



A novel inverse method for determining the refractive indices of medium and dispersed particles simultaneously by turbidity measurement

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ABSTRACT

The refractive indices of particles and dispersion medium are important parameters in many colloidal experiments using optical techniques, such as turbidity and light scattering measurements. These data are in general wavelength-dependent and may not be available at some wavelengths fitting to the experimental requirement. In this study we present a novel approach to inversely determine the refractive indices of particles and dispersion medium by examining the consistency of measured extinction cross sections of particles with their theoretical values using a series of trial values of the refractive indices. The colloidal suspension of polystyrene particles dispersed in water was used as an example to demonstrate how this approach works and the data obtained via such a method are compared with those reported in literature, showing a good agreement between both. Furthermore, the factors that affect the accuracy of measurements are discussed. We also present some data of the refractive indices of polystyrene over a range of wavelengths smaller than 400 nm that have been not reported in the available literature.

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1. Introduction

Optical techniques, due to their non-invasive, non-contact properties are well suited to studies of colloidal suspensions. In applications of these techniques, such as static light scattering, dynamic light scattering and turbidity measurement [1–8], it is usually required to know the optical properties of materials through which electromagnetic waves propagate. Among these optical properties, the refractive indices of materials are particularly important. For instance, when the turbidity measurement is used to determine the coagulation rate constant, the extinction cross sections or the optical factors have to be evaluated theoretically [5–8]. To accurately calculate the extinction cross sections, the refractive indices n_2 and n_1 of the particle and the medium have to be predetermined with sufficient accuracy.

Taking for example the turbidity measurement of the coagulation rate, it has been shown [6–8] that the degree of response of the turbidity change to the coagulation varies significantly with particle size and operating wavelength; at a certain wavelength, the change in turbidity completely loses its sensitivity to the coagulation process (the so-called blind point), rendering measurement impossible. Therefore, selecting proper operating wavelengths to perform the rate constant measurements is very important. In general, however, the refractive indices n_2 and n_1 vary with the oper-

ating wavelength. Recent studies [6,7] have shown that even a tiny error in the refractive indices may result in significant errors in calculations of the optical factor in the turbidity measurement, which may lead to large error in measuring the coagulation rate constant. Therefore, how to determine the values of n_2 and n_1 at desirable wavelengths poses a challenging problem.

For some commonly used materials in colloids such as polystyrene (PS) and water, the refractive indices are available at some discrete wavelengths [9–14]. When the experiment is performed at the wavelengths where the values of n_2 and n_1 are unknown, one has to resort to some empirical formulas or fitting formula [7,10,13]. Data obtained via such methods for n_2 and n_1 may have significant uncertainty if the fitting data points are sparse or far away from the operating wavelength. For instance, even for polystyrene there is basically no data available, to our knowledge, on its refractive indices at shorter incident wavelengths (such as those smaller than 370 nm [13] in vacuum). This situation may be even worse for some other materials. More data on refractive indices are required for producing accurate fitted formulas for those materials. Furthermore, the introduction of ions or polymers into the medium may change the refractive index of the medium such that the data for the pure medium may not suit the environment in the actual experiment.

The best way to obtain the data of refractive indices is to measure them in situ at the desired wavelength λ . As a general approach for this purpose, the refractive index at different wavelengths can be measured from the refraction of the prism shaped

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sample [11,12]. But the refractive indices of the medium and the particles (such as water and PS) [11,12] have to be measured separately. On the other hand, Ma et al. [13] have introduced an inverse method for determining the refractive indices of PS microspheres by measuring the reflectance and transmittance of colloidal suspension, combined with Monte Carlo modeling in conjunction with Mie theory. In this method, however, the refractive indices of water (the medium) at the measuring wavelengths have to be known first. Therefore, these methods are somewhat intricate in terms of the experimental procedure if we need only refractive indices at a specified wavelength, which is the case for many light scattering and turbidity experiments.

In this paper, we will describe a new method in which the refractive indices of both the dispersed particles and the medium can be inversely deduced based on Mie theory from the extinction cross sections of monodispersed particles through the turbidity measurement. As well known, for spheres the extinction cross section can be calculated exactly from the Mie theory as long as the refractive indices n_2 and n_1 are chosen correctly. On the other hand, the extinction cross section can also be experimentally determined by the turbidity measurement. Therefore we can try a series of values of n_2 and n_1 to compare their calculated extinction cross section by Mie theory with the experimental cross section to find out the desired pair of n_2 and n_1 .

