

# **Estimation of Complex Refractive Index of Polydisperse Particulate Systems from Multiple-Scattered UV-Vis-NIR Measurements**

**M. A. Velazco-Roa and S. N. Thennadil\***

School of Chemical Engineering and Advanced Materials

University of Newcastle upon Tyne,

Newcastle upon Tyne, NE1 7RU, United Kingdom

A method to extract the complex refractive index of spherical particles from a polydisperse suspension at concentrations where multiple light scattering effects are significant, is presented. The optical constants are estimated from total diffuse reflectance and transmittance measurements and inverting the measurements using the Radiative Transfer Equation (RTE) and the Mie theory for scattering by polydisperse spherical particles. The method is tested by applying it to three different polydisperse polystyrene suspensions and extracting the optical constants of polystyrene particles in the wavelength range of 450 – 1200nm. The effect of particle size, concentration and polydispersity on the estimated values of the optical constants is also discussed.

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## 1. Introduction

Characterisation of colloidal systems using spectroscopic techniques has been a topic of great interest in recent years. This is due to the fact that characteristics of particulate systems such as particle size and size distribution, volume fraction and chemical composition are extensively used to monitor processes and quality of suspensions, slurries and dispersions [1]. Apart from volume fraction and particle size, the optical constants ( $m=n(\lambda)+ik(\lambda)$ ) may provide significant information to aid in controlling processes for the production of particulate systems. Further, in order to estimate particle size and size distribution using methods based on light scattering theories, accurate values of the optical constants are required [2].

Ma *et al* [3] used Monte Carlo simulations in combination with Mie theory and experimental measurements of diffuse reflectance and transmittance to determine the complex refractive index of polystyrene microspheres. They reported values for the range 370 – 1600 nm as an average over the values estimated for fairly low concentration of 0.07405%, 0.1278% and 0.2919% by weigh of solids using monodisperse suspensions of 966 nm diameter. In many practical situations, it is necessary to deal with higher concentrations and polydisperse/multimodal systems. In addition, the sensitivity of estimated  $n(\lambda)$  and  $k(\lambda)$  to particle size, size distribution and concentration is not known and need to be examined.

This paper presents a general method for the estimation of optical constants in the UV-Vis-NIR region, for a polydisperse (broad and/or multimodal) suspension at concentrations where multiple scattering effects are appreciable. The optical constants  $n(\lambda)$  and  $k(\lambda)$  were obtained by an inversion technique using the adding-doubling method to solve the Radiative Transfer Equation (RTE) [4] in combination with the Mie theory to describe light scattering by a single particle [5] and measurements of total diffuse reflectance and transmittance using a single integrating sphere setup. This method is first applied to

monodisperse suspensions of polystyrene latex particles under the assumption that particle interactions are negligible. In principle, if the method (which assumes that inter-particle interactions are negligible) is exact, the values of the extracted optical constants will be independent of the particle size and concentration of the samples. The optical constants are extracted using samples with different particle sizes and concentrations to investigate whether they are indeed independent of these parameters. The method is then extended to polydisperse dispersions of polystyrene particles and the results compared with the values obtained using monodisperse suspensions.

The method of extracting the optical constants from the diffuse reflectance and transmittance is described in the next section.

## 2. Method for extraction of optical constants

The inversion method compares values of total diffuse reflectance,  $R_{tdm}$ , and transmittance,  $T_{tdm}$ , measured using a single integrating sphere method against the values of simulated total diffuse reflectance,  $R_{tds}$ , and transmittance,  $T_{tds}$ , calculated using the RTE to model multiple scattering in turbid media [6, 7]. The RTE is given by:

$$\frac{dI(r, \hat{s})}{ds} = -\mu_t I(r, \hat{s}) + \frac{\mu_s}{4\pi} \int_{4\pi} p(s, \hat{s}) I(r, \hat{s}) d\omega \quad (1)$$

where  $I(r, \hat{s})$  is the specific intensity at a point  $r$  with radiation along the direction  $\hat{s}$ ,  $\mu_t (= \mu_s + \mu_a)$  is the bulk extinction coefficient,  $\mu_s$  is the bulk scattering coefficient and  $\mu_a$  is the bulk absorption coefficient.  $p(s, \hat{s})$  is the phase function which is a measure of the angular distribution of the scattered light.

The bulk scattering and absorption coefficients are functions of the particle concentration and the scattering and absorption cross-sections of the species at wavelength  $\lambda$  of the incident beam, and are written as:

$$\begin{aligned} \mu_a(\lambda) &= \mu_{a,p}(\lambda) + \mu_{a,w}(\lambda); \mu_{a,p}(\lambda) = c\tilde{\sigma}_a(\lambda); \mu_{a,w}(\lambda) = \frac{4\pi k_w(\lambda)(1-c)}{\lambda} \\ \text{and } \mu_s(\lambda) &= \rho\tilde{\sigma}_s(\lambda) \end{aligned} \quad (2)$$

where  $c$  is the particle volume fraction,  $\tilde{\sigma}_a$  is the absorption cross-section of the particles, and  $k_w$  is the imaginary part of the complex refractive index of water. The optical constants for water were taken from values reported by Hale and Querry [8].  $\tilde{\sigma}_s$  is the scattering cross-section. The scattering cross-section for a polydisperse suspension is given by:

$$\tilde{\sigma}_s(\lambda) = \int_0^\infty \int_0^{2\pi} \int_0^\pi \rho(D) F(\theta, \phi, D, m, \lambda) S(\theta, V_T, \lambda) \sin \theta \cdot d\theta \cdot d\phi \cdot dD \quad (3)$$

where the differential cross-section  $F$  is function of diameter  $D$ , the relative complex refractive index  $m$ , which is the ratio of the particle refractive index and the refractive index of the medium (in this case water),  $\theta$  is the scattered angle and  $\phi$  is the azimuth angle. The differential cross-section is computed using Mie theory [5]. The static structure factor  $S$ , is a function of the inter-particle interaction energy  $V_T$  and represents the microstructure of the suspension. For suspensions where inter-particle interactions are negligible, the value of  $S$  is set to 1. In this study, it is assumed that the inter-particle interactions are negligible since moderately low concentrations are used. The number density of particles with diameter  $\rho(D)$  is given by:

$$\rho(D) = \frac{6}{\pi} \int_0^\infty \frac{\rho_{\text{medium}}}{D^3 \left[ \rho_{\text{medium}} + \frac{\rho_{\text{particles}}}{c} - \rho_{\text{particles}} \right]} f(D) dD \quad (4)$$

where  $\rho_{\text{medium}}$  is the density of the medium which in this case is de-ionised water at room temperature (= 1g/ml) and  $\rho_{\text{particles}}$  is the density of the polystyrene particles (=1.05 g/ml - specified by the manufacturer).

The phase function  $p(s, \hat{s})$  is required to solve the RTE. The exact Mie phase function for spherical particles was used for this study. The Mie phase function for a polydisperse system of spherical particles is given by:

$$p(\cos \theta) = \int_0^{\infty} \frac{2}{x^2 \sigma_{\text{ext}}(D)} [ |S_1(\cos \theta)|^2 + |S_2(\cos \theta)|^2 ] dD \quad (5)$$

Given the coefficients  $\mu_s$ ,  $\mu_a$  and the phase function the RTE can be solved. The adding-doubling method (ADD), was used to solve the RTE for plane-parallel geometries [7,9]. Finally the Mie re-distribution phase function was implemented in the ADD as [4,10]:

$$p(s, \hat{s}) \approx \frac{1}{2} \int_0^{2\pi} p(\cos \theta) P_m(\cos \theta) \sin \theta \cdot d\theta \quad (6)$$

where  $P_m$  is an m-term series of Legendre polynomials.

This method is an accurate numerical technique for solving the RTE which accounts for multiple scattering, and takes into consideration anisotropic scattering and Fresnel boundary conditions for arbitrarily thick samples with relatively fast computations compared to the Monte Carlo method.

The optical constants were estimated by minimising the objective function given by the absolute deviation of the theoretical total diffuse reflectance and transmittance ( $R_{\text{tds}}$  and  $T_{\text{tds}}$ ) from the measured values ( $R_{\text{tdm}}$  and  $T_{\text{tdm}}$ ):

$$\Sigma = \text{abs}(R_{\text{tdm}} - R_{\text{tds}}) + \text{abs}(T_{\text{tdm}} - T_{\text{tds}}) \quad (7)$$

For a given set of optical constants, the theoretical values of total diffuse reflectance and transmittance are computed using (1)-(7). For this study, the optimisation was carried out using the function “fmincon” of the MATLAB<sup>®</sup> Optimisation toolbox.

### 3. Experiments

#### 3.1 Monodisperse Suspensions

Total diffuse reflectance,  $R_{tdm}$ , and transmittance,  $T_{tdm}$ , of monodisperse polystyrene suspensions were measured using an integrating sphere of diameter 150mm (DRA-2500, Varian Instruments) attached to a UV-Vis-NIR spectrophotometer (Cary 5000, Varian Instruments) in the wavelength region 450 - 1200 nm at 20 nm intervals. Polystyrene microspheres suspensions of 10% by weight of solids of narrow particle size distributions with coefficient of variance, CV, 3% of mean diameter of  $0.45\mu m$  and  $0.22\mu m$ , and with coefficient of variance, CV of 12% with mean diameter of  $0.14\mu m$  were purchased from Duke Scientific Co. The samples were prepared by diluting the original suspension with de-ionised water to 5%, 2.5%, 1.53%, 0.3%, 0.15% and 0.075% by weight of solids. The samples with concentration lower than 1.53% were placed in a special optical glass cuvette of 2mm path length, and 1mm path length cuvette was used for the samples with a concentration higher than 2.5%. The number density of these suspensions were calculated using the density of de-ionised water at room temperature,  $\rho_{medium} = 1g/ml$ , and the density of the polystyrene particles,  $\rho_{particles} = 1.05 g/ml$ .

