Enhanced Photon-Migration Methods for Particle Sizing in Concentrated Suspensions

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This article presents a new method for determining particle size distribution in undiluted suspensions from spectral measurement of transport-scattering coefficients using continuous-wave photon migration techniques. Particle size distribution (PSD) for concentrated suspensions is determined by a regularized inverse algorithm, which makes it possible to incorporate a synthesized scheme of Marquardt and Tikhonov regularizations. Spectral measurements of dense TiO_2 suspensions with three different particle concentrations were used to recover the suspensions' size distributions. Our results are in excellent agreement with the size distribution measured with X-ray sedimentation. These reconstructions of PSDs are obtained both with and without a priori distribution function assumptions.

Introduction

Particulate suspensions are common in a variety of industries including ceramics, metals, foods, medical research, pharmaceuticals, pesticides, cosmetics, and paints and pigments. The two major categories of control parameters for the processing of particle/fluid suspensions are particle physics and interparticle chemistry (Funk and Dinger, 1994). One of the most important particle physics parameters to measure and control is the particle size distribution (PSD) of the powder. In suspensions and in powder processing in general, PSD affects many process and product properties (Dinger, 1996; Allen, 1990): particle packing densities, the nature and number of interparticle contacts within a compact, the interparticle porosity and pore size distribution in a compact, suspension rheology and viscosity, drying and firing behavior, and so forth.

Control of the PSD of powders in a body is effectively complete when the powders have been poured into the mixing device. Frequently, fluctuating body properties caused by variations in powder PSDs are adjusted using additive chemicals, that is, body property variations caused by one parameter (particle physics) are corrected by adjusting the other parameter (interparticle chemistry). Adjusting one control parameter to overcome variations caused by another is not advisable but common. To successfully process any particulate system, it is important that particle physics variations be controlled by adjustments to particle physics. Interparticle chemistry imbalances can then be controlled by adjustments to chemistry and the whole suspension can function as designed. To do this, one must be able to quickly and accurately measure the complete PSD of all constituent powders used in a batch formulation.

A major problem with all of the common particle size analysis techniques available today, including sedimentation, Coulter principle, dynamic light scattering, and turbidity measurement (Allen, 1990; Kourti et al., 1990; Elicabe and Garcia-Rubio, 1990; Vavra et al., 1995; Wang and Hallet, 1996), is the requirement of extremely dilute suspensions. These techniques cannot be used at normal suspension densities and require careful sampling followed by dilution and further sampling to achieve the small, highly dilute samples required for the analyses. In addition, these techniques often require calibration on the process stream they are intended to monitor.

To overcome the problems associated with the present techniques for particle sizing, a new optical method based on frequency-domain measurements of photon migration in scattering suspensions has recently been proposed (Jiang et al., 1997; Sevick-Muraca et al., 1997). Because this technique depends upon multiply scattered light, it is particularly suitable for non-dilute suspensions and has great potential for on-line process monitoring. In addition, transport scattering and absorption coefficients can be measured separately. Wavelength-dependent absorbances do not distort scattering

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measurements; hence, the technique does not require calibrations on the suspensions.

However, the measurements we conducted were based on a frequency-domain Ti:Sapphire laser system, which does not provide a light beam in a wide range of spectra. Furthermore, the procedures for optical data collection were relatively slow since measurements at multiwavelength were needed. In this paper, we demonstrate particle sizing in concentrated TiO_2 suspensions, using continuous-wave–based photon migration techniques. Compared with the frequency-domain techniques, this method allows faster and simpler measurements of optical properties in a scattering medium with the same accuracy as the frequency-domain techniques (Wang and Jacques, 1995; Nichols et al., 1997; Lin et al., 1997; Kienle et al., 1996). In addition, the cost for a continuous-wave-based system is lower than its frequency-domain counterpart.