To verify the feasibility of this new method, a system composed of polystyrene particles dispersed in water was used in this study. Absorption of polystyrene material is quite small in the most range of the UV–visible–near infrared wavelengths. The absorption, however, becomes stronger in the short wavelength region. Actually, there is an absorption peak at wavelength of 260 nm. Even for this absorption peak the magnitude of the imaginary part of refractive index of polystyrene is still as small as 0.0103 [15]. Considering both imaginary parts of water [9] and polystyrene are small enough in the UV–visible–near infrared region used in most optical techniques in colloidal science, we assume that the neglect of imaginary parts of the refractive indices in our method would not cause significant error.

Our experiments have confirmed that there was a good consistency between the results obtained from the new method and known data from the literature. The values of the refractive indices of PS were also measured by this new method over a range of wavelengths smaller than 400 nm. In addition, the factors that affect the accuracy of measurements are analyzed and discussed. This approach is simple and efficient in various applications of optical methods requiring data on the refractive indices of the medium and dispersed particles, especially in turbidity measurements because there is no need for any additional instrument.

2. Materials and methods

We suppose that the refractive indices n_2 and n_1 to be determined are associated with polystyrene and water, so the system considered below consists of polystyrene particles dispersed in water. In order to inversely evaluate n_2 and n_1 , first we need to determine the extinction cross sections of particles with different sizes in water by turbidity measurement.

In our experiments, a UV–vis dual-beam spectrophotometer (Purkinje TU-1901, Beijing) was employed to measure the transmission percentage $T\%$ of monodispersed latex solution at temperature 20 °C. For each latex dispersion and incident light wavelength, over five independent experiments were performed to achieve the average value of the transmission percentage. Then, the transmission percentages were transformed to turbidity by the equation:

$$\tau = -\ln(T\%/L), \quad (1)$$

where L is the path length through the dispersion. If the colloidal system is monodispersed, the extinction cross section of single

particle C can be obtained from the turbidity τ and the number concentration N :

$$C = \tau/N. \quad (2)$$

This equation holds based on the assumption of single scattering so that the light scattering properties of a single particle are expected to represent the behavior of the entire ensemble. To ensure that our experiments were performed at conditions in which the single scattering approximation holds, the volume concentration used in our study was much smaller than 0.1%. For such small concentrations, the multiple scattering effect can be neglected, as predicted by theory [16]. The experimental results also proved that the single scattering approximation is applicable as the plot of τ vs N is linear until the volume concentration becomes much larger than the volume concentration used in our study [8].

The particle radii used in the experiments were $a = 115, 266, 250, 500$ and 4000 nm. The initial particle number concentration N of the stock solution was determined according to the particle size and dry weight of the dispersions of a certain amount of the sample solution.

The method discussed above assumes that all particles in an experimental sample have the same size. To reduce the effect of polydispersity of the particle size, some commercial products for “monosized PS sphere size standard” (Duke Scientific Corporation, USA) were employed in our experiments.

To protect the particles in dispersion from coagulation, the transmission percentages were measured and recorded for more than one hour by using different wavelengths of the incident light. We confirmed that $T\%$ did not change with time for each test wavelength. The dispersion remained monodispersed during the experiment period, assuring that Eqs. (1) and (2) would hold.

The extinction cross section, as well as the particle radius a and the incident wavelength λ can be determined experimentally. On the other hand, the extinction cross sections for different values of n_2 and n_1 at wavelength λ can also be theoretically calculated based on Mie theory [17,18]. Then, the theoretically calculated values can be compared with the measured extinction cross sections of particles with different radii. The true values for n_2 and n_1 should be able to make the calculated extinction cross sections coincide with the experimental ones for different radii. Therefore, to search the valid n_2 and n_1 at desired wavelength, different values of refractive indices should be tested through a series of comparisons described above.

However, we cannot test different values of refractive indices without limitations. Therefore, the first remedy we can apply is to narrow down the test range of the refractive indices. To do so, we can make use of some data known in the literature. Considering that the refractive index (real part) decreases with the increase of the wavelength in the UV–visible–near infrared region (the commonly used Cauchy refractive index formula also reflects this fact), some known data of the indices at the wavelength near the wavelength λ , at which the refractive indices are to be determined, were used as a reference to limit the range of n_2 and n_1 . As the refractive indices for different materials have, in general, already been reported more or less over some wavelengths, it is usually practical to obtain a reference value to confine the testing range.