#### 3.2 Polydisperse Suspensions

Total diffuse reflectance,  $R_{tdm}$ , and transmittance,  $T_{tdm}$ , of polydisperse polystyrene suspensions were measured the wavelength range 450 to 1200 nm at 20 nm interval using the same set-up as for monodisperse suspensions. The samples were placed in a special optical glass cuvette of 1mm for samples B and C, and 2mm pathlength for sample A (See Table 1). Polystyrene microspheres suspension of 10% by weight of solids of narrow particle size

distributions with coefficient of variance (CV), 3% (specified by manufacturer) of mean diameter of 220 nm, 450 nm, 490 nm, 500 nm and 510 nm were purchased from Duke Scientific Co. Two different multimodal polydisperse samples were prepared by diluting the original suspensions with de-ionised water and mixing them in the proportion 1:1:1 by weight. In addition to these two samples, an “unmixed” sample A was used which had a narrow size distribution as a baseline to evaluate the effect polydispersity could have on the extracted optical constants. Table 1 shows the characteristics of the samples and concentrations used. The samples were prepared and measured three times to estimate the error due to concentration. Figure 1 shows the size distribution of samples A, B and C generated and used for the estimation of the optical constants.

#### **4. Results and Discussions**

The optical constants  $n(\lambda)$  and  $k(\lambda)$  determined by the integrating sphere method using the rigorous Mie theory and Mie phase function for monodisperse and polydisperse suspensions are presented. The values of  $n(\lambda)$  calculated were compared with values published by Nikolov and Ivanov [11] for polystyrene determined by refractometry measurement for eleven different wavelengths in the wavelength range 442 and 1060 nm. In addition, the results are compared with those of Ma et al [3]. The mean values of  $n(\lambda)$  and  $k(\lambda)$  were determined by averaging  $n(\lambda)$  and  $k(\lambda)$  values from triplicates of the same concentrations and particle size distribution, and triplicates of measurements of reflectance and transmittance for every sample with the error bars indicating two times the standard deviation.

## 4.1 Monodisperse Suspensions

Figure 2(a) and 2(b) present the variation of  $n(\lambda)$  and  $k(\lambda)$  estimated for three different particle sizes  $0.45\mu m$ ,  $0.22\mu m$ , and  $0.14\mu m$ , at the same concentration 0.3% (weight of solids). From figure 2(a) it is observed that the values of  $n(\lambda)$  are overestimated in comparison with the values published by Ivanov and Nikolov [11] and Ma et al [3]. Given the different instrumentation, experimental and computational technique used this difference (<2% over the wavelengths considered) is small and it can be concluded that there is good agreement with the published data. The curve of  $n(\lambda)$  values of the samples with particle sizes  $0.45\mu m$  and  $0.22\mu m$  have a similar tendency in the entire region of the spectra considered. However the sample with mean diameter  $0.14\mu m$  has an anomalous behaviour around the wavelength of 800 nm. For this sample, the transmittance was lower than the other two samples around this wavelength resulting in a much noisier measurement. It is believed that this higher noise in the transmittance measurements leads to the problems in convergence of the optimisation in the estimated refractive index. There is a small but significant increase in the estimated  $n(\lambda)$  with increase in particle size over the wavelength range considered. However, this systematic variation is sufficiently small to be negligible from a practical standpoint.

Figure 2(b) shows the  $k(\lambda)$  values extracted from these samples. It is seen that there is good agreement with the values published by Ma et al [3]. Unlike  $n(\lambda)$ , there is no discernible systematic variation with particle size.

Next, the effect of concentration on the estimated optical constants were studied. Figure 3(a) and (b) present the values of  $n(\lambda)$  and  $k(\lambda)$  determined for suspensions of particles with mean diameter of  $0.45\mu m$  with concentrations (weight fraction of particles  $c$ ): 0.1, 0.05, 0.025, 0.015, 0.003, 0.0015 and 0.0075. From Figure 3(a), it is seen that the



estimated  $n(\lambda)$  shows a strong dependence on concentration above a weight fraction of about 0.025. It appears that the dependence on the particle concentration is stronger at the lower wavelengths and the estimated  $n(\lambda)$  decreases with increasing concentration. The imaginary part of the complex refractive index,  $k(\lambda)$  is presented in the figure 3(b). The values show a clear concentration dependence over the wavelength range considered with  $k(\lambda)$  decreasing with increasing concentrations. The concentration dependence of  $n(\lambda)$  and  $k(\lambda)$  could be due to the effect of inter-particle interactions. According to the manufacturers, the latex suspension is stabilised using dispersants i.e. they are electro-sterically stabilised. This leads to a soft-sphere potential [12, 13]. The data presented here indicates that this potential becomes significant and cannot be neglected for particle concentrations of greater than about 1%. In such cases, the appropriate expression for the static structure factor [12] should be included in Eq. (3).

## ***4.2 Polydisperse Suspensions***

The effect of polydispersity was taken into account by including the information of the particle size distribution through  $f(D)$  in Eq. (4) and using Eq. (3) and (5). As explained previously 3 samples were used (see Table 1). Sample A has a narrow distribution (mean diameter  $0.14\mu m$  and CV 3%). In the previous section, such samples were considered to be monodisperse suspensions with a diameter equal to the mean diameter of the size distribution. In general, it is customary to assume the suspension is monodisperse when estimating the optical constants using suspensions with narrow size distributions. The effect of this assumption on  $n(\lambda)$  and  $k(\lambda)$  was studied. The impact of particle size distribution even when they are narrowly distributed was examined by including the size distribution information in the calculations. Figure 4(a) and (b) show the estimated optical constants when sample A is considered as monodisperse and when the size distribution is taken into account. There is a

significant difference in the estimated  $n(\lambda)$  with the values being closer to that reported by Ivanov and Nikolov [11] when the size distribution is included in the calculations. This suggests that the  $n(\lambda)$  is sensitive to size distribution even when the variance of the distribution is small though from a practical standpoint this effect appears to be small enough to be negligible. From figure 4(b), it is seen that  $k(\lambda)$  does not change significantly when the size distribution is taken into account.