Photon migration measurements monitor the characteristics of *multiply scattered light* as it consecutively scatters from particle to particle in tissue. Through the spectral measurement of isotropic or reduced scattering coefficient of the tissue, PSD can be recovered using a regularized inverse algorithm (Jiang et al., 1997). The photon migration technique is unique in two aspects: it can analyze particles in dense suspensions without dilution since it depends on multiply scattered light and is thus suitable for on-line process monitoring, and transport scattering and absorption coefficients of the suspensions can be measured separately, so that wavelength-dependent absorbances do not distort scattering measurements. This enables accurate solution of the inverse problem for determining PSD.

In this article, the principle of continuous-wave–based photon migration measurements for determination of the transport-scattering coefficient is described. We also summarize our inverse algorithm for reconstructing PSD in concentrated suspensions. Using our regularized inverse algorithm, we have reconstructed PSDs of TiO_2 suspensions with three different concentrations. The results are in excellent agreement with the size distribution measured with x-ray sedimentation. These reconstructions of PSDs are obtained both with and without *a priori* distribution function assumptions.

Spectral Measurements of Continuous-Wave Photon Migration

The continuous-wave photon migration techniques involve launching time-independent light into a highly-scattering medium and measuring the relative intensity of reflected or transmitted light (for reviews, see Farrell et al., 1992; Nichols et al., 1997; Lin et al., 1997). In highly scattering media, the propagation of light can be described by the well-known time-independent diffusion equation (Duderstadt and Hamilton, 1976; Ishimaru, 1976; Chandrasekhar, 1960). By fitting experimentally measured relative intensity of reflected or transmitted light to the solution of the diffusion equation under the condition of semi-infinite sample geometry, the spectral measurements of the transport scattering and absorption coefficients are obtained. The spectral measurements can be achieved by a simple fitting procedure (Nichols et al., 1997), or by an oblique incident reflectometry (Wang and Jacques, 1995; Lin et al., 1997). The data used in this work were collected by the latter approach.

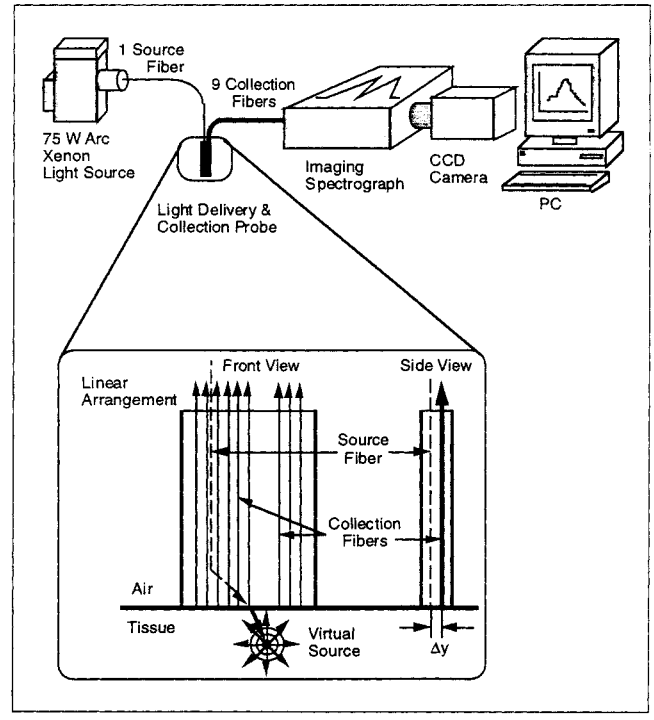

Figure 1. Experimental apparatus.

White light was coupled to the oblique-incidence optical fiber probe. A source fiber delivered light to the gel phantoms at a 45° angle and the diffuse reflectance was collected by nine collection fibers. The source fiber was 0.116 cm away from the collection fiber plane. The source-detector distances were 1.33, 1.13, 0.92, 0.18, 0.39, 0.59, 0.79, 1.00 and 1.20 cm, respectively.

