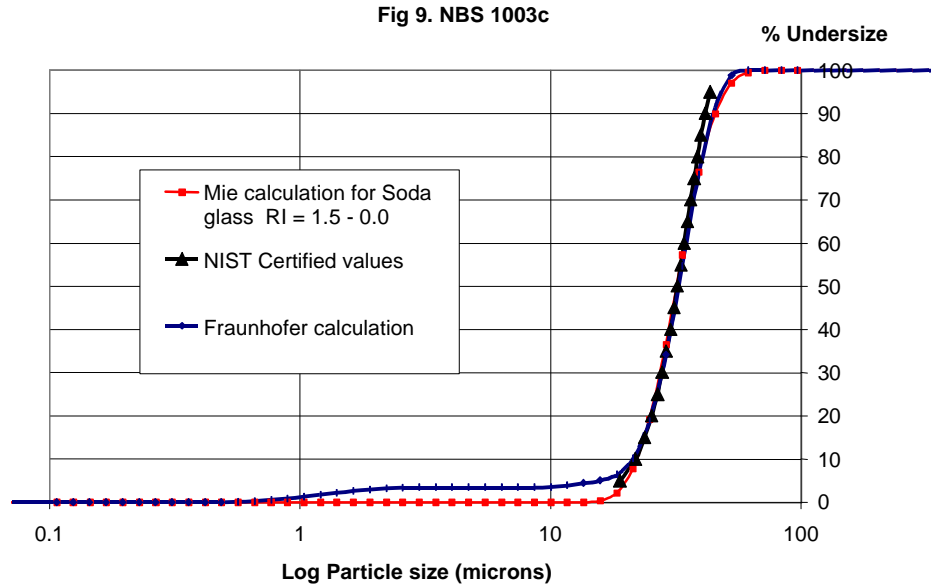
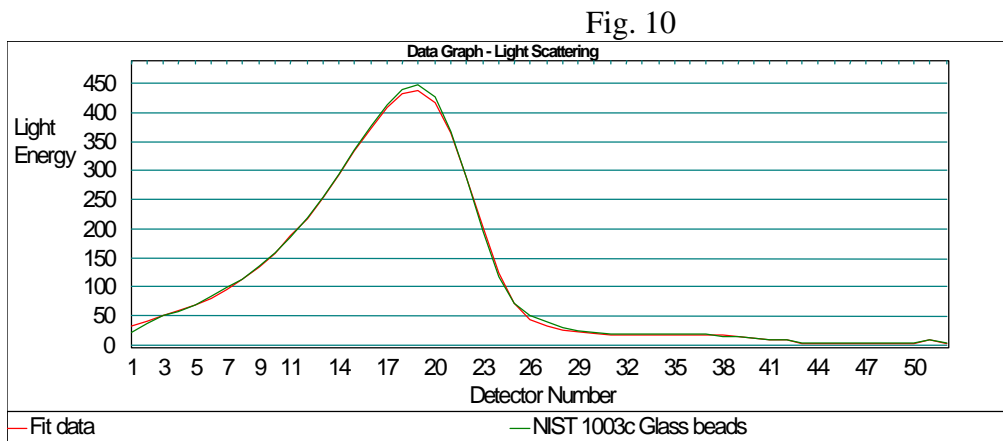


**Examples of getting it wrong**

**Example #1:** In Figure 9 the Fraunhofer result shows an artefact quantity of particles between 1 µm and 10 µm. Why might this be?



**Fig.9** Percent undersize of NBS 1003c CRM analyzed using light scattering using Mie theory and the correct RI values compared with an analysis using the Fraunhofer approximation. The certified values are also plotted.



