Instruction Manual for
BI-DCP
Disc Centrifuge Photosedimentometer
&
BI-DCPLW Line Start Software

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Please Read

This is your instruction manual for your Brookhaven Disc Centrifuge Photosedimentometer system and BI-DCPLW Line Start control software. Please read it carefully before attempting to plug in and use the equipment to make measurements. The **Installation** section, Section II, describes procedures for checking that the instrument and the software are working properly. Cleaning and changing discs, repositioning the detector and other maintenance procedures are described in the appendices. You may familiarize yourself with some of the features of this software by loading sample data files (Files/Database/Sample Data). You can run the Modeling Utility, view results, display distribution tables and graphs to test and understand the operation of the software. In Section VI, **Making a Measurement**, all the detailed procedures of preparing a sample, making a measurement and printing reports are given. If you have any questions or suggestions, please contact Brookhaven Instruments.

This 32-bit program requires Windows 98, 2000, NT, XP or higher and at least 16 Mb of RAM.

DO NOT PUT STRONG SOLVENTS IN THE STANDARD DISC. THAT WILL RUIN THE DISC. The standard disc is made of poly (methyl methacrylate), PMMA. Also known as Plexiglas, Lucite, and Perspex, this material will be attacked by strong acids or bases and many common organic solvents such as acetone and toluene. It is resistant to water, simple alcohols, and to aqueous solutions of sucrose, ethylene glycol and glycerol. If in doubt, contact the factory for advice. Brookhaven Instruments cannot be responsible for warranty replacement of PMMA discs ruined by the use of incorrect solvents.

Software is never really finished: There are always additions and changes. As these become available, they will be added to the back of this manual as appendices. Please look at the appendices if you cannot find the answer to your questions in the main part.

Remember the old saying: "When in doubt, read the instruction manual." Sometimes the solution to your problem has already been addressed. You just need to find it. Thanks for purchasing a Brookhaven.

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Warranty

Brookhaven Instruments Corporation, hereinafter known as BIC, warrants that the product is free from defective material and workmanship. Under the terms of this warranty BIC agrees to correct by repair or at BIC's election by replacement, any parts which prove to be defective through no fault of the user.

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The BIC warranty extends for a period not exceeding the warranty period of the original equipment manufacturer where applicable. The typical warranty period on printers and computer peripherals is 90 days, and on photomultiplier tubes it is 180 days. Please contact BIC for copies of applicable OEM warranties.

The BIC warranty does not cover scratches or haze which may develop in disc cavities as a result of improper sample preparation or use. Nor does the warranty cover damage to a disc from the use of incorrect solvents. SEE PAGE 2 OF THIS MANUAL.

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Information produced by using this BIC software and its manual, including the resulting displays, reports, and plots, are believed to be accurate and reliable. However, Brookhaven Instruments Corporation assumes no responsibility for any changes, errors, or omissions.

Table of Contents

I. Introduction

General Description I-1

Specifications I-1

Disc Specifications I-3

II. Installation

Software II-1

Testing the Software II-1

Analyzer II-3

Cooling requirements for the DCP II-4

Contacting Brookhaven for Help……
II-5

III. Principles of operation

Basic Operation III-1

Theory: Stokes' Law.....III-1

Error Calculations Using Stokes' Law…….. .III-2

Disc Cavity Geometry …….. III-3

Errors from Spin Fluid Volume and Alignment Errors……..III-4

Turbidity and Distribution Calculations: Mie Scattering Corrections..... III-4

IV. Software Overview

Starting View Window IV-1

Instrument Setup Window……..IV-2

Modeling Utility Window: Run Time, Spin Fluid Volume…….. IV-3

Parameters Window…….. IV-5

Scattering Corrections Window…… IV-6

Normal View Window…….. IV-7

Detailed Results Window……. IV-8

Database & How To Use It…….. IV-9

Printing Options Window ……... IV-11

V. Sample & Gradient Preparation

Items You Need To Make A Measurement V-1

Syringe Kit V-2

Sample Preparations: General Comments..... V-3

Sample Preparation: 1 Micron PS Latex..... V-4

Sample Preparation: Carbon Black..... V-5

Gradients V-6

Forming An Internal Gradient: Water/MeOH…… V-7

VI. Making A Measurement

Running A Sample..... VI-1

Monitoring the Run..... VI-2

Stopping the Run VI-3

Cleaning the Disc..... VI-3

VII. Advanced Data Analysis

Setting the Baseline Manually..... VII-1

Detailed Distribution View VII-2

Specialty Graphs: Compare Measurements VII-3

Specialty Graphs: Build SPC Chart..... VII-3

Specialty Graphs: Compare V/S/N Distributions..... VII-4

Specialty Graphs: Bimodal Analysis VII-5

Custom Mie Scattering Corrections..... VII-6

Appendices

Removing and Replacing Discs..... Appendix I-1

Detector Alignment Procedure for the BI-DCP ..... Appendix II-1

Concentration Definitions and Calculations ..... Appendix III-1

ASCII Data File Format..... Appendix IV-1

Distribution Statistics, Definitions and Calculations..... Appendix V-1

Section I: Introduction

General Description

Absolute particle size distributions for latex, carbon black, catalysts, and many other types of small particles are readily obtainable by disc centrifugation. Using the line start technique (LIST), a small volume of suspension is injected into a spinning disc with a spin fluid and gradient. A tiny amount of a low vapor pressure liquid is layered on top to prevent evaporative cooling. Larger particles move faster through the spin fluid than slower ones, thus creating a fractionated sample. A narrow-band LED shines light through the disc. A diode is placed behind the disc to receive the light. When particles pass through the beam, the light is attenuated either by scattering or absorption or both. The time it takes particles to arrive is used to determine particle size. The extinction of the light is used to determine the relative concentration after light scattering corrections. From size and mass concentration, a volume- or mass-weighted particle size distribution of high resolution is determined. Surface area- and number-weighted distributions can be derived and presented.