The experimental system used in this study is schematically shown in Figure 1, which was based on oblique incident reflectometry (Wang and Jacques, 1995; Lin et al., 1997). White light from a 75-W Xenon Arc Lamp was delivered, and the diffuse reflectance was measured as a function of source-detector distance by a fiber-optic probe. The source fiber was oriented at a 45° angle of incidence, and the nine collection fibers, arranged in a linear array, collected the diffuse reflectance. To correct for slight variations in collection efficiency from one detection fiber to the next, a correction factor was calculated for each fiber based on a calibration procedure using standard phantoms. The detection system was composed of an imaging spectrograph, a CCD camera, and a PC to automatically record the spectrum of the collected light through the wavelength range of 400–800 nm. The spectral resolution of the measurements was 0.5 nm.

The fiber probe was placed on the surface of the concentrated suspensions. An exposed x-ray film was attached to the top of the suspensions to approximate a matched boundary condition for diffusion theory. Four measurements were performed with the probe oriented at 0°, 30°, 60°, and 90° with respect to an arbitrary reference orientation. The transport-scattering spectra were evaluated for each diffuse reflectance measurement, and the results were averaged. The concentrated suspensions were a mixture of TiO_2, India ink, and polyacrylamide gel (Lee, 1997) that produced TiO_2 concentration values of 8.8×10^{-3}, 11.7×10^{-3}, and 14.6×10^{-3} wt. %, respectively. Note that while the addition of the India ink

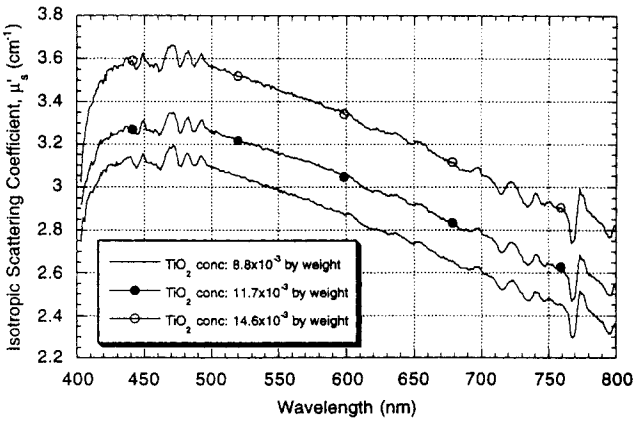

Figure 2. Transport-scattering spectra [μ_s' (cm^{-1}) vs. wavelength, λ (nm)] determined by oblique incident reflectometry.

is not necessary for the purpose of particle sizing, an appreciable absorption can exist in particle suspensions. The photon migration techniques used are capable of separately measuring scattering and absorption coefficients; thus, wavelength-dependent absorbances did not distort the scattering measurements. The mixture was poured into a plastic container 8 cm in diameter and 6 cm in height before gelling. Figure 2 presents the transport-scattering spectra measured for the TiO_2 suspensions with three different concentrations. The standard deviations between the source fiber orientation angles for each concentration are 0.16, 0.25, and 0.37 for the concentrations of 8.8×10^{-3}, 11.7×10^{-3}, and 14.6×10^{-3} wt. %, respectively.

Regularized Inverse Algorithm

Our inverse algorithm casts particle sizing as an optimization problem in which the optimization parameters are fully variable, discretely classified PSDs or coefficients in a probability function (such as a lognormal or Gaussian distribution function) using *a priori* assumptions. The details of our inverse algorithm have been given in Jiang et al. (1997) and Sevick-Muraca et al. (1997). We present a brief overview here for context.

It is known that PSD in a multiply scattering medium is correlated with the transport-scattering coefficient of the medium by the following relationship (Van de Hulst, 1983; Bohren and Hoffman, 1983):

$$(1-g)\mu_s(\lambda) = \mu_s'(\lambda) = \int_0^\infty \frac{3Q_{\text{scat}}(x,n,\lambda)[1-g(x,n,\lambda)]}{2x}\phi f(x)dx \quad (1)$$

where $(1-g)\mu_s$ is the transport-scattering coefficient, g is the mean cosine of the scattering angle from a single particle, Q_{scat} is the scattering efficiency, n is the refractive index of the medium and λ is the wavelength of light, $f(x)$ (x is the diameter of the particles) is the particle volume size distribution and ϕ is the total volume fraction of the particles. Both quantities of g and Q_{scat} can be computed using the Mie theory (Bohren and Hoffman, 1983). To use Eq. 1 correctly, we have assumed that no particle–particle interaction exists and that it applies only to spherical particles.