The results for the multimodal polydisperse suspensions are presented in figures 5(a) and (b). The variation of the real part of the complex refractive index i.e.  $n(\lambda)$  for different particle size distributions of polystyrene is shown in the figure 5(a). From this figure it is observed that the  $n(\lambda)$  values estimated for both multimodal polydisperse samples B and C in the region 450 to 800 nm are in good agreement with theoretical values. In the region 800 to 1200 nm there is a small but systematic difference between  $n(\lambda)$  values estimated and the  $n(\lambda)$  values published, though the two samples with different distributions lead to estimations which are statistically indistinguishable as indicated by the error bars which represent two times the standard deviation about the mean value.

Figure 5(b) shows the  $k(\lambda)$  values for the sample A, B and C. The estimated values appear to be slightly influenced by the particle size distribution especially at the lower wavelengths.

## 5. Conclusions

A general method to extract the optical constants  $n(\lambda)$  and  $k(\lambda)$  of spherical particles from multiply scattering of monodisperse and polydisperse suspensions in the UV-Vis-NIR region of the spectrum was presented. The results were compared with published data and found to be in good agreement with them.

The effect of particle size and concentration on the estimated values of the optical constants were investigated. There was a small but significant increase in the estimated  $n(\lambda)$  with increase in particle size over the wavelength range considered. However, this systematic variation is sufficiently small to be negligible from a practical standpoint. Unlike  $n(\lambda)$ , there is no discernible systematic variation with particle size. The estimated  $n(\lambda)$  shows a strong dependence on concentration above a weight fraction of about 0.025. The estimated  $k(\lambda)$  show a clear concentration dependence over the wavelength range considered. This concentration dependence of  $n(\lambda)$  and  $k(\lambda)$  indicates that the effect of inter-particle interactions should be taken into account for electrosterically stabilised suspensions even at moderately low concentrations.

The inversion method using the exact Mie calculations is very computationally intensive and takes several hours for obtaining the desired convergence. As a result, the calculations were carried out only at 20 nm intervals. The computations could be speeded up significantly by using a simple phase function such as the Henyey-Greenstein function [4] if the error due to this approximation is sufficiently small. This will be investigated in the near future. The method presented could also be used to extend the approach proposed by Frontini and Fernandez [14] for simultaneously estimating the complex refractive index and the particle size distribution to systems where multiple scattering is significant.

## **6. Acknowledgements**

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Table 1. Characteristics of the polydisperse polystyrene samples.

<b>Sample</b>	<b>Mean Particle radius, (nm)</b>	<b>Standard deviation (nm)</b>	<b>Concentration (%) by weight of solids</b>
A	225	6.75	0.15
B	245:250:265	7.5: 7.55: 7.75	0.19
C	110:225:250	3.3: 6.75: 7.5	0.138