In order to calculate particle size from arrival time, use is made of Stokes' Law in a centrifuge. The particle and liquid density and the liquid viscosity are also required to complete the calculation as well as the spin fluid volume and internal dimensions of the spinning disc. To transform from the extinction (turbidity) of light to mass concentration, the refractive index of the particle and liquid are required.

Specifications

The BI-DCP consists of the analyzer and control software. The analyzer system includes the following: motor and controller; keypad entry with LCD readout; disc and disc injection port; 650 nm red LED; diode detector; and built in stroboscope. (The built in strobe has two separate uses. First, it is used to confirm the stable rotation of the shaft. For this reason it is not synchronized to the rotation of the shaft. Rather it is synchronized to the motor drive circuit. Second, it is used for detecting unstable sedimentation during the measurement.)

The analyzer drive system has a microprocessor controlled, digitally driven electronic motor and a digital read-out for setting and monitoring speed. With the PMMA disc, the BI-DSC, the speed can continuously vary from 600 to 15,000 rpm. For use with some solvents that might harm the BI-DSC, there is an optional disc, the BI-DSCR that can be operated from 600 to 10,000 rpm.

The BI-DSCR is made from homolite, a type of polycarbonate. It shatters more easily than the PMMA disc. This is the reason the maximum speed is less for the BI-DSCR. To prevent mistakes, the hub of the BI-DSCR is black and that of the BI-DSC is shiny. An internal light with receiving diode detects the back reflected light from the mounted disc's hub. If the level is low, the maximum speed allowed is 10,000 rpm; if the level is high, the maximum speed allowed is 15,000 rpm.

The rotational speed accuracy and stability are better than ± 0.01%. The disc is dynamically balanced over the range of operating speeds and can hold spin fluid volumes from 10 to 25 ml. With too low a spin fluid volume, the accuracy of determining the geometrical parameters needed for use in Stokes' Law calculations is low. With too high a spin fluid volume, liquid overflows when the disc is stopped. The most typical spin fluid volume is 15 mL.

A Windows-based software package for data acquisition, analysis, and management is included. A PC is required and may be supplied by the user or optionally by Brookhaven Instruments Corporation.

The BI-DCPLW software is designed for use with the BI-DCP particle size analyzer. It is a 32-bit, C++ program requiring Windows 98, 2000, NT, XP or higher operating systems. We recommend the use of at least 16 MB of RAM and a Pentium PC. The program acquires data from the analyzer, calculates the results, manages a library of data files, and allows the user to plot different graphs and reports.

Windows Software Version

Listed below are some of the features of the system:

- Real-time data plotting on the monitor during measurement.
- Provides on-screen and hardcopy reports of selected statistical measures of the volume- (mass-), surface area-, and number-weighted distribution and tables of the cumulative distribution.
- Generates on-screen and hardcopy plots of the raw data curve with baseline and the differential and cumulative forms of the various distributions.
- Distributions can be displayed on a logarithmic or linear scale.
- Up to six distributions can be graphically overlaid and compared.
- A complete database management system by folders and files.
- Ability to design various report printouts, including a preview feature.
- Generates statistical process control chart with printouts.
- Ability to see the detail results on the screen.
- Can import old DOS runs and save them in the Windows' datafile system.
- Graphs and results can be viewed as volume- (mass-), surface-area- or number-weighted distributions.
- Display of cumulative distributions either separately or with differential distributions on the same graph.
- Detailed size distribution tables can be viewed on the screen or printed as a report.
- Ability to reanalyze measurements.
- Graphs can be scaled automatically or manually and as log or linear functions.
- Automatic calculation of viscosity and density as a function of temperature for several common liquids.
- Modeling utility to quickly optimize run time and disc speed for a given size range.

Please transfer the disc specifications included with every disc onto this sheet for future reference. When contacting the factory for help, you may be asked to include this information. A common mistake when working with more than one disc is to leave the previous disc's specifications in the software. This leads to small but noticeable calculation errors.

DISC SPECIFICATIONS

Number 1: Standard (BI-DSC) or Solvent Resistant (BI-DSCR)

Serial Number:

Disc Cavity Width in cm:

Disc Cavity Radius in cm:

Detector Radius in cm:

Number 2: (BI-DSC) or Solvent Resistant (BI-DSCR)

Serial Number:

Disc Cavity Width in cm:

Disc Cavity Radius in cm:

Detector Radius in cm:

Original Purchaser

Organization

Address

_

Section II: Installation

Software

If Brookhaven supplied the computer, the software is already installed on your hard drive.

If you supplied the computer, insert the CD with the BI-DCPLW software into the CD drive. In the DCPLW subdirectory, find and double click on Setup.Exe. Follow the suggestions on screen. When you are finished, the software can be found under START/PROGRAMS/Brookhaven Instruments Win (32) or in the Windows Explorer. You may find it convenient to drag a copy to your desktop.

Testing the Software

Depending on how you have setup the computer, either click or double click on the icon or dcplw32.exe to start the program. The Main Window should appear as shown here in Figure II-1.

