles (highly dilute limit) are measured and the particle size is inferred from the angular scattering pattern. In DLS techniques one measures the time autocorrelation function of the scattered intensity and infers the average displacement of the particles in the colloid due to Brownian motion. From this displacement and using the theory for Brownian motion of colloidal particles, one infers the hydrodynamic radius of the particles which in many cases is very close to the actual radius of the particles. ST and SLS are limited to medium sized particles which exhibit clear features in their angular scattering pattern as well as in the extinction spectrum. SLS and DLS techniques are limited to very low densities (well below 1% in volume fraction) to avoid, in the first case, multiple scattering of light among particles, and hydrodynamic interactions between particles, in the latter case. ST and SLS require *a priori* knowledge of their refractive index. If particles are sufficiently large, the inversion of the particle size is a well-conditioned inverse problem. However, as the particles size gets smaller the problem becomes very sensitive to experimental errors and uncertainty in the refractive index [3]. In many cases the refractive index of the particles is not known with certainty or simply not known, often resulting in important errors. For instance, if the particles were formed through a chemical reaction, the exact chemical composition may not be well known, or the particles may be porous to some degree. Therefore, when using ST or SLS the refractive index of the particles can only be guessed. Also, when particles are very small, their refractive index may differ from that of larger particles made of the same material due to an increase of surface area relative to the particles' volume [4].

Among ST, SLS and DLS, the latter has proved more effective for routine characterization of colloidal particles. Most of the commercial instruments for particles sizing are based on this technique. Possibly the relative insensitivity of DLS to the particles' refractive index and because it can handle smaller particles are the main reasons why DLS is preferred. The main disadvantage is that the sample should be highly diluted and, thus, it can not be used in many complex systems *in situ*.

We have already proposed a new methodology to size particles in suspension using the effective refractive index of a colloid per unit volume fraction occupied by the particles by measuring directly the angle of refraction and using adequate extensions of the Snell's law [5,6]. Although the method is also limited to dilute samples, in comparison with SLS and DLS the proposed method may handle much higher densities. Many important colloidal materials have a particle density within the range where the present method may be applicable. On the other hand it is not necessary to know *a priori* the refractive index of the particles because the present method also determines it. The determination of average size and refractive index by the present technique is a well-conditioned problem even for very small particles. However, at the moment, this method can only determine an average value of the particle size and not its size distribution. On the other hand, the technique requires measuring the particles volume fraction which is not a trivial measurement and may some times be the largest source of errors. This latter measurement can be made immediately after the optical measurements and it is done *in situ*. The purpose of the present work is to assess experimentally the feasibility of the proposed method in the case of non-absorbing particles.

## 2. Sizing colloidal particles from their contribution to the effective refractive index

Let us briefly summarize the theory behind the proposed method and consider the case of monodisperse colloids. This means that the colloidal particles have a narrow size distribution. Suppose we have a colloid of spherical particles or nearly spherical particles of radius  $a$ , all with the same real refractive index  $n_p$  dispersed in a transparent liquid of real refractive index  $n_m$ . Let us suppose that the volume fraction of the particles is not known and it is denoted by  $f$ . One may define an effective refractive index of the particle suspension as the effective refractive index,  $n_{eff}$ , seen by the "coherent wave" at a specific wavelength ( $\lambda$ ). The coherent wave is the wave of the average field (usually

considered as the “configurational” average). In addition to the coherent wave there is also a diffuse field. Recently, the correct theoretical foundations of this effective refractive index were understood (and published) by our research group, ending with the generalized confusion about the existence and correct use of such an effective refractive index. In particular, the effective refractive index of a colloid comes from a non-local effective medium. The non-locality of the effective electromagnetic response has important consequences. For instance, the coherent reflectance from a flat interface between a colloidal medium cannot be calculated in general using the well known Fresnel reflection coefficients with the effective refractive index. This means that, depending on the size and refractive index of the particles, the effective refractive index may not be measurable with common techniques relying on the measurement of the reflection coefficients (such as modern Abbe refractometers widely used in the industry) [1].