How to take advantage of known indices as the reference data at certain wavelengths in determining the unknown index at desired wavelengths depends on the wavelength positions of the former relative to that of the latter. We suppose that the sought index is positioning at the wavelength λ and the reference indices at λ_a (if $\lambda_a < \lambda$) or λ_b (if $\lambda_b > \lambda$) for a specified material. If we have known the index data of the material at λ_a ($< \lambda$), as well as at λ_b ($> \lambda$), the solution (index) we seek is in the “intermediate range” of the wavelength, that we call as “intermediate case.” If there is no known refractive index at λ_a ($< \lambda$), or λ_b ($> \lambda$), it is

called a “low side case” or “high side case,” respectively. For different cases, the problem-solving procedure is a little different and will be discussed below.

2.1. Determination of refractive indices for the “intermediate case” of both water and PS material

We suppose the refractive indices of water and PS particles (denoted by n_1 and n_2 for water and PS, respectively) to be determined at the wavelength λ . Let the refractive indices of water at wavelengths of λ_a and λ_b ($\lambda_a < \lambda < \lambda_b$) be known as n_{1_a} and n_{1_b} , respectively. Likewise, PS particles are known as n_{2_c} and n_{2_d} , respectively, at λ_c and λ_d ($\lambda_c < \lambda < \lambda_d$).

Because the refractive index decreases with the increase of the wavelength, we have $n_{1_b} < n_1 < n_{1_a}$ and $n_{2_d} < n_2 < n_{2_c}$, respectively. In our algorithm to obtain the required refractive index, we use a series of trial pairs of n_1 and n_2 to calculate the cross sections to compare with the experimental values for different sized particles (radius $r = 115, 266, 250, 500$ and 4000 nm, respectively). This calculation started with $n_1 = n_{1_b}$ and $n_2 = n_{2_d}$ at the increment step of $\Delta n_1 = 0.0001$ and $\Delta n_2 = 0.0001$ to increase the value of n_1 and n_2 until they reach n_{1_a} and n_{2_c} .

Due to presence of experimental errors, we cannot expect to find a pair of n_1 and n_2 to make the calculated values of extinction cross sections to accurately match their experimental values for all the different-sized particles. The average difference ε_j of the extinction cross sections calculated theoretically according to the j th trial pair of n_1 and n_2 and the experimental values, was defined as:

$$\varepsilon_j = \frac{1}{M} \sum_{i=1}^M \frac{|C_{ca_i} - C_{ex_i}|}{C_{ex_i}}, \quad (3)$$

where i indicate i th type of particles (with different radii), C_{ca_i} and C_{ex_i} are the calculated and experimental values of the extinction cross sections for the i th type of particles. M is the number of different types of particles used in the study.

We should have the experimental values C_{ex_i} close to that calculated theoretically by using the true values of n_1 and n_2 (if known). On the other hand, if Δn_1 and Δn_2 are sufficiently small, there should be one or more pairs of n_1 and n_2 closely approximating their true values. Since the true values are to be determined, we can take the experimental values as the basis for comparison. In this case, an error range \mathcal{E} should be allowed in the comparison procedure. In practice, we screened out those pairs of n_1 and n_2 making $\varepsilon_j < \mathcal{E}$ (those are called contributing pairs hereafter) and used their averaged value to determine the true value of n_1 and n_2 . To appropriately choose the value of \mathcal{E} , we first find the minimum value from all ε_j to be ε_{\min} . As \mathcal{E} is used to screen out the trial pairs, making ε_j small, any value could be appropriate as long as it is a little larger than ε_{\min} . In this study we took $\mathcal{E} = 1.1 \times \varepsilon_{\min}$.

Based on the above considerations, the procedure for implementation can be summarized below:

- Determine the range for the test refractive indices as $n_{1_b} < n_1 < n_{1_a}$ and $n_{2_d} < n_2 < n_{2_c}$.
- Determine ε_{\min} over all steps.
- Screen out the contributing pairs satisfying $\mathcal{E} = 1.1\varepsilon_{\min}$.
- Average all contributing pairs to determine the value of refractive indices at wavelength λ .