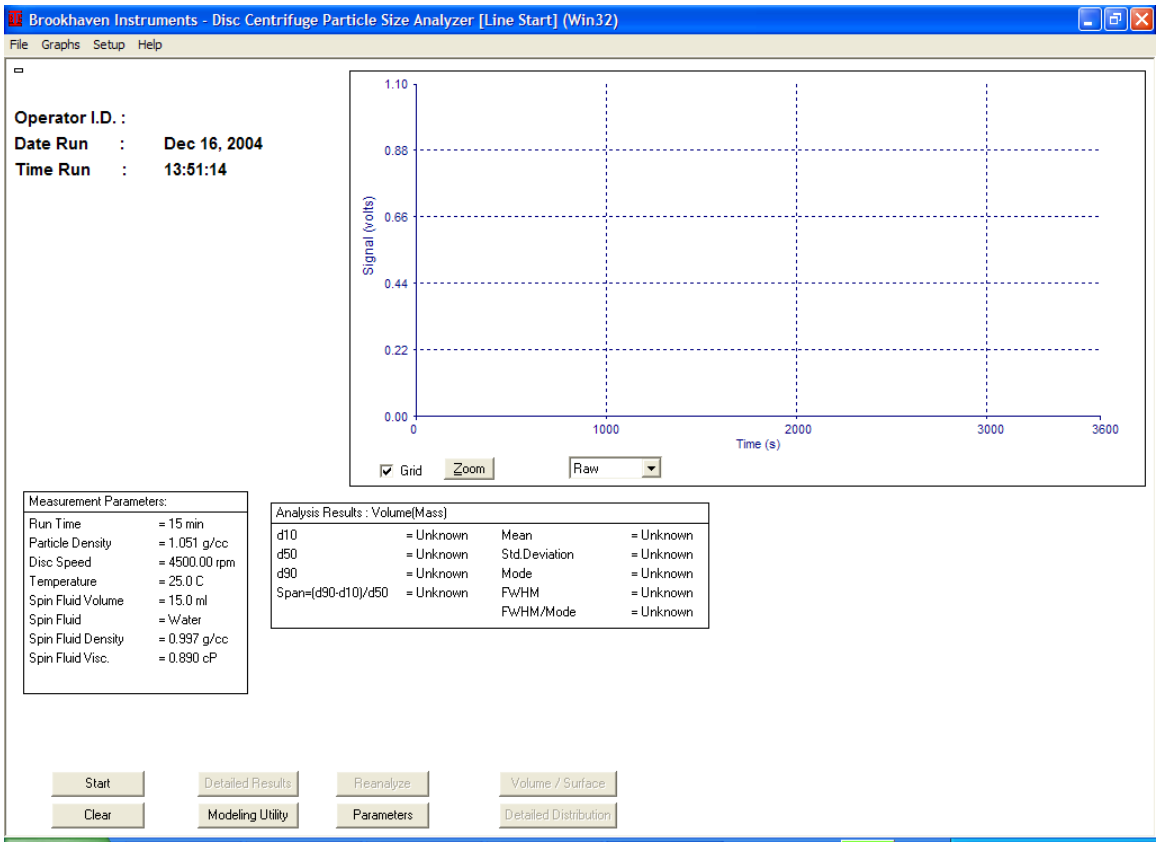


Figure II-1: Starting window when software first installed.

Click on **File** in the Main Window Menu bar and then on **Database**. By double clicking on a FOLDER, it opens and the files therein are shown in the bottom half of the window. Open the folder entitled Sample Data. Open a demo file by double clicking it. Now you will see the raw data graph in the right corner of the screen and the results below it. The Sample I.D., date, and other input parameters are displayed in the left corner of the screen. Click on **Zoom** to see a bigger graph. Various graphs, detailed results, and size distribution tables are displayed. Similarly, distributions weighted by volume, surface area or number can be seen. Click on **File** and **Print Report**, you will get a print out of the summary of results for the current file. You can print other reports.

Click on **Setup** in the Main Window Menu bar, and then click on **Instrument Parameters**. Figure II-2 shows an example. Make sure the disc parameter values agree with the disc you will mount on the instrument. These are given on a data sheet that comes with every disc. The default values should be close to, but not equal to, the actual disc values. Verify that these parameters are the same as the disc parameters given in Section I, Introduction. If not, type in the correct values now. The default connection between the analyzer and the PC is through the COM1 port. You may change to COM2 using the drop-down list-box. With a standard, BI-DSC with the shiny hub, 15,000 rpm is the maximum speed. With an optional, BI-DSCR solvent resistant disc with the blackened hub, 10,000 rpm is the maximum. Select the appropriate maximum speed using the drop-down list-box. {NOTE: The color of the hub is detected automatically and prevents going over the maximum speed; however, it is a good check to select the maximum in this window.} Click the command button labeled SAVE.

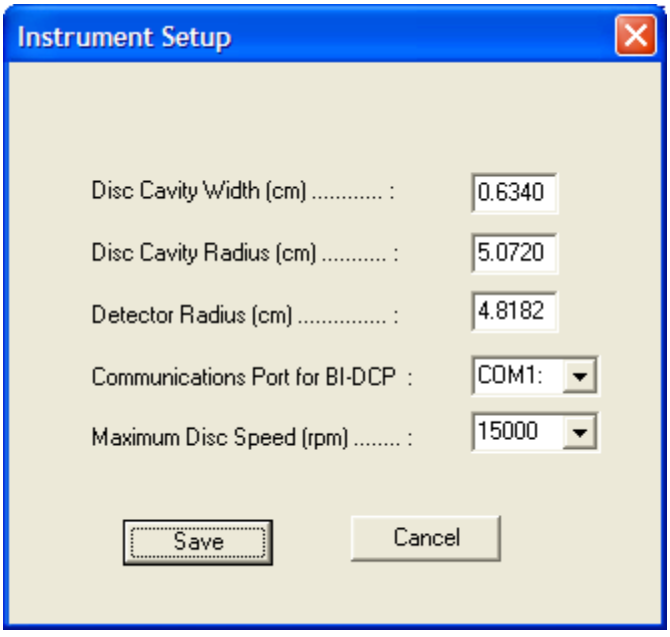


Figure II-2: Instrument Setup Window. Enter disc parameters to match the disc mounted.

Analyzer

Install the centrifuge disc as outlined in Appendix I.

Plug the power cord into the rear of the analyzer. Plug the other end into a suitable source of power.

Turn on the power of the analyzer. The LCD display should light up.

Align the detector as outlined in Appendix II.

Enter 3000 on the keypad. Each digit entered is shown on the last line of the LCD, the COMMAND LINE. Use either the left arrow or the ERASE LINE key to make corrections. Press the RPM button to implement your choice. The exact rotational speed, a value very close to 3000 RPM is displayed on the first line of the LCD.

Press the red button marked MOTOR. Verify that the disc rotates. Press MOTOR again to stop the disc. It should stop very quickly. There is an electronic brake for safety. Start the disc rotating again.