The effective refractive index of a dilute colloid is given by the so called van de Hulst formula [7],

$$n_{eff}(\omega) \approx n_m(\omega) \left[ 1 + i \frac{3}{2} \frac{f}{x_m^3} S(0) \right], \quad (1)$$

where  $x_m = k_m a$  is the size parameter in the matrix,  $k_m = n_m(2\pi/\lambda)$ ,  $\lambda$  is the wavelength in vacuum of the light and  $S(0)$  is the forward scattering amplitude of the particles (given by Mie theory for spherical particles) and is complex. Notice then that the effective refractive index is a complex number, regardless the dielectric properties of the particle. The real part is related to the refraction of the coherent wave and its phase delay, whereas the imaginary part is related to the attenuation of the coherent wave due to scattering and to absorption, as it travels through the colloid. This means that the effective refractive index of colloids has an imaginary part even in the absence of optical absorption. It is not difficult to show that the imaginary part of the effective refractive index is related to the so called extinction cross section of the particles,  $C_{ext}(\omega)$ . We actually have that,  $(4\pi/\lambda) \text{Im}[n_{eff}(\omega)] = \rho C_{ext}(\omega)$  where  $\rho$  is the number density of particles and  $C_{ext}(\omega)$  is the extinction cross section of an isolated particle (obtained from Mie theory for spherical particles).

In [8] a methodology to obtain the size and refractive index of non-absorbing colloidal particles with a narrow size distribution from measurements of the effective refractive index of the colloid was proposed and analyzed on theoretical grounds. Extension of the proposed methodology to highly absorbing particles (in a non-absorbing matrix) was also discussed in Ref. [8], but here we will consider only the simpler case of non-absorbing particles. This methodology requires measuring the volume concentration of the colloidal particles ( $f$ ), the real and the imaginary parts of the refractive index difference between the colloid ( $n_{eff}$ ) and the pure matrix liquid ( $n_m$ ). From  $\text{Re}(n_{eff} - n_m)/f$  and  $\text{Im}(n_{eff} - n_m)/f$  it is possible to retrieve the radius ( $a$ ) and refractive index of the particles ( $n_p$ ) uniquely as long as the particles are not too large.

The inversion problem remains well conditioned even for very small particles. The extinction coefficient,  $\rho C_{ext}(\omega)$ , and therefore, the imaginary part of the effective refractive index of a colloid, can be obtained from the attenuation of a collimated light beam through a known distance through the colloid, just as it is regularly done in spectro-turbidimetry techniques. The main problem is to measure the increment of the real part of the effective refractive index of a colloid due to the presence of the colloidal particles. As already said, differential refractometers are, in principle, an attractive possibility for measuring  $\text{Re}(n_{eff} - n_m)$ . However, we need first to understand the special requirements of these refractometers for their use with colloidal samples. Also, we have argued that the simplest and safest way of measuring the effective refractive index in turbid colloids, with some

precaution, is by refraction or by phase delay (interferometry). Being the former simpler while still offering a high sensitivity on refractive index increments, here we use a coherent refraction scheme to measure the real part of the effective refractive index increment,  $\text{Re}(n_{\text{eff}} - n_m)$ . The measurement of the volume fraction occupied by the particles is done with, possibly, a less developed methodology. Here we use a gravimetric volumetric method which may be used whenever there is no “excess volume” in the mixture of the matrix and the colloidal particles, that is, when the volume of the particles and matrix is additive.

As shown in Ref. [8] to retrieve the values of  $a$  and  $n_p$  from the measurements of  $\text{Re}(n_{\text{eff}} - n_m)/f$  and  $\text{Im}(n_{\text{eff}} - n_m)/f$  we can use a graphical method. We first plot theoretical curves of  $\text{Re}(n_{\text{eff}} - n_m)/f$  versus  $\text{Im}(n_{\text{eff}} - n_m)/f$  using Eq. (1) for increasing values of the particle radius and for different values of the particles refractive index. Then, the experimental point with coordinates  $(\text{Re}(n_{\text{eff}} - n_m)/f, \text{Im}(n_{\text{eff}} - n_m)/f)$  is localized on the theoretical curves finding the corresponding values for  $a$  and  $n_p$ .

### 3. Experimental

Our experimental arrangement is shown in Fig. 1. A laser beam is split in two. One of the resulting beams is sent through a rectangular cell, 1 mm thick, in order to perform differential measurements of the coherent extinction-per-unit-length coefficient and the other beam is sent through a prismatic cell to measure the refraction of the coherent light. From the first measurement we obtain the imaginary part of  $n_{\text{eff}}$  and from the second one we obtain the real part of  $n_{\text{eff}}$ . The prismatic cell was made of silicate glass slabs with an apex angle of  $\theta_p = 48.1^\circ \pm 0.1^\circ$ . This angle was chosen so that a laser beam incident normally to the entrance side of the cell, will exit the cell on the other side close to the critical angle defined by the refractive index of water and air ( $\theta_c = 48.69^\circ$ ). A CCD camera mounted in a linear micrometric stage is used to record the lateral displacement of the output beam due to refraction. A laser beam at the wavelength  $\lambda = 475$  nm is incident near the normal to the entrance side of the cell.