2.2. Evaluation of refractive indices for the “low side case” (or “high side case”) for both water and PS

The basic considerations for dealing with these two cases are similar, so only the “low side case” will be considered below to

demonstrate how to solve the problem and implement the experimental procedure. For this “low side case,” we suppose the values of n_1 and n_2 are known only at wavelength $\lambda_b > \lambda$ and $\lambda_d > \lambda$, respectively, as n_{1_b} (for water) and n_{2_d} (for PS). We cannot define a testing range of the refractive indices as described in Section 2.1.

We noticed that ε_j has the tendency of decreasing as the refractive indices increase from the low limit n_{1_b} and n_{2_d} to their true values, and increasing as the indices increase further to larger values. Therefore, the testing range for the refractive indices can be determined by making use of this tendency.

Similar to Section 2.1, the trial pairs of n_1 and n_2 started from the low limit n_{1_b} and n_{2_d} at the incremental step of $\Delta n_1 = 0.0001$ and $\Delta n_2 = 0.0001$. For each trial value of n_1 , ε_j will have the tendency to increase with the increase of the trial value of n_2 after ε_j reaches a certain value, ε_{PS_limit} . Therefore, the trial value of n_2 that makes $\varepsilon_j > \varepsilon_{PS_limit}$ could be used as the up limit of the testing range of the refractive index of PS for the testing value of n_1 . According to the changing tendency of ε_j , the value of ε_{PS_limit} should be quite larger than the measurement error. If we denote $\varepsilon_j(n_{1_b}, n_{2_d})$ as the ε_j for the trial pair of n_{1_b} and n_{2_d} , ε_{PS_limit} should also be larger than $\varepsilon_j(n_{1_b}, n_{2_d})$ for ensuring some trial value of n_2 to be tested before the trial value of n_1 reaches its true value. Therefore, any value that is larger than the measurement error and $\varepsilon_j(n_{1_b}, n_{2_d})$ could be taken as ε_{PS_limit} . In this study, the ε_{PS_limit} is taken as the maximum of 20% and $1.1 \times \varepsilon_j(n_{1_b}, n_{2_d})$ without losing universality.

Now we consider how to determine the up limit of the testing range of water. First, the testing refractive index of water should reach the value (denoted as $n_{1_decrease}$) around which ε_j has the tendency of decreasing with the increase of testing value n_1 . For the value of $n_{1_decrease}$, there exist some refractive indices of PS in the testing range determined above that could give rather small ε_j , which is determined as $\varepsilon_j < 10\%$ in this study without losing universality. After the decreasing tendency around $n_{1_decrease}$, the tendency of ε_j will become increasing. Therefore, the refractive index of water will reach the value (denoted as $n_{1_increase}$) at which all the refractive indices of PS in the testing range give $\varepsilon_j > 10\%$. The value of $n_{1_increase}$ is then determined as the up limit of the testing range for the refractive index of water.

After the testing range is determined, the evaluation of the true value of n_1 and n_2 is similar to that in Section 2.1 such that the procedure for implementation can be summarized below:

- Determine the low limit of the testing range for the refractive indices of water n_{1_b} and PS n_{2_d} .
- The refractive index of water changes at a step of $\Delta n_1 = 0.0001$.
- For each test value of the refractive index of water, the refractive index of PS changes at a step of $\Delta n_2 = 0.0001$, until the calculated ε is larger than ε_{PS_limit} . By this means, the testing range for the refractive index of PS is determined for each test value of the refractive index of water.
- Repeat (b) and (c) until at one refractive index of water, the minimum ε_j calculated for the range of PS is smaller than 10%.
- Repeat (b) and (c) until at one refractive index of water, the minimum ε_j calculated for the range of PS is larger than 10%. By this means, the range for the refractive index of water is determined.
- Determine the minimum value of the error ε_{\min} in the above procedure.
- Screen out the contributing pairs satisfying $\mathcal{E} = 1.1\varepsilon_{\min}$.
- Average all contributing pairs to get the value of the refractive indices at wavelength λ .