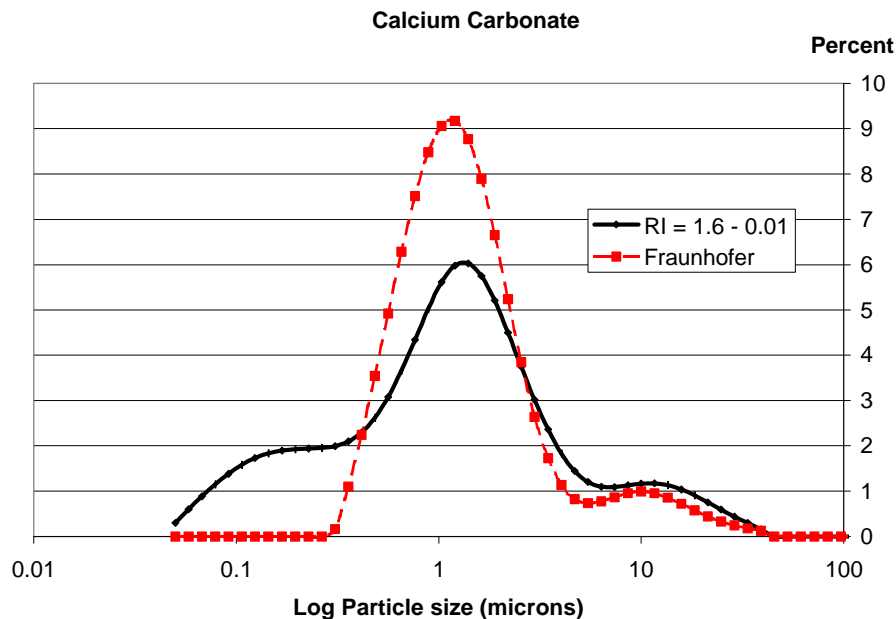
**Fig. 10,** shows the measured light energy distribution and the fitted curve created as a result of the data inversion using Mie theory with RI = 1.5 – 0.0, the NIST stated value.

As explained above the light scattered from the ensemble of particles in the measuring cell are recorded as currents or energy from a series of detectors in the instrument. In Fig. 9, detector 1 is

the detector closest to the laser beam, the lowest angle measured. The increasing detector number corresponds to increasing angles of observation. NBS 1003c is a distribution of transparent soda-glass beads. The laser light that passes through these beads forms a constructive interference with the light diffracted from the edge of the beads and is the cause of the signals recorded by detectors 29 to 43. Mie theory predicts that this will happen in view of the refractive index values chosen and thus only reports only the sizes we know to be present. The Fraunhofer approximation (which does not model transparency) interprets the signal observed by detectors 29 to 43 as the presence of a quantity of small particles.

**Example #2:** Calcium Carbonate is used as filler in plastics as well as in the making of paper. It is a natural product dug out of pits, processed and classified into grades. It is optically bi-refracting and has a range of refractive index values depending upon the temperature and pressure conditions that were pertaining when it was created. The example shown in Fig. 11 is a mixture of three size fractions

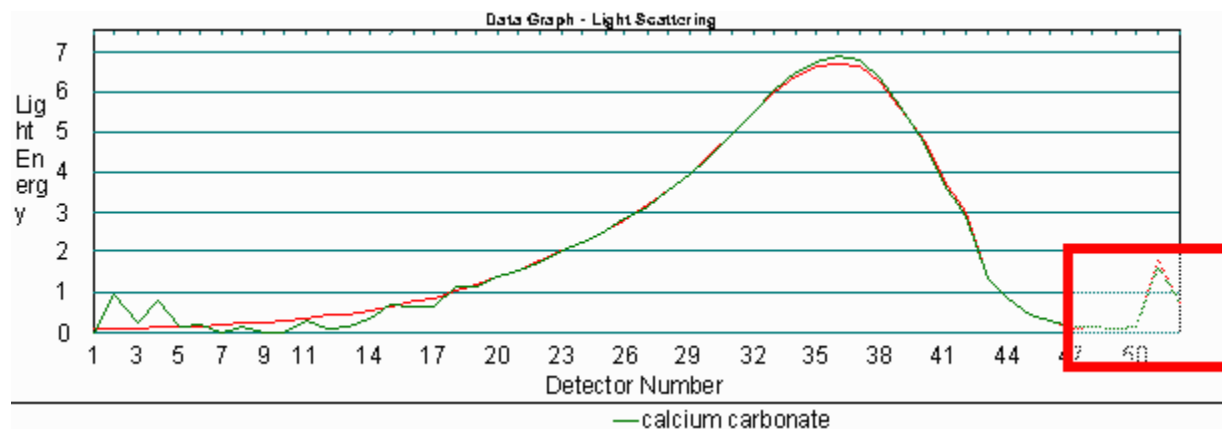
Fig. 11



**Fig. 11,** these results were analysed from a single measurement using the conditions labelled.

As was seen in Fig. 4 extinction and hence the scattering is very weak for tiny particles. It is particularly weak below  $0.2\ \mu\text{m}$ . Mie theory can account for this and continues to report the presence of the sub- $0.2\ \mu\text{m}$  material. The Fraunhofer approximation disregards such small scattering contribution relative to the rest of the light energy and in this instance fails to report any quantity of particles less than  $0.2\ \mu\text{m}$ .