Press the button marked STROBE. Verify stable operation by noting that the disc position is apparently frozen. If it wobbles back and forth, stop the motor and contact the factory.

Verify stable operation at 4000, 5000 and 6000 rpm. Speeds may be entered on the keypad and implemented by pressing the RPM key while the disc is rotating. This will not affect the operation of the instrument as long as a measurement is **not** in progress. Note: The strobe automatically shuts off after 5 minutes to prolong its life. To reactivate the strobe, just press the key again.

Set the speed to 3000 rpm.

Open the door of the analyzer. Verify that the motor stops rapidly and automatically. Note the small switch at the top left hand side of the opening.

Turn the analyzer off.

Connect the analyzer to the computer using the flat cable supplied for this purpose. The connectors are polarized, and care should be taken to install them correctly. You can use either the COM1 or the COM2 port on the computer. The

analyzer uses a 25 pin connector, and the PC uses a 9-pin adapter. Brookhaven supplies as standard a 25-pin to 9-pin adapter cable.

Cooling requirements for the BI-DCP

The BI-DCP is air-cooled. Room temperature air enters through a filter installed in the top panel at the rear of the machine, and it directly flows over the disc. As it does so, it removes the hot air built up by the friction of a high-speed disc rotating in air. The air is then pulled through the motor by a special set of fan blades built into the motor itself. The air exits through rear panel openings assisted by two fans.

NOTE: NEVER BLOCK THE FANS OR THE INTAKE FILTER. LEAVE AT LEAST 10 cm BETWEEN THE REAR PANEL OF THE INSTRUMENT AND THE BACK WALL.

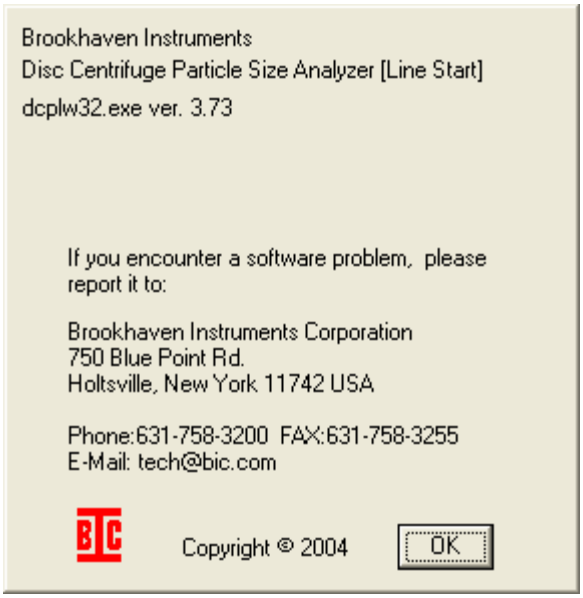
Remove, clean and replace the filter every 3 months.

The installation of the BI-DCPLW software and the BI-DCP analyzer are complete:

- The computer works;
- The program can be executed;
- You can print out results;
- The analyzer works and is connected to the desired COM port.

Contacting Brookhaven For Help

Click HELP in the main menu window. The window shown in Figure II-3 appears. The telecommunication numbers for Brookhaven are shown. When contacting Brookhaven, please specify that you are using the BI-DCP with software version dcplw32.exe ver. 3.73 or whatever version is currently running. Please specify in detail the problem. Attach a binary file to demonstrate the problem. To make a binary file click FILE/DATABASE. Then double click on the Folder that contains the file of interest. Click once on the folder to highlight it. Do not open the file. Just highlight it. Then click on ARCHIVE FILE. Do not EXPORT the file creating an ASCII file. Just ARCHIVE the file creating a binary file that can be read here at Brookhaven using the RELOAD command.



One last piece of advice:

MAKE FREQUENT COPIES OF YOUR DATA FILES

If any of the hardware fails, Brookhaven Instruments can repair it. Corrupted or lost programs can be replaced. We cannot, however, recover your lost data files. That is your responsibility. After all, that distorted looking size distribution may turn out to be the founding piece of evidence in a new branch of nanotechnology, if only you had a copy of it. So remember this: File/Database/Open Folder/Select File(s)/ARCHIVE (not Export).

Section III: Theory

Basic Operation

A beam of light is passed through the disc and used to clock the arrival time of particles as they move through a spin fluid of known viscosity and density. With the disc spinning, a small volume of particle suspension is injected onto the spin fluid-air interface, the meniscus. From the time, the particle size is calculated using Stokes' Law in a centrifuge. In addition, the attenuation of the beam, either by absorption or scattering, is used to determine the concentration.

To avoid hydrodynamic instabilities, the spin fluid is modified to obtain a gradient in viscosity and density that allows the particles to pass smoothly through the meniscus while maintaining laminar flow, a requirement for the use of Stokes' Law. When properly established, the gradient can be used over and over allowing multiple injections and the saving of time for multiple runs. In addition, when properly established, the gradient's effect on the spin fluid's density and viscosity is negligible.

Theory: Stokes' Law

Using Newton's Laws of motion, and assuming laminar flow, it is easy to derive the following equation:

$$t = \frac{18\eta_f \ln(R_d/S)}{\omega^2(\rho_p - \rho_f)\cdot d^2}$$

where:

t = arrival time
η_f = viscosity of the liquid medium without particles
R_d = radial position of source and detector
S = radial position of suspension surface (meniscus)
ω = radial velocity of the centrifuge disc, the rotational speed
ρ_p = density of particle
ρ_f = density of liquid medium without particles
d = particle diameter

Stokes' Law determines the fundamental relationships between particle size and the other parameters. For a size range of 10:1, the arrival times vary from 1:100, with the longest time corresponding to the smallest particle. If large particles sediment too rapidly to be timed with accuracy, one can change any of the following parameters, within practical limits, to slow down the sedimentation:

Increase the spin fluid's viscosity and density by choosing a more viscous liquid or by making mixtures of known properties (e.g. water and ethylene glycol). Note that the

smaller particles are slowed down as well. The change in viscosity is the bigger effect, with the change in density not counting for much typically, unless the liquid's density is close to that of the particle's density. A change in viscosity causes a linear change in arrival time. Working with liquid viscosities higher than approximately 100 centipoise is inconvenient.