Now the inverse problem becomes to find the particle size distribution, $f(x)$, and the volume fraction, ϕ, from measurements of the transport-scattering coefficients at multiple wavelengths. Using our regularized optimization methods, we obtain the following system of equations leading to the inverse problem solution (Jiang et al., 1997, 1998; Sevick-Muraca et al., 1997):

$$(\mathfrak{J}^T\mathfrak{J} + \alpha I)\Delta\zeta = \mathfrak{J}^T[(\mu_s')^o - (\mu_s')^c] \quad (2)$$

where the Jacobian matrix $\mathfrak{J}$ represents the sensitivity of transport-scattering coefficients measured at multiple wavelengths, the elements of which are numerically computed using Eq. 1. I is the identity matrix and α may be a scalar or a diagonal matrix. The vectors, $(\mu_s')^o$ and $(\mu_s')^c$, contain the observed and computed values of transport-scattering coefficients at the wavelengths of interest.

The numbers of the elements of $\Delta\zeta$ and $\mathfrak{J}$ depend on whether we use *a priori* knowledge about the number of modes and their size distribution functions or not. If we use a lognormal distribution in this study for TiO_2 suspensions (Crow and Shimizu, 1998)

$$f(x) = \exp[-(\ln x - a)^2/2b^2]/\sqrt{2\pi}bx$$

where parameters a and b denote the mean and variance of the distribution, respectively, then the number of the elements of $\Delta\zeta$ is three (we choose ϕ as the third parameter) and the number of elements of $\mathfrak{J}$ is $M\times3$, where M is the number of wavelengths; if we do not use *a priori* knowledge about the number of modes and their size distribution functions, then the numbers of the elements of $\Delta\zeta$ and $\mathfrak{J}$ become N and $M\times N$, respectively, where N is the number of intervals that are equally discretized for the product $\phi f(x)$ (Sevick-Muraca et al., 1997).

Thus, the basic method for determining $f(x)$ and ϕ is to measure the transport-scattering coefficient of the suspensions at multiple wavelengths. Then the particle sizing task is to make estimates (which are updated and improved through the solution of Eq. 2) of parameters a, b, and c or discretized $f(x)$ and ϕ that are required for the measured scattering coefficients to be sustained. Since the matrix $\mathfrak{J}\mathfrak{J}^T$ is known to be ill-conditioned (Wang and Hallet, 1996; Jiang et al., 1997, 1998), a way to regularize or stabilize the decomposition of $\mathfrak{J}\mathfrak{J}^T$ is needed. We used a hybrid technique that synthesizes the standard Marquardt and Tikhonov regularization schemes (Jiang et al., 1997, 1998; Sevick-Muraca et al., 1997).

Results

We have used the inverse algorithm described in the "Regularized Inverse Algorithm" section to reconstruct the particle size distributions for dense TiO_2 suspensions with three different concentrations. To reconstruct a typical PSD shown below, only a few seconds were needed with a SunSparc 5

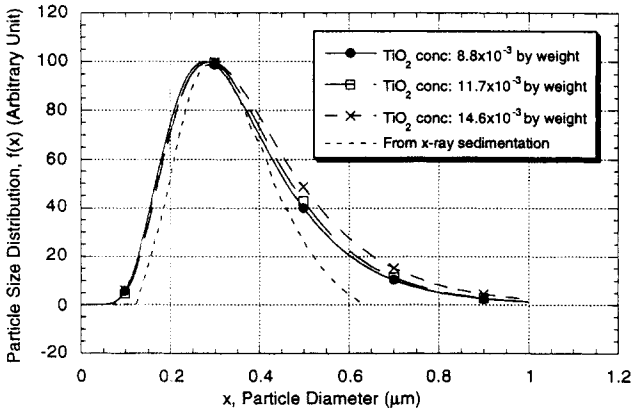

Figure 3. Particle-size distribution, $f(x)$ (arbitrary unit), as a function of diameter, x, (μm) for TiO_2 samples.