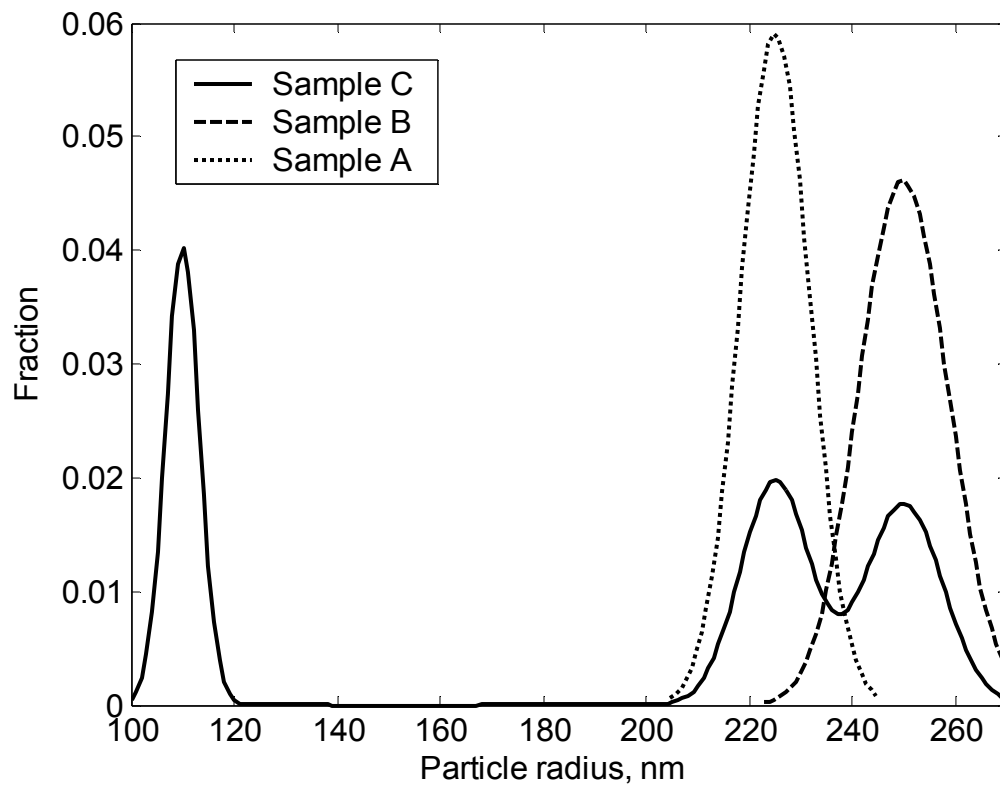


Figure 1. Particle size distribution of samples A, B and C.

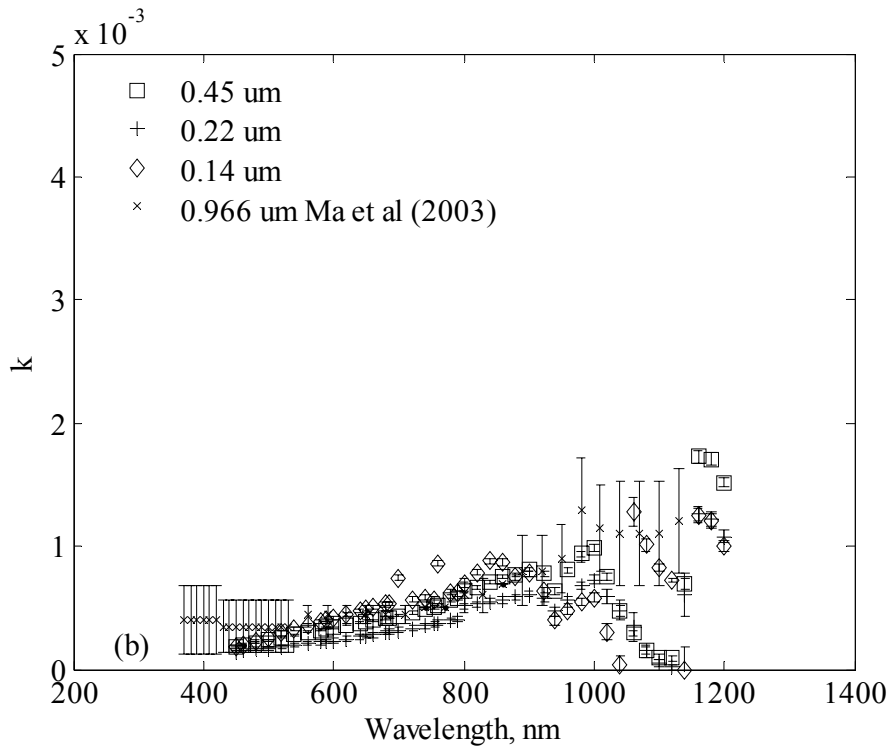
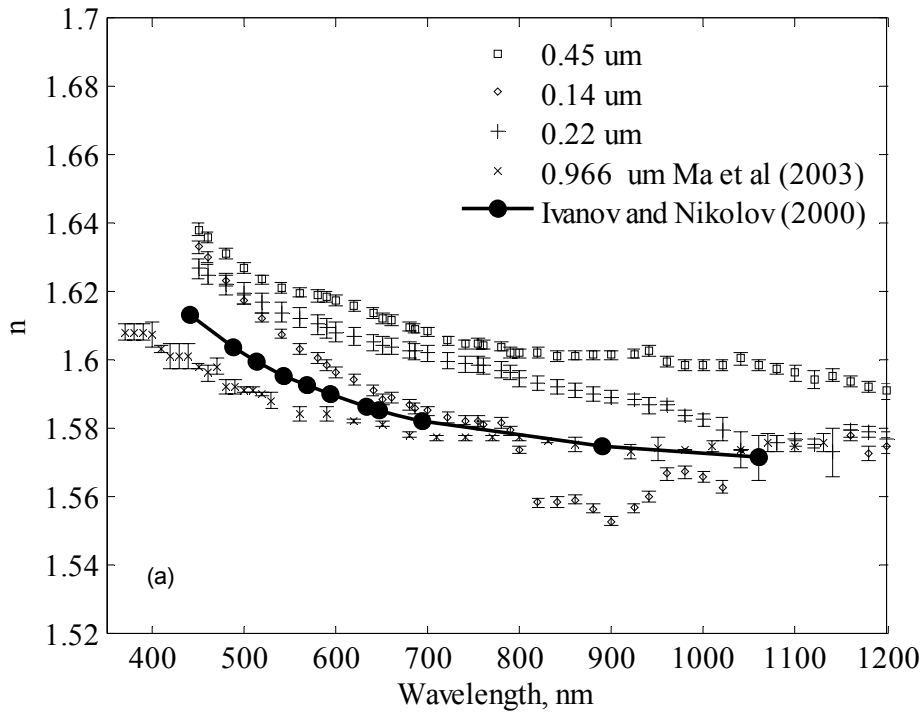


Figure 2. Complex refractive index,  $m=n(\lambda)+k(\lambda)i$ , obtained by the inverse method for monodisperse polystyrene microspheres in aqueous suspension of different particles sizes ( $0.45\mu m$ ,  $0.22\mu m$  and  $0.14\mu m$ ). (a) Real part of the complex refractive index,  $n(\lambda)$ . (b) Imaginary part of the complex refractive index,  $k(\lambda)$ .