Decrease the rotational speed of the spinning disc. This has a dramatic effect since the arrival time is inversely proportional to the square of the speed: halving the speed increases the arrival time by a factor of four. Since the BI-DCP allows for semi-continuous control over the rotational speed, changing this variable is often the best way to effect a change. Note that below about 600 rpm, depending on the spin fluid's viscosity and density, the gradient and integrity of the spin fluid's composition will be compromised leading to mixing.

Increasing the spin fluid's volume will decrease S, the radial position of the meniscus. This decreases the arrival time since the particles have to travel through a longer distance in the liquid. The calculation of S depends on the disc's inner dimensions. Furthermore, the change in arrival time is a weak function of the change in spin fluid since the variation depends on the logarithm of S-1. Using more than 25 to 30 mL of spin fluid becomes inconvenient since, upon stopping the disc, the liquids slosh out of the disc's center hole.

If small particles sediment too slowly, one can either decrease the spin fluid viscosity, increase the rotational speed, or decrease the spin fluid volume.

For broad distributions, it is important to reach a compromise that allows at least many seconds of flat baseline at the beginning of the experiment (early times correspond to larger sizes) with the need to complete the experiments in a reasonable time (long times correspond to smaller particles). The Modeling Utility feature is useful in this regard and will be discussed in Section IV: Software Overview.

Error Calculations Using Stokes' Law

Stokes' Law also affords one the opportunity to estimate errors in the calculation of diameter from estimated errors in the various other parameters. To illustrate the errors, it is best to rewrite the equation as follows:

$$d = \sqrt{\frac{18\eta_f \ln\left(R_d / S\right)}{\omega^2\left(\rho_p - \rho_f\right)\cdot t}}$$

The relative error in d is inversely proportional to the relative error in rotation speed. Since the speed is digitally controlled to better than +/- 0.01%, this error is insignificant.

The relative error in d is inversely proportional to the square root of the relative

error in the density difference. In most cases, the error contribution is less than a few percent in d. For example, for a polymethylmethacrylate (PMMA) latex, with density of 1.20 +/- 0.02 g/cm^3, in water at room temperature, with a density of 0.997 +/- 0.001 g/cm^3, the difference and propagated error in the density difference is 0.203 +/- 0.02 g/cm^3. While this represents a nearly 10% error in the density difference, it only represents a nearly 5% error in the calculated diameter because of the square root relationship.

As the density difference becomes smaller (e.g. polystyrene latex in water: (1.051 – 0.997) g/cm^3), the relative error becomes larger; and as the density difference becomes larger (e.g. TiO2 in water: (4.20 – 0.997) g/cm^3), the relative error becomes smaller.

The relative error in d is inversely proportional to the square root of the relative error in t. While the time is known accurately, it is the error in determining the starting time that contributes most to this error. There is a finite time to inject the sample and press the start button. In the worst case, this error might be 1 second. If there is a baseline of 10 seconds before the signal begins to change, then the error is 10% at this time with a corresponding 5% in diameter. As time increases, this error drops significantly, reaching just 1% at t = 50 seconds. Remember: These estimated errors are based on the maximum estimated error in the starting time.

The relative error in d is proportional to the square root of the error in viscosity. The biggest error in viscosity comes from its variation with temperature. For most liquids around room temperature, the viscosity varies by about 2%/^{o}C. Thus, the error in calculating d will vary by 1%/^{o}C. This means that if the sample is actually at 22 ^{o}C or 24 ^{o}C and you input 23 ^{o}C for the temperature, the viscosity is calculated at 23 ^{o}C and the propagated error is approximately 1%.

For short runs at any speed, or long runs at low rotational speeds, the temperature of the sample during the run is fairly constant and can be estimated by reading the value on the LCD and using that in the calculation. For longer runs or high speed runs, it is worthwhile preheating the instrument by running it at the higher speed and preheating the spin fluid and suspension liquid to bring all these temperatures to within 1 ^{o}C. An alternative approaches is to actively remove the heat by placing a suitably-shaped plenum over the exit filter on the top, rear of the machine and attach the other end to a fan pulling the air up and out of the instrument.

Before estimating the errors in d from the errors in the radial positions Rd (detector) and S (meniscus), it is necessary to describe how these values depend on the disc cavity parameters.

Disc Cavity Geometry

The disc cavity is a cylinder with a radius Rc that is much larger than its height w. The distance w is the distance between the inner walls of the disc. The total volume of the disc cavity is therefore equal to $\pi Rc^2 w$. When spinning and partially filled with a volume

of liquid V, the total volume of the disc cavity is the sum of V plus the volume of the smaller, empty cylinder determined by the meniscus's radius S. This simple relationship is given algebraically by the following equation:

$$V + \pi S^2 w = \pi R_c^2 w$$

When Brookhaven calibrates a disc, we determine w and R_c. Once these values are known, the radius of the meniscus, S, can be determined for any injected spin fluid volume V. When V = 5.00 mL, the radius of the meniscus is called R_d, and this is the position of the detector after the instrument is properly aligned. (See Appendix II for alignment procedures.) A typical set of values is w = 0.6340 cm, R_c = 5.0720 cm, and with V = 5.00 mL, a calculated R_d = 4.8182 cm.

Errors from Spin Fluid Volume and Alignment

Where do the errors come from with disc cavity dimensions and the spin fluid volume? The errors in w and R_c are approximately +/- 0.001 cm. These are small and lead to insignificant errors in the calculated diameters d. The larger errors come if one does not use a Grade A volumetric pipette for the 5.00 mL used in alignment of the disc. DO NOT USE A SYRINGE. The ability to read the volume in a typical syringe is limited to perhaps 0.2 mL. Thus, instead of a spin fluid volume of 15.0 mL, you might inject 14.8 or 15.2 mL. What are the consequences?