Fig. 12



**Fig. 12** The fit of computed scattering energy and measured values for calcium carbonate. Detectors 51 and 52 (highlighted within the red-bordered square) are not light energy scattered but the extinctions due to red light and blue light respectively.

The values shown in channels 51 (red extinction) and 52 (blue extinction) in the Fit graph Fig. 12 demonstrate good agreement for the extinction values for both red and blue sources. A common refractive index value for the light scattering prediction for both red and blue light was used. Both colour extinction values are in good agreement and this helps to confirm that the light scattering from this material had no extra wavelength dependence.

As will be explained later the agreement, or lack of agreement, of the fit to the measured value of extinction provides strong confirmation of an appropriate choice of optical properties. You will have an unjustified sense of security if you place your hope in the assumption that all will be well if the Fraunhofer approximation is utilised, because such a model does not take into account the optical properties.

### How can appropriate refractive index values be determined?

**The real part of the refractive index:** Several alternative optical methods are available to determine refractive indices. If the material is a liquid, (i.e. the droplet phase in an emulsion) the refractive index can simply be determined by refractometry using an Abbé or similar refractometer. If the material is a soluble solid, an Abbé refractometer can also be used to determine the refractive index of the solid by measuring the refractive index of three or four different known concentrations of solution. The measurement values are then extrapolated to the 100% concentration value. This has been found to give reasonably accurate results.

Index-matching immersion fluids are available to determine refractive indices for insoluble solids with RI between 1.3 and 2.1. This range covers most materials (apart from some pigments and inorganic compounds – metal oxides etc). If a particle is dispersed in a fluid of matching refractive index, it will seem to be invisible (glass beads in benzene are the classic example of this). For absorbing materials the measured obscuration goes through a crisis even when the sample doesn't disappear so you can still detect the matching point. Matching index fluids can thus be used to determine at which point the particles become effectively invisible or cause a minimum of scattering. There are two ways of using such fluids. It is possible to buy index-

matching oils that are supplied in small bottles and these can be used in conjunction with a microscope and applying the Becke line (Ref. 3,4) test. However, these oils tend to be expensive and are only available in small quantities so it is a more practical proposition to use two miscible liquids of differing refractive index. A typical choice for this would be propan-2-ol, (isopropyl alcohol, RI = 1.39) and methylnaphthalene (RI = 1.62). Using these two liquids, it is possible to create a wide range of different mixtures of which the RI is known (e.g. a 40% propan-2-ol: 60% methylnaphthalene mix has a RI = 1.528).

$$(RI_{material1} * Volumefraction_{material1}) + (RI_{material2} * Volumefraction_{material2}) = RI_{mixture}$$

To carry out a determination of the RI of a material, a number of mixtures should be created. A laser diffraction measurement should be performed using each of these mixtures, care being taken to ensure that equal weights of sample are added to each mixture to ensure that the sample concentration is identical in each case. By plotting the obscuration value obtained from each mixture the minimum obscuration with respect to matching liquid refractive index can be established. It should be noted that the obscuration will not always be zero since if the material has a non-zero imaginary refractive index, it will absorb light even when immersed in a liquid of equal refractive index. Determination of the imaginary refractive index will be discussed later in this paper.

Crystallographers and mineralogists favour the technique which uses index matching fluids in conjunction with a phenomenon known as “Becke lines” to determine the refractive index of materials. A material with a refractive index which is significantly different to its surroundings (higher or lower index) acts as a lens (this effect is more marked in the case of crystals which tend to be thicker in the centre and thinner towards the edges – like lenses). There will also be internal reflection of light due to internal grain boundaries. Therefore, rays of light coming from the bottom surface of a sample of a mineral appear to come from a slightly higher point. Such materials appear to stand out in relief from their surroundings. This phenomenon is responsible for the creation of Becke lines. The Becke line is a band of light visible along a particle boundary in plane-polarised light. There are two thin lines on the particle boundary, one dark and one light. The light line moves into the medium of higher refractive index. If the focus is moved up, the line will move into the centre. If the dispersant RI is varied, the crossover point (between the sample having a higher refractive index than the dispersant and vice versa) can be determined.