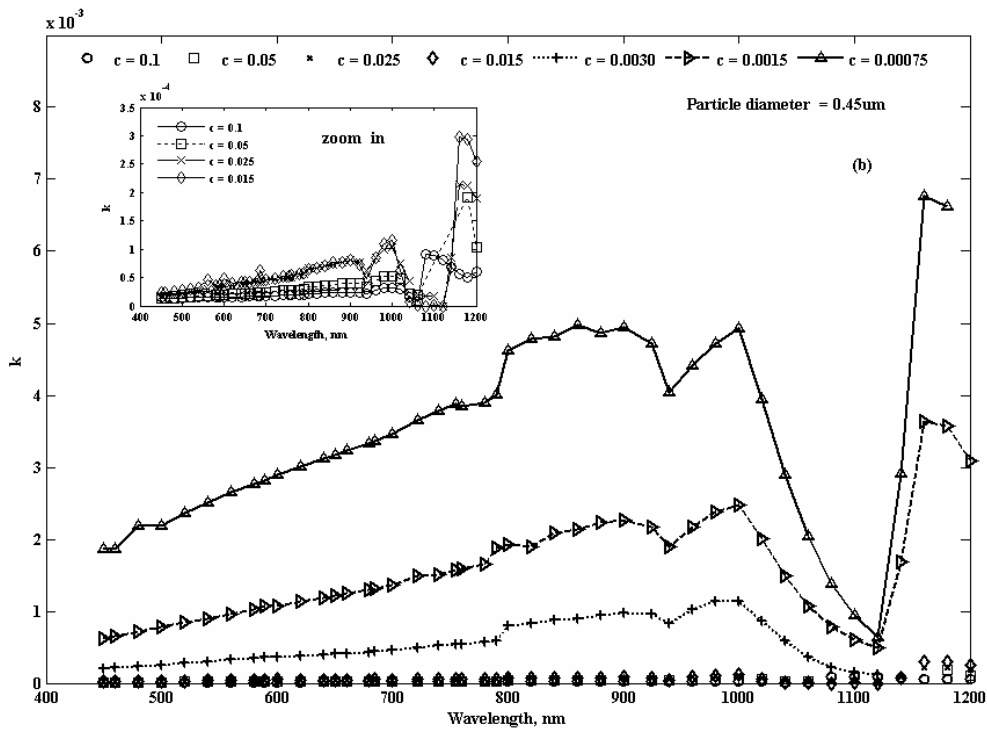
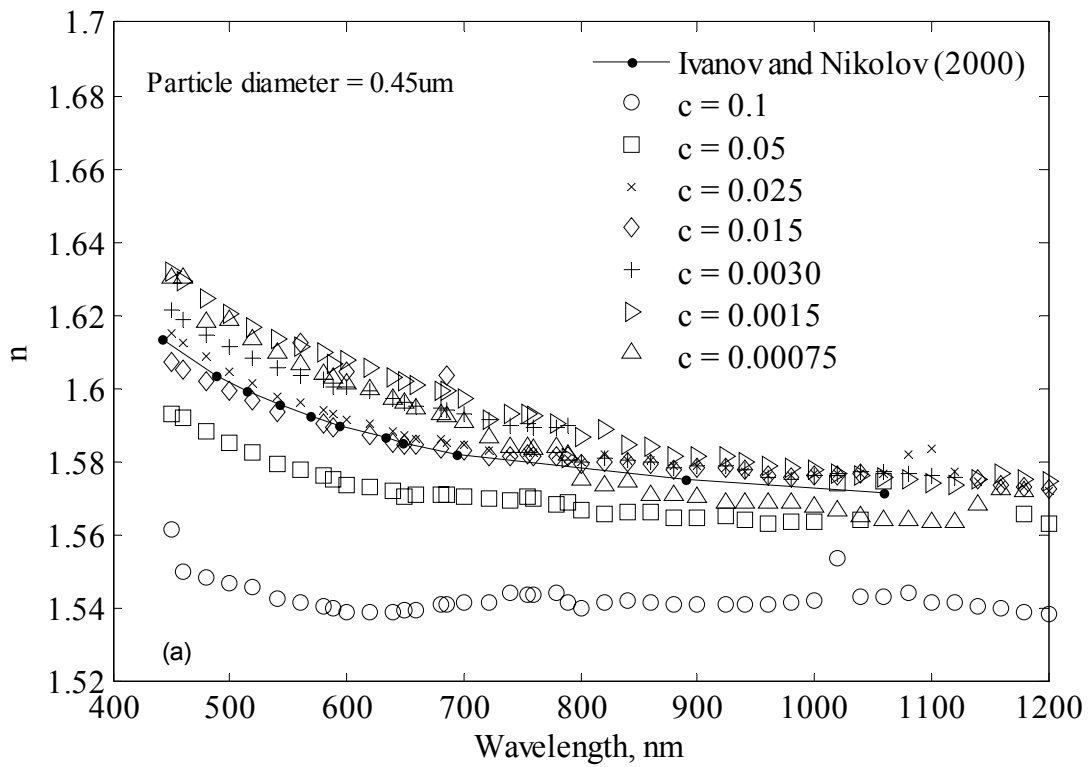