Given w = 0.6340 cm and R_c = 5.0720 cm, when V = 15.0 mL, S = 4.265 cm. And when V = 15.2 mL, S = 4.254 cm. The difference in S is small because it is the result of subtracting a smaller number off the larger number (R_c^2) and then further dampening the effect by taking the square root. Furthermore, d varies in proportion to the square root of the natural logarithm of (R_d/S). So the error in d from a 0.2 mL error in V, using R_d = 4.8182 cm, is only 1%. That is acceptable. But do not compound it by using a syringe to determine accurately the 5.00 mL required during alignment. Always use a calibrated pipette that is good to 1% or better (+/- 0.05 mL in 5.00 mL).

Turbidity and Differential Volume Distribution Calculation: Mie Scattering Corrections

Stokes' Law relates the arrival time of the particle at the detector's position to the particle diameter. The extinction of the light is also used to determine the amount of material at that diameter. Both diameter and amount are required to produce a distribution.

The incident light intensity I_o is related to the transmitted intensity I by the Lambert-Beer law:

$$I = I_o e^{-\tau \cdot L} = I_o e^{-\sigma \cdot Q_{ext} \cdot L},$$

Where, τ is the turbidity, σ is the particle's scattering cross section, Q_{ext} is the extinction efficiency, and L is the width of the cavity. The intensities are proportional to the signal

voltages. $Log_e(I_o/I)$ is proportional to τ. Thus, with no further corrections, a disc centrifuge photosedimentometer results in the differential turbidity-weighted size distribution.

It can be shown that σ is proportional to the differential volume distribution, a result first noted by Treasure as due to the finite slit width of the detector; however, Treasure's analysis was incomplete. For more details, see Chapter 10, "Detector Slit Width Error in Measurement of Latex Particle Size Distributions with a Disc Centrifuge", by Devon et. al., in Particle Size Distribution II: Assessment and Characterization, edited by T. Provder, 1991, American Chemical Society, Washington D.C.

Therefore, if the turbidity is divided by Q_{ext}, the differential volume distribution, dV/dD[1], is obtained. The integral of this as a function of diameter yields the cumulative distribution by volume. If dV/dD is divided by D, the differential surface area distribution, dS/dD (also called dA/dD), is obtained from which its cumulative distribution is obtained by integration. Finally, the differential number distribution, dN/dD is obtained by dividing dV/dD by D^3. In this way, once the proper Q_{ext} is determined, and continuing with the spherical assumption, all distribution information can be calculated.

Q_{ext} can be calculated from light scattering theory, specifically spherical Mie theory[2]. In order to calculate it, the wavelength, particle diameter, and the relative refractive index must be known. Fortunately, the BI-DCP determines the particle diameter. In addition, the wavelength of the light source is known (650 nm). Therefore, to complete the calculation, the refractive index of the particle and the spin fluid must be known, their ratio determining the relative value required by the theory. The relative refractive index is the ratio of the particle's refractive index and that of the liquid. If the particle absorbs light at 650 nm, then the square root of the sum of the squares of the particle's real and imaginary refractive indices is used in the ratio.

Until Brookhaven introduced the exact spherical Mie theory for calculating Q_{ext}, it was either ignored or assumed to vary as the diameter raised to some power. Thus, to compare BI-DCP results with legacy measurements, you may wish to choose no correction or one of the common powers if the historical data indicates what was used.

For strongly absorbing particles –carbon black is a primary example—from zero to perhaps 300 nm, Q_{ext} varies linearly with diameter. For white, non-absorbing latexes from approximately 50 nm to 350 nm, Q_{ext} varies as the cube of the diameter. Above 350 nm, but well before the first peak in the exactly calculated Q_{ext} from full Mie theory, such

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[1] Here D represents particle diameter to prevent confusion with the differential notation.
[2] Chapter 12, "Particle Size Analysis with a Disc Centrifuge: Importance of the Extinction Efficiency", by Weiner, Fairhurst, and Tscharnuter, in Particle Size Distribution II: Assessment and Characterization, edited by T. Provder, 1991, American Chemical Society, Washington D.C.

low-density, white, non-absorbing particles exhibit D^2 dependence for Q_{ext}. For all these reasons, Brookhaven also includes the option to use these historical approximations for Q_{ext}. However, it must be emphasized that they are no longer necessary and should not be used whenever the most accurate results are required.

Section IV: Software Overview

A general overview of the program and some of its important features are presented in this section. Double click on the BIC icon labeled BI-DCPLW Particle Size Analyzer. The main window with the last used set of parameters but no results is displayed as shown in Figure IV-1. Command buttons at the bottom of the screen enable the user to initiate measurements, reanalyze data, and visualize detailed tabular and graphical results. The menu bar of the main window has file utilities for the working with the database, various printout selections, and setup parameters.