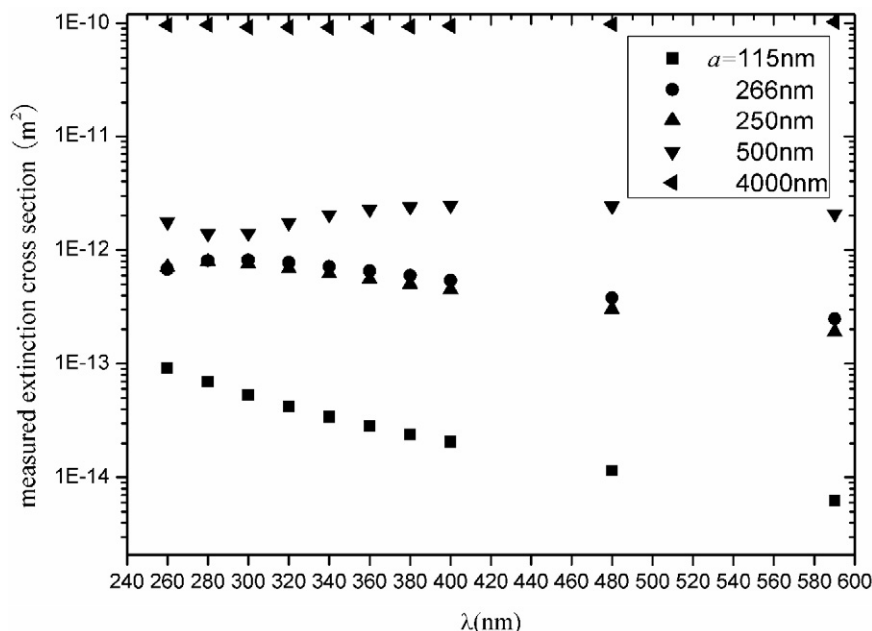


Fig. 1. The measured extinction cross sections for different sized particles with different incident wavelengths.

2.3. Evaluation of refractive indices for the combination case (either the water or PS material is an “intermediate case” and the other is a “side case”)

Under such conditions, the range for the refractive indices of water and PS can be determined by combining Sections 2.1 and 2.2.

Based on the algorithms described above, the relevant computer code can easily be written. To obtain the values of n_2 and n_1 at desired wavelength, the following parameters should be inputted:

1. The desired wavelength λ .
2. The known (reference) values of n_2 and n_1 .
3. Input “1,” “2” or “3” depending on the condition defined by (1) and (2) matches which case described in 2.1, 2.2 and 2.3.
4. The experimentally measured extinction cross sections for different sized particles (using the experimental procedure as described in Section 2).

To obtain the output, only a couple of minutes running on PC are needed.

3. Results

3.1. Determination of refractive indices for the “intermediate case” of both water and PS material

The refractive indices to be determined at wavelength of 480 and 590 nm were taken as verification examples of the algorithm in Section 2.1. The measured extinction cross sections for different sized particles at these two wavelengths are shown in Fig. 1. For a wavelength of 480 nm, the measured extinction cross sections for particles of radii 115, 266, 250, 500 and 4000 nm are 1.15×10^{-14} , 3.79×10^{-13} , 3.03×10^{-13} , 2.43×10^{-12} and 9.77×10^{-11} m², respectively. It was reported in a recent study [11] that the refractive index of water at 404.77 nm is 1.343113 and at 546.227 nm is 1.334825. For PS, the refractive index at wavelength 442 nm is 1.6135 and at 543 nm is 1.5957 [12]. By using these parameters, the average difference ε_j for different trial pairs of n_1 and n_2 and the contributing pairs can be calculated by using the algorithm

in Section 2.1, which are shown in Fig. 2. And the refractive indices at wavelength 480 nm were obtained as 1.3361(0.0009) and 1.611(0.002), respectively, for water and PS. The values shown in the brackets are the error intervals of the refractive indices evaluated from the contributing pairs. Compared with the reported refractive indices 1.337811 for water at wavelength 480.126 nm and 1.6037 for PS at wavelength 488 nm, it can be seen that the results are very close.

For $\lambda = 590$ nm, the measured extinction cross sections for particles of radii 115, 266, 250, 500 and 4000 nm are 6.28×10^{-15} , 2.48×10^{-13} , 1.91×10^{-13} , 2.07×10^{-12} and 1.02×10^{-10} m², respectively. It was reported [11] that the refractive index of water at 546.227 nm is 1.334825 and at 656.454 nm is 1.331509. And the refractive index at 543 nm is 1.5957 and at wavelength 632.8 nm is 1.5867 for PS [12]. The refractive indices evaluated by means of our inverse method at wavelength 590 nm are 1.333(0.001) and 1.592(0.002), respectively, for water and PS. The reported results for wavelengths near 590 nm are: 1.333399 for water at wavelength 587.725 nm and 1.5901 for PS at wavelength 594 nm. The evaluated results are very close to reported ones.