Figure 3. Complex refractive index for monodisperse polystyrene microspheres of  $0.45\mu\text{m}$  diameter of particle concentrations: 0.1, 0.5, 0.25, 0.15, 0.030, 0.0015, and 0.00075 weight fraction of solids. (a)  $n(\lambda)$  and (b)  $k(\lambda)$ .



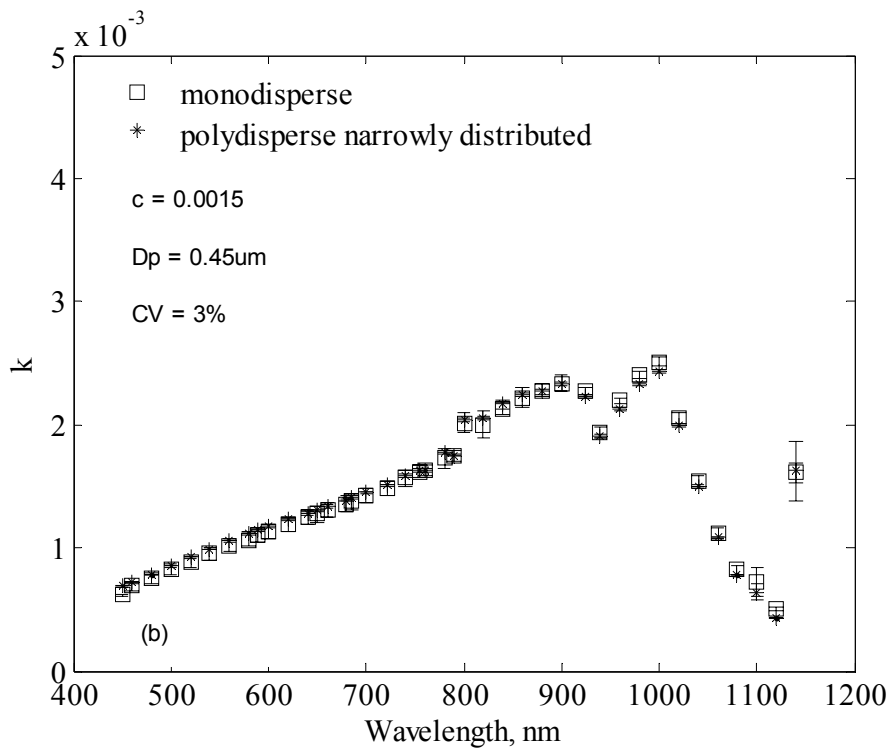
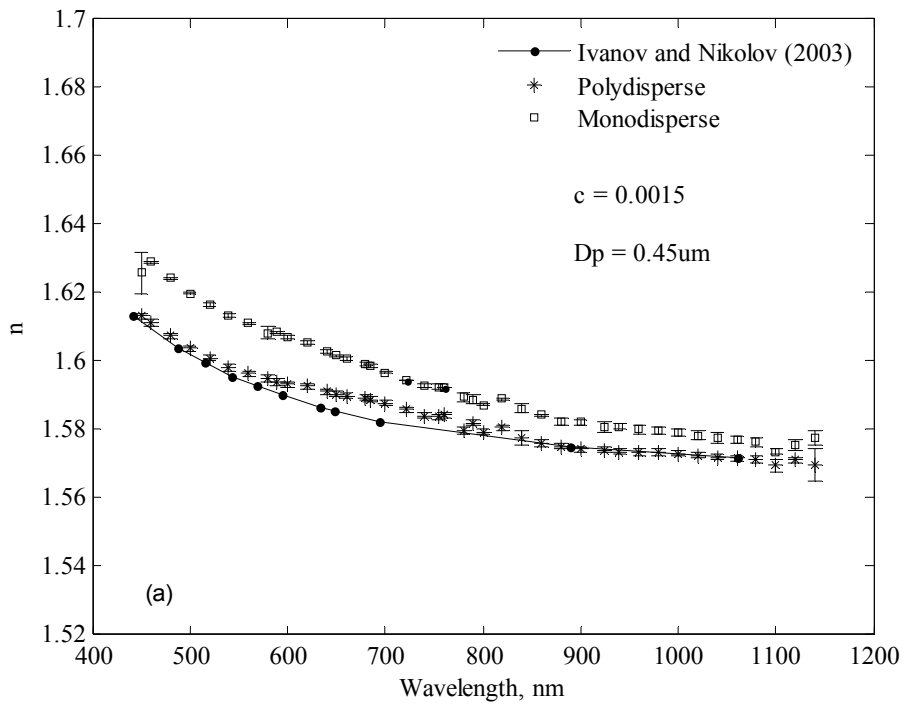


Figure 4. Comparison of complex refractive index of narrowly distributed polystyrene microspheres obtained by assuming the particles as monodisperse with that when size distribution is taken into account. Mean diameter  $0.45 \mu\text{m}$  and  $\text{CV} = 3\%$ . (a)  $n(\lambda)$  and (b)  $k(\lambda)$ .