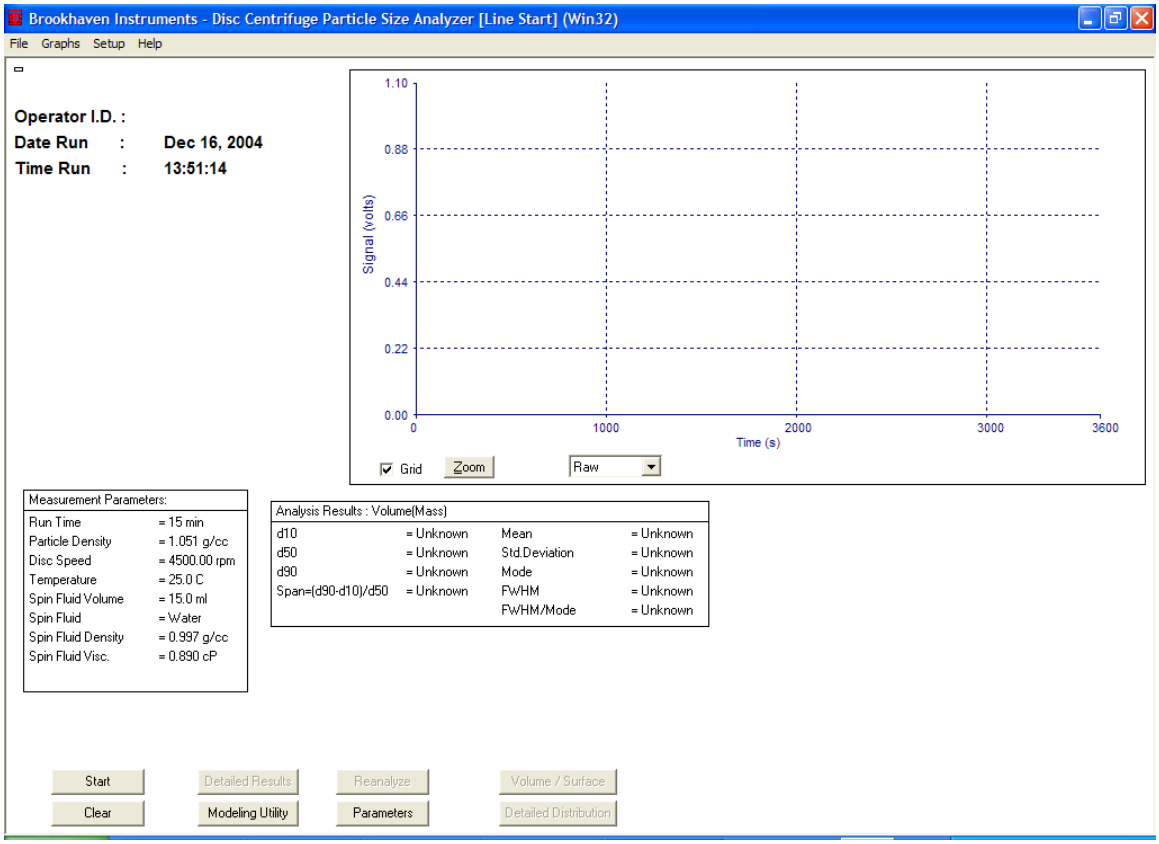

Figure IV-1: Start view when first running the program.

In the menu bar of the main window, click on **Setup/Setup Instrument Parameters**. The screen shows the disc parameter values. See Figure IV-2. These should be those that correspond to the ones for the disc that is actually mounted on the BI-DCP analyzer. Verify that these parameters are correct, and then click **Save** to preserve them for use with subsequent measurements. Occasionally, people leave the default values from an initial installation of the software, or, more commonly, they leave the set corresponding to a previous disc. While the errors doing this may amount to a few percent, it is good practice to verify that the disc parameters used for calculation (in the

Setup Instrument Parameters window) correspond to those of the mounted disc.

Each time your raw data is saved, the parameters at run time are saved with it. When you reanalyze you can alter the Sample I.D., particle density, etc., but you cannot change disc parameters.

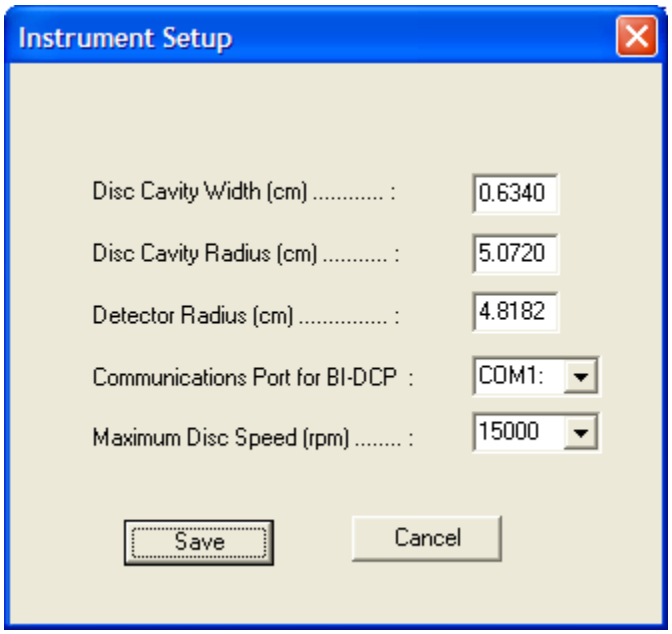

Figure IV-2: Instrument parameters setup window.

The disc calibration parameters (width, radius, detector radius at 5.00 mL) in centimeters are provided with each disc. Make sure these match what you see in this window. The detector radius must be determined (see Appendix II) using 5.00 mL.

The RS232 (serial) communications port is used for data transfer between the computer and the analyzer. From the pull down list box, select the communications port, used on the PC. If you don't select the correct communications port, then when you start the measurement, you will see a ″Com port initialization failed″ error message. You only have to input this parameter one time as long as you click **Save** when exiting.

With the PMMA disc the speed can continuously vary from 600 to 15,000 rpm. There is an optional, solvent resistant disc made of polycarbonate (brand name homolite). This is the BI-DSCR that can spin continuously from 600-10,000 rpm. From the pull down list box, select the maximum disc speed that corresponds to the mounted disc. In addition to selecting the maximum in software, there is a failsafe mechanism using an internal light source and diode looking at the reflection off the disc's hub. Shiny hubs correspond to the higher maximum speed standard disc; dark hubs correspond to the lower maximum speed optional, solvent resistant disc. You only have to input this parameter one time as long as you click **Save** when exiting.

Modeling Utility Window

If you are not sure how to setup the run conditions in the **Parameters** window, click first on the **Modeling Utility** command button on the bottom of the screen. The information displayed on this page is, for the most part, the same as that entered in the **Parameter** window. An example is shown in Figure IV-3.