3.2. Evaluation of refractive indices of a “low side case” for both water and PS

For PS, the refractive indices for wavelengths smaller than 400 nm are lacking to our knowledge (although Ref. [13] have measured the refractive indices for wavelengths larger than 370 nm, the values were not listed so that we cannot obtain the accurate data), while for water, the refractive indices are available in the literature for a rather wide range of wavelengths [11]. Therefore, for water there is no “low side case” as mentioned in Section 2.2 in the UV–visible–near infrared region. However, we can still use the procedure in Section 2.2 to evaluate the refractive indices for wavelengths smaller than 400 nm by supposing a “low side case” for water.

The measured extinction cross sections for particles with different radii for wavelengths from 400 to 260 nm with a wavelength interval of 20 nm are shown in Fig. 1. For $\lambda = 400$ nm, the extinction cross sections measured for particles of radii 115, 266, 250, 500 and 4000 nm are 2.06×10^{-14} , 5.41×10^{-13} , 4.51×10^{-13} , 2.48×10^{-12} and 9.50×10^{-11} m², respectively. Considering that

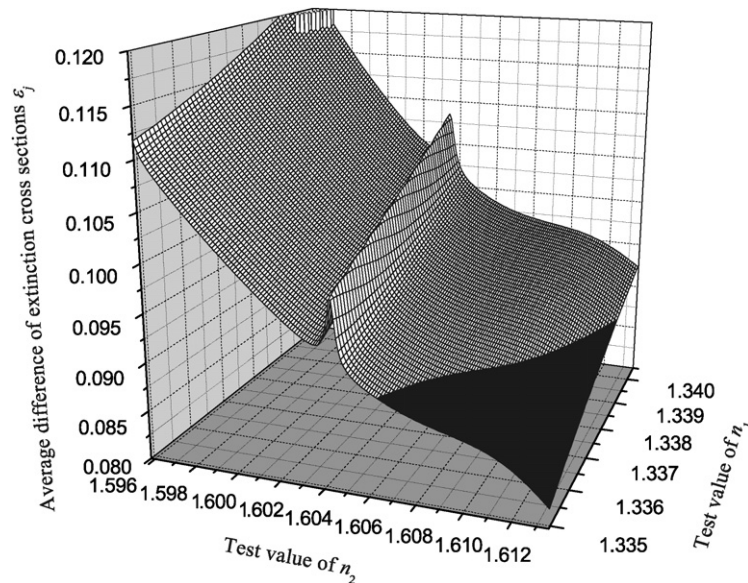


Fig. 2. The average difference ε_j for different trial pairs of n_1 and n_2 at wavelength 480 nm. The black part shows contributing pairs.

Table 1

The evaluated refractive indices for different wavelengths by using the algorithm in Section 2.2 with a wavelength interval of 20 nm

λ (nm)	400	380	360	340	320	300	280	260
n_1	1.341 (0.001)	1.344 (0.002)	1.349 (0.004)	1.356 (0.004)	1.359 (0.006)	1.362 (0.002)	1.364 (0.002)	1.366 (0.003)
n_2	1.641 (0.002)	1.644 (0.002)	1.664 (0.003)	1.673 (0.002)	1.688 (0.006)	1.707 (0.002)	1.725 (0.002)	1.761 (0.003)

the refractive index of water at 435.957 nm is 1.340578, and for PS the refractive index at 442 nm is 1.6135. Taking these parameters and using the procedure for a “low side case,” we get the refractive indices of water and PS at wavelength 400 nm 1.341(0.001) and 1.641(0.002), respectively. At 404.770 nm the reported refractive index for water is 1.343313, which is close to the evaluated result of 1.34103.

By taking the evaluated results of 400 nm as the low limit of the range for the test values of n_1 and n_2 , we can then determine the refractive indices of 380 nm from the experimental results by the procedure in Section 2.2. The result gives $n_1 = 1.344$ and $n_2 = 1.644$. By repeating the procedure iteratively with a wavelength interval of 20 nm, we can obtain the results for smaller wavelengths (360, 340 nm, etc.), which are listed in Table 1.

Using the value in Table 1, we compared the calculated extinction cross sections with and without the imaginary part of refractive index of polystyrene at wavelength 260 nm (at which there is a absorption peak). The result shows that the average difference is only about 1.7%. This difference should be much less at longer wavelengths, therefore we can reasonably infer that the neglect of the imaginary part of refractive index should be allowable.