The measurements are made as follows: first the prism is filled with the liquid matrix so the beam refracts as it exits the prism and it is centred on the CCD camera and the image of the laser beam spot is recorded (dashed line in Fig. 1). Next the water is replaced by the colloid and the beam further refracts (solid line in Fig. 1) making that the laser’s spot beam shifts sideways a distance  $\Delta x$ . The distance that the laser’s spot moves is proportional to the distance to the plane of measurement and to the increment of the angle of refraction due to the presence of the particles.  $\Delta x$  is measured as the cumulative macro displacement of the stage and the micro displacement calculated by the pixel position shift of the image. Under these conditions the change in the real part of the effective refractive index is calculated as:

$$\text{Re}(n_{\text{eff}} - n_m) = n_m \cdot \tan \theta_s \cdot \Delta x, \tag{3}$$

where  $\theta_s$  is the output angle change of the beam refracted by the colloid in the prism (see Fig. 1).

Next, the extinction coefficient is measured simultaneously using the parallel-slabs cell in this case we use a Si-based photodetector. We obtain the extinction coefficient by measuring the ratio between the laser beam’s power transmitted through the matrix liquid ( $P_m$ ) and that transmitted through the colloid ( $P_p$ ). The imaginary part of the effective refractive index is calculated as:

$$\text{Im}(n_{\text{eff}} - n_m) = \frac{\lambda}{4\pi} \rho C_{\text{ext}} = \frac{\lambda}{4\pi d} \ln \left( \frac{P_p}{P_m} \right) \tag{4}$$

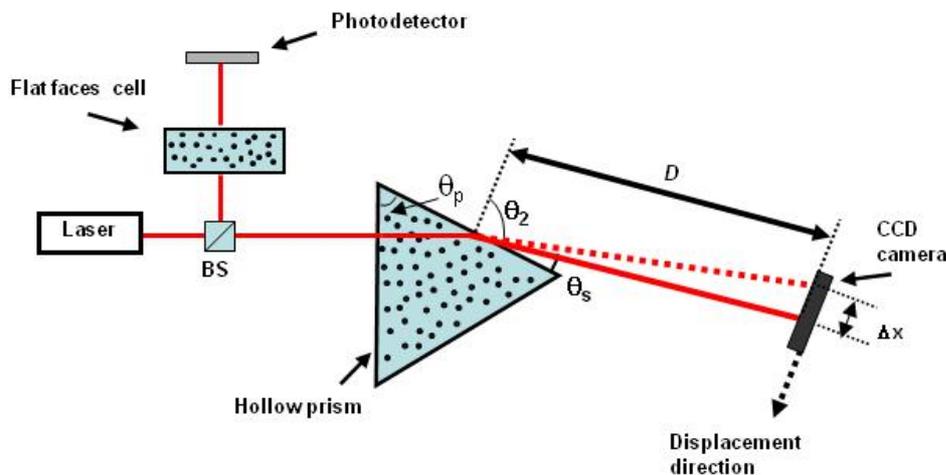


FIGURE 1. Experimental setup for refraction and extinction measurements.

Finally, the volume fraction of the particles in the colloid, is determined by a volumetric and weight analysis using a micro-balance with a resolution of  $10^{-4}$  g. Using a precision-graded syringe we put a drop of 50 $\mu$ l of the colloid on a microscope cover-slide and register its weight. The sample drop is kept on the balance and we let the liquid matrix (distilled water) evaporate and register the remaining particles' weight. Since we know the density of the liquid matrix, we can infer the volume of the liquid evaporated and calculate the volume occupied by the particles.