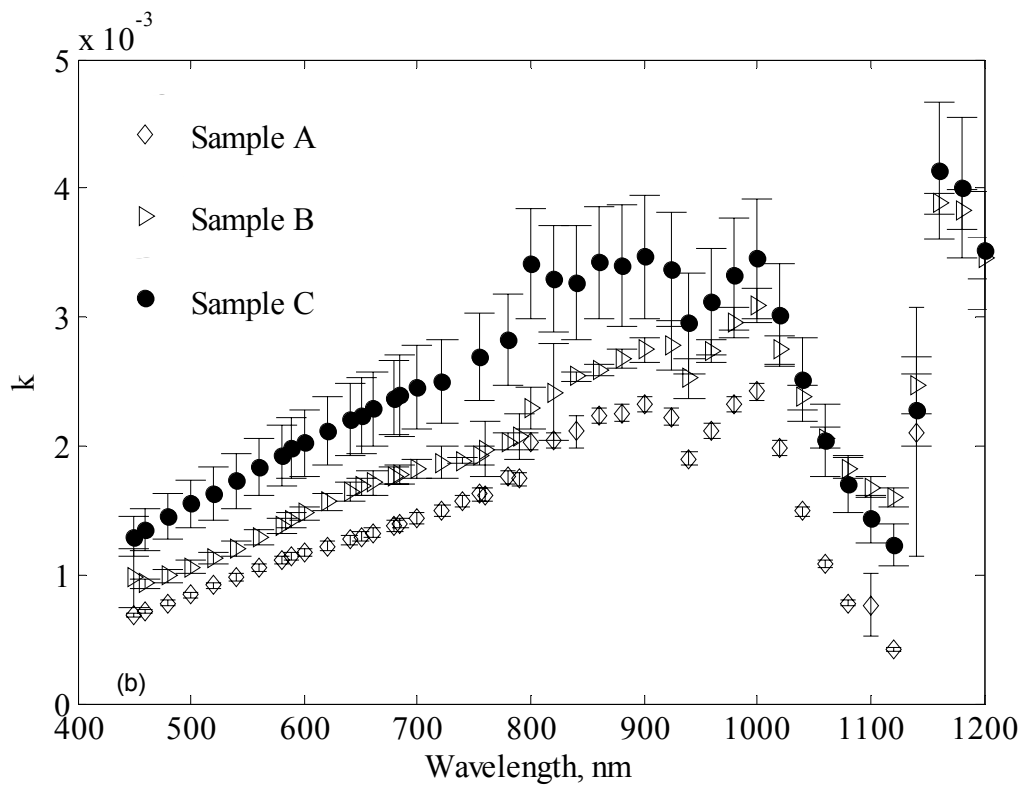
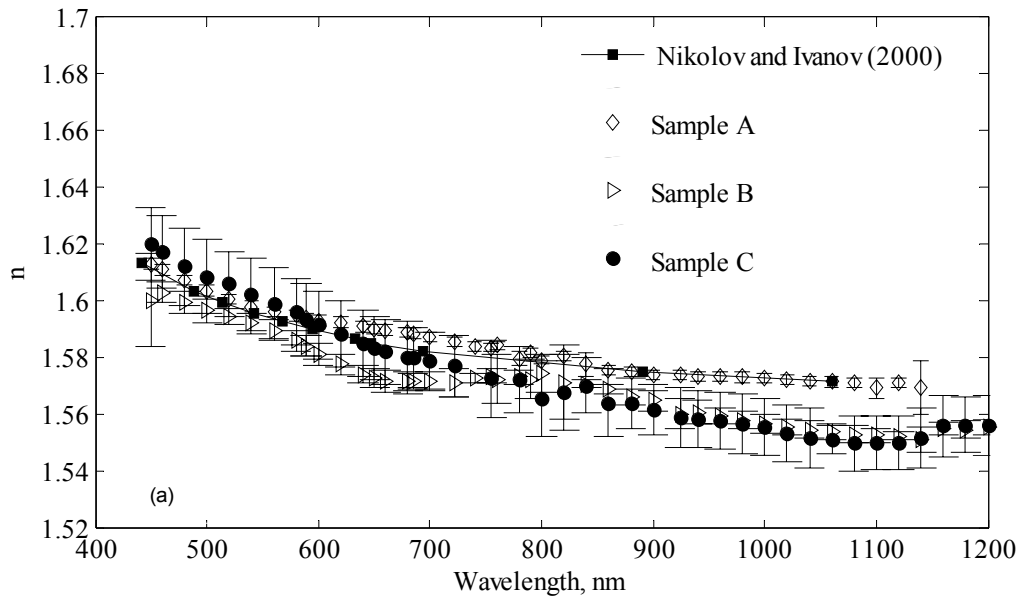


Figure 5. Complex refractive index, of polystyrene microspheres for samples with different size distributions (a)  $n(\lambda)$  and (b)  $k(\lambda)$ .