Comparing the evaluated refractive indices of water with the reported data [11] at nearby wavelengths, it can be concluded that the error of this method is very small, so that the results of the refractive indices would be applicable for optical methods such as turbidity measurement and light scattering experiments.

3.3. Evaluation of refractive indices at the wavelengths which are “low side case” for PS and “intermediate case” for water

For the wavelengths in the last section, we can also use the procedure in Section 2.3 for evaluating refractive indices at wavelength only “low side case” for PS. The results are listed in Table 2.

Table 2

The evaluated refractive indices for different wavelengths by using the algorithm in Section 2.3

λ (nm)	400	380	360	340	320	300	280	260
n_1	1.344 (0.002)	1.345 (0.001)	1.348 (0.002)	1.351 (0.001)	1.354 (0.001)	1.3597 (0.0003)	1.366 (0.001)	1.3737 (0.0007)
n_2	1.643 (0.002)	1.644 (0.010)	1.663 (0.002)	1.669 (0.002)	1.682 (0.002)	1.706 (0.002)	1.727 (0.002)	1.774 (0.003)

Compared with the results listed in Table 1, it can be seen that the refractive indices for different wavelengths are quite close.

4. Discussion

The inverse method presented above is based on the assumption that all particles in an experimental sample are monosized. Apparently this assumption is not applicable in most practical situations. The polydispersity, i.e. the width of the particle size distribution, of the primary particles will certainly cause additional error. So it is necessary to consider the possible effect of polydispersity in primary particle size on the result obtained by using our method. Since the normal (or Gaussian) distribution is one of the most commonly observed in many natural phenomena or processes, it has widely been adopted as a starting point for modeling studies. Now we assume that the particle size distribution follows a Gaussian distribution with a mean of particles' radii of a and a standard deviation of σ . We calculated the average extinction cross sections, respectively, for monosized particles (radii of a) and particles with Gaussian size distribution (the mean radius a and the standard deviation σ). By using the inverse method we can achieve the refractive indices for both cases and according to their difference to evaluate effect of polydispersity of the particle size. By using the inverse method we can achieve the refractive indices for both cases and then evaluate the effect of polydispersity of the particle size according to their difference. Our result showed that when the relative standard deviation (σ/a) is 5%, the relative differences of average extinction cross sections for monosized and Gaussian distributed particles are smaller than 2.5% for all particles used in this study. Particularly, for the cases of particles with $a = 500$ and 4000 nm, the differences in average extinction cross sections are less than 0.25% at wavelengths smaller than 400 nm. The relevant (relative) differences in the refractive indices

Table 3

The evaluated refractive indices for different wavelengths by using the algorithm in Section 2.2 with a wavelength interval of 40 nm

λ (nm)	400	360	320	280
n_1	1.341 (0.001)	1.348 (0.003)	1.354 (0.002)	1.360 (0.004)
n_2	1.641 (0.002)	1.664 (0.002)	1.682 (0.002)	1.724 (0.002)

Table 4

The evaluated refractive indices for different wavelengths by using the algorithm in Section 2.2 with a wavelength interval of 60 nm

λ (nm)	400	340	280
n_1	1.341 (0.001)	1.344 (0.004)	1.345 (0.004)
n_2	1.641 (0.002)	1.660 (0.003)	1.714 (0.003)

are smaller than 1%. Therefore we can reasonably assume the polydispersity of particle size should not introduce significant error for the method.

In this inverse method, the experimental extinction cross sections are taken as the basis to calculate ε_j for each testing pairs. Because of the measurement errors of the extinction cross sections, there may be some pairs that have obviously unreasonable (too large or too small) values of refractive indices but still give very small ε_j . The occasional presence of these “unreasonable pairs” may severely mislead the minimization process in our inverse method, resulting in an incorrect evaluation of refractive indices. Therefore, the first steps in the procedure for all different cases (Sections 2.1, 2.2 and 2.3) are to determine the testing range of the refractive indices. These steps could solve the above mentioned problem by excluding the unreasonable values of the refractive indices.

Similarly, the pair of refractive indices that give ε_{\min} in the testing range may also have large error comparing with the true values. Some pairs giving ε_j a little larger than ε_{\min} in the testing range may still be good approximations to the true values. Considering this, we average the contributing pairs that give $\varepsilon_j < \mathcal{E}$ to determine n_1 and n_2 instead of simply choosing the pairs giving ε_{\min} in testing range.