It was inverted from the diffuse reflectance measurements (lines with symbols) and as measured from the sedimentation (dashed line) using *a priori* distribution function assumption.

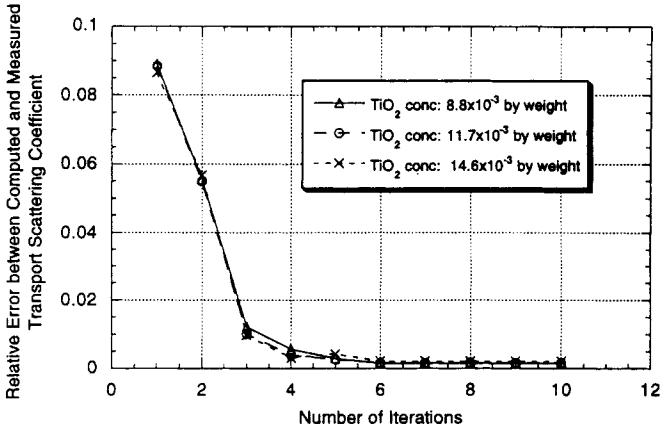

Figure 4. Relative error between the computed and measured transport scattering coefficients vs. the number of iterations.

Using *a priori* distribution function assumption convergence of the inverse solution is achieved with a maximum of three iterations.

workstation. We found that the inversion results were not very sensitive to the choices of the uniform initial estimates of the discretized size distribution or parameters in the known probability distribution function, which were up to 100% greater than the true values, depending of course on the optical property measurements.

Figure 3 shows the particle size distributions recovered for all three TiO_2 suspensions with *a priori* lognormal distribution function assumption. The lines with symbols denote the reconstructed values from the photon migration measurements and the dashed line represents the size distribution obtained from the sedimentation measurement for comparison. The figure shows that an excellent agreement between our results and those yielded by the sedimentation has been reached. The relative error between the computed and the measured transport-scattering coefficients at each iteration, defined as

$$\left(\sqrt{\sum_{i=1}^{M}\left[(\mu_s')_i^o-(\mu_s')_i^c\right]^2}\right)_{J\geq 1}\Bigg/\left(\sqrt{\sum_{i=1}^{M}\left[(\mu_s')_i^o-(\mu_s')_i^c\right]^2}\right)_{J=0}$$

M is the number of wavelengths and J is the number of iterations ($J = 0$ denotes that the calculation is performed before the iterative procedure begins), as shown in Figure 4. In this case, the reconstructed volume fractions (ϕ) are 0.92%, 1.24%, and 1.61%, respectively.

Figure 5 presents the particle size distributions recovered for all three TiO_2 suspensions where no *a priori* distribution function assumption was used. Again, a very good agreement has been achieved between these results and x-ray sedimentation. Figure 6 gives the relative error of the inverse solution in this case. The recovered volume fractions (ϕ) are 0.90%, 1.21%, and 1.59%, respectively.

Discussion and Conclusions

The results presented in the previous section clearly indicate that we are capable of determining particle size distribution in concentrated suspensions with and without *a priori* distribution function assumptions using continuous-wave photon migration measurements. Since we made optical property measurements at 800 wavelengths between 400 nm and 800 nm, we have obtained PSD in concentrated suspension without *a priori* distribution function assumption for the first time. This approach allows us to reconstruct PSD with an arbitrary shape. This is an important advancement of our approach because we may not have such *a priori* information in many practical situations. In addition, the inverse solution procedure in our reconstruction was quite stable, whereas an unstable solution procedure has been experienced using frequency-domain photon migration techniques (measurements