For validation purposes we applied our methodology to a colloid of polystyrene particles dispersed in distilled water from Duke Scientific Co. The particles have a commercially graded radius of 10.5 nm  $\pm$  1.5 nm. Results of our measurements are shown in Fig.3a) where the theoretical curves correspond to particles of refractive index from  $n_p=1.50$  to  $n_p=1.55$  at steps of 0.01. The three last solid symbols on each of the curves correspond to particles of radius  $a$  of 8, 10 and 12 nm, respectively, and the star symbol indicates three independent experimental values made for the same sample. As we can see from the plots we obtained consistently a radius  $a=10.5$  nm  $\pm$  0.25 nm which indicates that the developed methodology offers a good accuracy on sizing the particles. Note that, although we retrieve the correct particles radius, our estimated value of the refractive index is between  $n_p = 1.51$  and 1.54, which is less than the refractive index reported for the bulk of a macroscopic object of polystyrene of 1.59. We speculate that the difference may be due to surface effects due to the small size of the particles or to porosity of the particles.

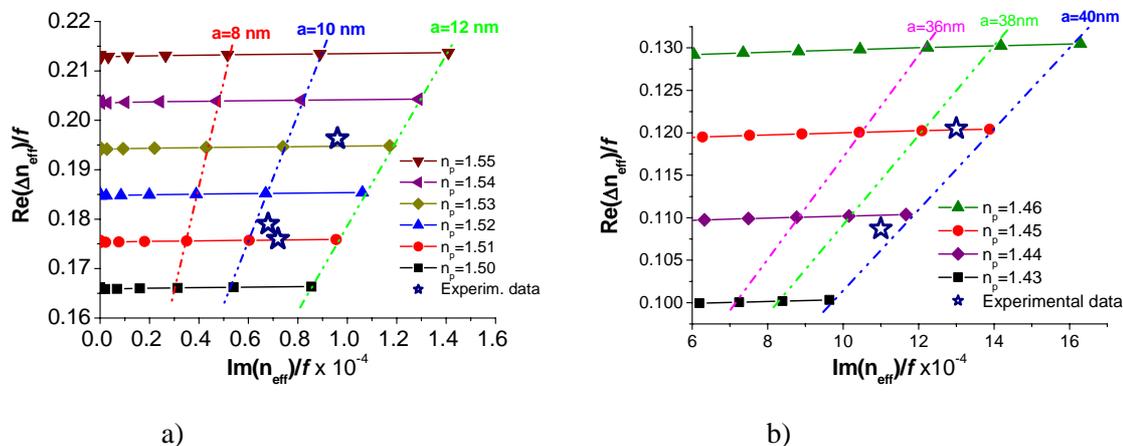
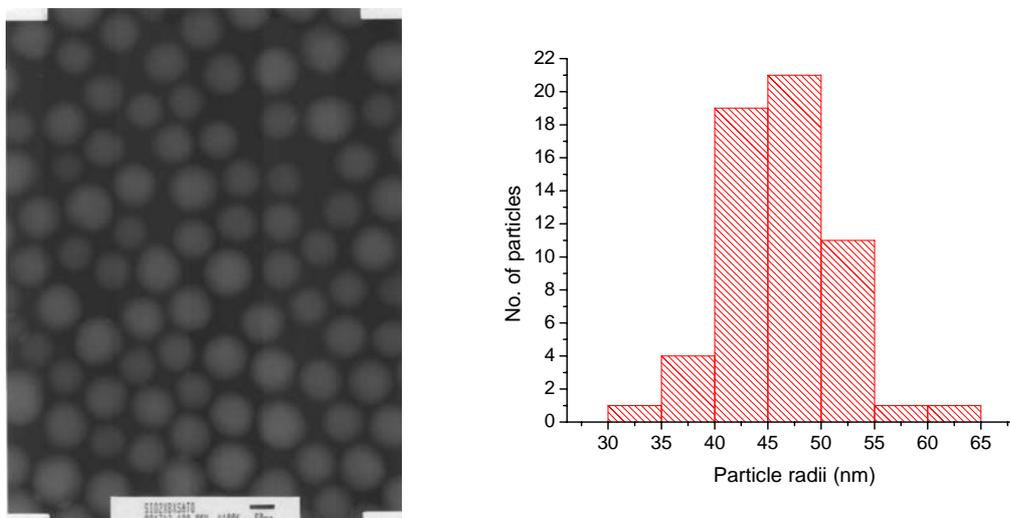


FIGURE 3. Theoretical curves and experimental data for  $\text{Re}(n_{\text{eff}} - n_m)/f$  versus  $\text{Im}(n_{\text{eff}} - n_m)/f$  for a) polystyrene particles immersed in distilled water and b)  $\text{SiO}_2$  particles immersed in distilled water of  $n_m = 1.33$  at the wavelength  $\lambda=475$  nm.