In this study, \mathcal{E} is chosen to be $1.1\varepsilon_{\min}$. We have repeated the procedures in Section 3 using some other values of \mathcal{E} a little larger than ε_{\min} to test the influence of \mathcal{E} on the results. When $\mathcal{E} = 1.2\varepsilon_{\min}$ and $1.05\varepsilon_{\min}$ are used, the percentage differences of the results comparing with the results for $\mathcal{E} = 1.1\varepsilon_{\min}$ shown in Section 3 are smaller than 0.6%. For some wavelengths, the differences are even smaller than 0.1%. This result confirms that the influence of choice of \mathcal{E} on the result is negligible.

It should be noticed that in Section 3.2, the refractive indices were evaluated gradually from larger to smaller wavelengths. In the experimental procedure, a wavelength interval of 20 nm was chosen. For each wavelength, the evaluated n_1 and n_2 of the wavelength 20 nm larger than the desired wavelength were used to determine the testing range as shown in Section 3.2 in order to obtain the required data. From previous discussion it can be seen that the testing range is important in this inverse method. Therefore, larger wavelength intervals might cause poorer accuracy. Considering this, we have repeated this procedure at 40 and 60 nm intervals. The results are shown in Tables 3 and 4. The results in Table 3 are still very close to the results in Tables 1 and 2. However, the relative error of the refractive index of water for wavelength 280 nm shown in Table 4 compared with that in Table 2 reaches 1.5%, which is larger than any other results. Therefore, if the wavelength is a “low side case” for both the medium and particles, one should measure the extinction cross sections of different

sized particles at an interval of wavelengths not too large (such as less than 60 nm) from the wavelength at which the indices are known, gradually to the desired wavelength λ . Then the refractive indices of the medium and dispersed particles at λ could be calculated gradually as mentioned in Sections 2.2 and 3.2.

The reason for the relatively large error when a large interval is used in evaluating the refractive indices by the procedure mentioned in Section 2.2 is that the range for the tested refractive indices are relatively large. Therefore, it is better to use the procedure in Section 2.3 if possible, such as particles dispersed in water. By this procedure, the refractive index of water is more strictly confined so that it will yield more accurate results even though the interval is relatively large.

In Ref. [12], the minimum wavelength for the indices of PS is 442 nm. If using the procedure in Section 2.3 to get the refractive indices at wavelength 340 nm, which is about 100 nm smaller than 442 nm, the range for the refractive index of water lays between 1.3474 and 1.351996 according to Ref. [11]. From these parameters, we get $n_1 = 1.350$ and $n_2 = 1.669$, which is very close to the results in Tables 1 and 2.

We can even obtain the refractive indices at 260 nm directly from the refractive index of PS at 442 nm and the reported refractive indices of water at different wavelengths. Here we choose the refractive index of water between 1.371483 and 1.375563 according to Ref. [11]. Then we can get $n_1 = 1.375$ and $n_2 = 1.775$, which are also compatible with Tables 1 and 2. Therefore, by using the method described in Section 2.3, one can directly get n_1 and n_2 although the interval of wavelength is up to 180 nm, which is due to the confinement of the range of water as the data for larger and smaller wavelengths are already known.

5. Summary

In this study, we described a novel method to inversely evaluate the refractive indices of the medium and dispersed particles simultaneously. The PS particles dispersed in water were used to demonstrate the method. In this method, the extinction cross sections of different sized particles were determined experimentally by turbidity measurement. Then a program based on Mie theory was used to inversely evaluate the refractive indices at different wavelengths. The evaluated results were compared with some reported values of the water and PS, showing that this method yielded satisfactory results. The influence of the related parameters on the accuracy of evaluation was also discussed.

Considering that the refractive indices of water have been rather widely measured, it becomes much easier to get the refractive indices for PS at small wavelengths as discussed in Sections 2.3 and 3.3. However, if the known data for the medium is absent, the procedures in Sections 2.2 and 3.2, which are a little more complex, can still be used to evaluate the refractive indices. Therefore, the method proposed in this study is valid and easy complemented for researchers in colloidal science. This method would be helpful for optical methods, including turbidity measurement and light scattering experiments, in which the values of the refractive indices with satisfactory accuracy at operative wavelength are usually crucial. In addition, this study presents the refractive indices of PS at wavelengths smaller than 400 nm, at which these data have not been reported elsewhere.

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