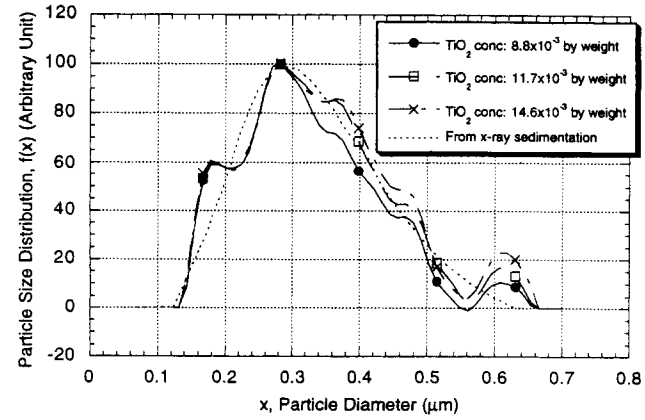

Figure 5. Particle size distribution, $f(x)$ (arbitrary unit), as a function of diameter, x, (μm) for TiO_2 samples.

It was inverted from the diffuse reflectance measurements (lines with symbols) and as measured from the sedimentation (dashed line). No *a priori* distribution function assumption was used.

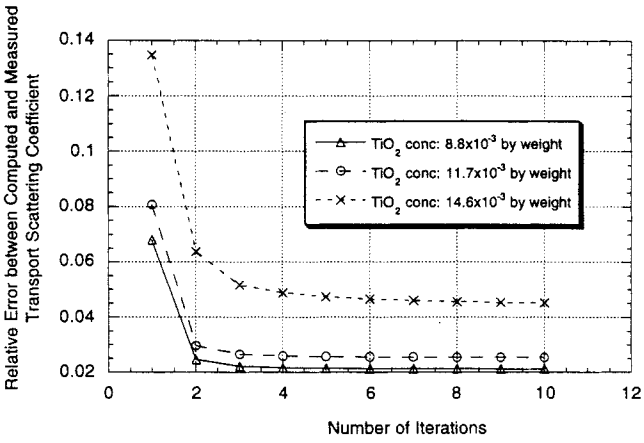

Figure 6. Relative error between computed and measured transport scattering coefficients vs. the number of iterations.

No *a priori* distribution function assumption was used. Convergence of the inverse solution is achieved with a maximum of two iterations.

at only 15 wavelengths were made (Jiang et al., 1997; Sevick-Muraca et al., 1997). This is clearly evidenced by the relative error or converging rate shown in Figures 4 and 6.

From Figures 3 and 5, one can observe that the increase of the particle concentration from 8.8×10^{-3} to 14.6×10^{-3} by weight does not make significant impact on the recovery of PSD. Although we do see a larger relative error between the computed and the measured transport scattering coefficients for the case of higher particle concentration in Figure 6, this does not affect the reconstruction of PSD significantly because the error shown is only relative. Clearly this observation should be restricted to the particle concentrations used in this study. The actual limits of the particle concentration for which our approach is applicable warrant future study. It is also interesting to note that, while the shape of particles in TiO_2 suspensions is not perfectly spherical, the spherical particulate-based Mie theory still provides us with accurate results from our inverse algorithm. This could be due to the use of the hybrid regularization in our iterative optimization procedure, which provides a compensation mechanism for the geometrical discrepancy that occurs in the theory. In Figure 3, we note some discrepancies at longer wavelengths between our results and those measured with x-ray sedimentation. We suspect that the discrepancies were due to the assumption of *a priori* lognormal distribution function since these discrepancies did not exist when we did not use the *a priori* assumption (Figure 5). While our solution employed 800 wavelength measurements, we have not yet tested the minimum number or choice of appropriate wavelengths required for a successful and optimal inverse solution. Studies regarding these interesting issues are currently under way.

In summary, we have used continuous-wave photon migration measurements of transport-scattering for particle sizing in concentrated suspensions. Our study shows that fast, simple continuous-wave photon migration measurements in a wide range of wavelengths, coupled with an efficient inverse algorithm, can provide PSD of concentrated suspensions in a matter of seconds. This indicates its potential for on-line process monitoring.

Acknowledgments

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