Next, we applied our methodology to a colloid of silica ( $\text{SiO}_2$ ) nano-particles immersed in distilled water. These particles were fabricated at our research center using the method proposed Stöber *et al* in 1968 [9]. In this method the synthesis of spherical silica nanoparticles is made from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as a catalyst. The size of the resulting particles depends on the type of silicon alkoxide and alcohol. In our case we made a solution of 50 ml of ethanol (99.99%, Aldrich), 3.0 ml of ammonium hydroxide solution (28%, Aldrich) and 1.5 ml of tetraethyl orthosilicate (TEOS) (99.99%, Aldrich), mixed and stirred for one hour at room temperature. We changed the initial ethanol matrix for distilled water by centrifuging the particles and rinsing with distilled water several time. We measured a volume fraction  $f = 2.2\%$ , and effective optical parameters:  $\text{Re}(n_{\text{eff}} - n_m)/f = 0.1205$  and  $\text{Im}(n_{\text{eff}} - n_m)/f = 0.0013$ , indicated by the star symbols in Fig. 3b. From the displayed theoretical curves in Fig. 3b we obtain a particle's radius of  $a = 38.5$  nm and a refractive index of the particles  $n_p = 1.45$ . We repeated the whole procedure and prepared a second sample in the exact same way as before. In this case we measured  $f = 2.4\%$  and the effective optical parameters,  $\text{Re}(n_{\text{eff}} - n_m)/f = 0.1087$  and  $\text{Im}(n_{\text{eff}} - n_m)/f = 0.0011$ . These values correspond to the lower star symbol in Fig. 3b. From these values we retrieve a radius of the particles  $a = 38.6$  nm and a refractive index  $n_p = 1.44$ . Here again, the refractive index  $n_p$  is less than that reported for the  $\text{SiO}_2$  material of macroscopic samples of 1.47, although the difference is smaller than for the polystyrene particles.

To compare our measurements of the radius of the  $\text{SiO}_2$  particles, we estimated their size by transmission electron microscopy (TEM) and using a commercial particle sizer (Z-Sizer by Malvern Instruments) which is based on DLS. A TEM microscopy image of the  $\text{SiO}_2$  particles is shown in Fig. 4a. The image was taken with particles drawn from the same sample of  $\text{SiO}_2$  particles prepared for the second sample and during the same day the effective parameters were measured. This image reveals that the sample actually had a wide size distribution plotted in Fig. 4b, ranging from 30 to 65 nm of radii. The retrieved value of 38.6 by our methodology lies within the diameter range between 70 to 80 nm which is somewhat smaller than the average value estimated from the TEM micrograph. Nevertheless, the TEM micrograph is for particles outside the matrix and their radius may be different than when they are within the matrix. Measurements with the Z-sizer give a mean radii of  $a = 57.8$  nm which is higher than the average radius obtained from the TEM image. However, this corresponds to the hydrodynamic radii.



**FIGURE 4.** Silica particles colloid a) TEM microscopy image and b) size distribution graph.

The three measurements done to compare the particle radii for SiO<sub>2</sub> particles done differ from each other by about 20% which could be due to the different conditions for measurements. Further work is needed to understand better these results as well as to diminishes the experimental uncertainties on measurements by our methodology. The largest uncertainty in our method was found in measuring the extinction coefficient and the volume filling fraction. In spite of this our methodology seems to have similar discrepancies comparing results obtained with TEM microscopy and Z-sizer which is currently used in many industries and research laboratories.

#### 4. Summary and Discussion

We assessed experimentally a new methodology to size non-absorbing colloidal particles *in situ* from the measurement of effective refractive index. The increment in effective refractive index can in fact be measured without much difficulty by coherent refraction using a prismatic cell and a well collimated laser beam. The imaginary part can be obtained as usual by coherent transmittance measurements at normal incidence on a rectangular cell. We performed experiments using commercial polystyrene particles and silica particles suspended in tridistilled water. The retrieved radius of the SiO<sub>2</sub> particles were compared with that obtained by TEM microscopy and a commercial DLS based Z-sizer system. The radius obtained by our methodology was 19% lower than the mean radius obtained by TEM and the radius obtained using the Z-sizer system is 20% higher than this last. Further developments in our methodology require an accurate way of measuring the volume fraction occupied by the particles as well as a more precise measurement of the extinction coefficient.

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