**The imaginary part of the refractive index:** In cases where light adsorption is significant both the real and imaginary components of the refractive index change significantly and continuously with wavelength, especially in the wavelength region near the adsorption maximum. Both components may be determined by measuring the quantitative adsorption spectrum of the material and applying the Kramers-Kronig transform (Ref. 5). For measurements that use a single wavelength (as when the light source is a laser) a single pair of values for the real and imaginary components are sufficient to compute the scattering and adsorption contributions to extinction at that particular wavelength. Such information is not easy to establish and is only suitable for a limited range of substances. One powerful method that has proved valuable is to test for a match between the measured and predicted extinction values. The value of extinction is one of the parameters reported by some laser diffraction instruments. It will be recalled the extinction = scattering + absorption. Provided that an appropriate value for the real part of the

refractive index is available and being applied, values of the imaginary part of the refractive index may be chosen and tested until a best match is observed between theory and observation.

Coloured pigments may have very strong resonance at or near the wavelengths used in the laser diffraction, measuring unit. Because of this any multiple-wavelength analysis may require distinctly different pairs of real and imaginary refractive index values at the different wavelengths.

### How can we finally confirm our choice of refractive index?

It has been shown by Lips et al. (Ref. 6) that the true phase volume of a system of suspended spherical particles whose scattering extinction efficiencies have been predicted by Mie theory can be measured correctly. It was shown that even for oblate spheroids with an aspect ratio 5:1, the error was only of the order of 10%. Experiments confirmed that: suspensions of known pre-determined phase volume were correctly reported by laser diffraction instruments that were able to report extinction values. In addition to producing a size distribution by analysing scattered light, some laser diffraction instruments report the zero angle obscuration measurement that can be used to calculate the volume concentration of particles present. Obscuration is the fraction of incident light intensity that is NOT detected at zero angle (due to scattering or adsorption of particles in the beam). That is, obscuration equals one minus the ratio of light intensity transmitted to the zero-angle detector when particles are present in the sample volume to the intensity transmitted when particles are absent. By combining the Mie theory of light scattering with the Beer-Lambert law the following equation is obtained:

$$c = \frac{100 \log_e(1 - \text{Obscuration})}{\frac{-3}{2} b \sum \frac{V_i Q_i}{d_i}} \quad \text{-----(1)}$$

Where

c is the concentration (%)

b is the path length of the measuring cell

$V_i$  is the volume in size band I

$Q_i$  is the extinction coefficient of size band I

$d_i$  is the mean diameter of size band I. T

Equation (1) shows the relationship between volume concentration and the obscuration measured as part of a normal experiment. This equation, is used by the some laser diffraction units, to calculate a theoretical concentration. For a stable size distribution (with no multiple scattering), comparison of the real and calculated concentrations can be used to establish that by successive approximation.

Some laser diffraction instruments, report the theoretical volume concentration using equation (1). To calculate the experimental volume concentration, follow the procedure below. The specific gravity or Archimedian density of the powder will be required for this measurement. A true density value as measured by gas pycnometry is NOT suitable for this test. Many particulate systems contain pores that remain un-wetted in a suspension. Such pores may still

contain gas; therefore a gas pycnometer-derived density is not appropriate. Measure the weight of sample added to achieve the recommended obscuration value when fully dispersed. This stage may require some iteration to get right. Divide the figure obtained by the specific gravity of the material and divide this again by the volume of dispersant liquid used in the measurement. Finally, multiply by 100 to give the result as a volume % (i.e. Phase volume). If the material is spheroid, the two volume concentrations (real and theoretical) should be within a few percent if the appropriate refractive index has been used. The degree of disparity depends on the sphericity of the material and the precision of the various measurements. Obviously for non-spherical material, this approach is less useful. It should be noted that the approximation continues to be valid for particles whose aspect ratio does not exceed about 4:1.

The specific gravity (if unknown) can be calculated by using weighing bottles or by Archimedian displacement. To do a displacement experiment, a large measuring cylinder with a magnetic bead in it should be placed on a magnetic stirrer. Liquid should be added to a known line on the cylinder. Weigh the container of the sample (including the bead), and then add sample until 1ml of material has been displaced. Weigh the container again. The weight of material needed to displace 1ml of water is the specific gravity. If the material is water-soluble, an appropriate non-solvent should be used and the weight should be divided by the density of the non-solvent liquid. This is to correct back to water (1ml of water weighs 1g as the density is 1 g/cm<sup>3</sup>) as the density of the dispersant will influence the amount added.

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