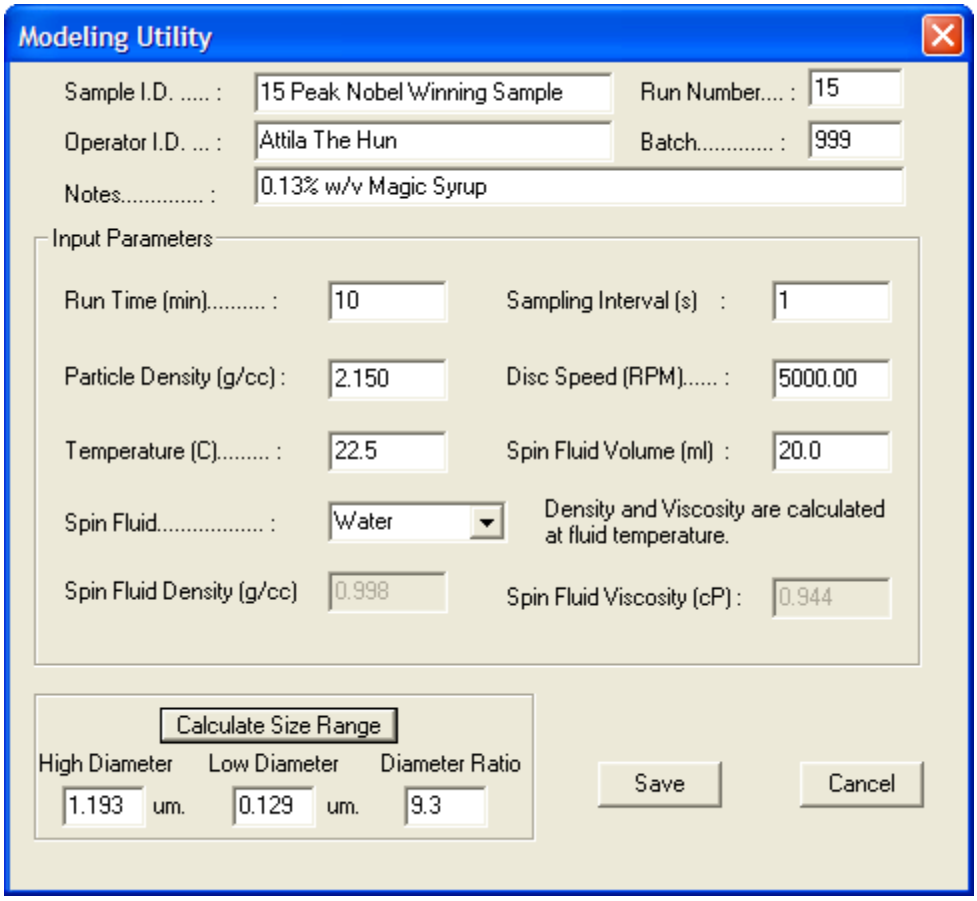

Figure IV-3: Modeling Utility variables and calculations.

The information in the top portion of this window is entirely for identification and labeling purposes. Enter whatever you wish. Note, however, that the Sample I.D. information is used to label files in the database. Therefore, to make it easier to recognize file contents, choose a Sample I.D. that will say enough to uniquely identify its contents. Labeling many files with "Latex" is a sure way to waste time trying to locate a particular file.

In the middle portion of this screen you enter variables. [Leave Sampling Interval at the default value of 1 second.] When finished, click **Calculate Size Range**. The high, low, and ratio are calculated and displayed. If you like the range, then click **SAVE**. This same information is then loaded into the **Parameters** window saving you time for preparing for the next measurement.

Here are some guidelines for optimizing the run conditions using the following guidelines:

Setting the Run Time

Except for narrow standards around a micron, use a minimum run-time of 5

minutes. For a narrow one micron standard, 3 minutes is sufficient. Increasing the run time will extend the low end of the size range measured.

Choosing the Spin Fluid Volume

Start with 15 mL for the spin fluid volume. Increase the volume to 20 or 25 mL to shift the high and low diameters to higher sizes. Decrease the volume to 10 mL to shift the high and low diameters to lower sizes. The High:Low ratio will remain constant.

Selecting a Spin Fluid

Please see the cover page of this manual for restrictions on fluids that may be used with the standard disc.

If the desired High Diameter cannot be achieved by using a slower rotational speed or higher spin fluid volume, consider using a different Spin Fluid for the run. Using a more viscous/dense liquid will slow the particles down as they sediment out of the suspension; thus, increasing the High Diameter measured in a run. For example, you can add sucrose, ethylene glycol (E. glycol), or glycerin (glycol) to water to increase the viscosity of the spin fluid. Choices with corresponding liquid density and viscosity are given in the pull down list box. If you select a composition not listed, or if you decide on using a completely different liquid, select first the **UNSPECIFIED** choice in the list box. Then write in the name of the liquid. Finally, you must then enter the liquid density and viscosity.

Whatever spin fluid is used it must be chemically and physically compatible to the extent that it does not cause aggregation or partially dissolve the particles. It must be reasonably easy to inject, and it must be easily removable from the disc when cleaning.

Depending on the density and viscosity of the liquid, somewhere between 600 -750 rpm, the spinning liquid will not be sufficiently pressed against the perimeter of the spinning disc to prevent mixing at the meniscus. You can easily observe this using the built in strobe and, if necessary, a little food coloring.

Input the particle's density.

Once you have found a satisfactory set of conditions, click on **Save** to save this information for the next run. This brings you to the main window again. From there, click the **Parameters** button at the bottom of the screen.

Parameters Window

Click on the **Parameters** command button in the lower part of the screen. Fill in the **Sample I.D.**, **Operator I.D.**, and **Notes** fields. The Sample I.D. is used in the Database section of the program for naming files, Therefore, care should be taken in

organizing files by the use of appropriate Sample ID's. Use the **Run Number** and **Batch** to distinguish between measurements made on the same sample.

Figure IV-4 shows the **Parameters** window. Unless you decide to change the values in this window, they will match exactly those from the modeling window. In this example, it was decided to change the run and batch numbers, the run time, and the temperature.

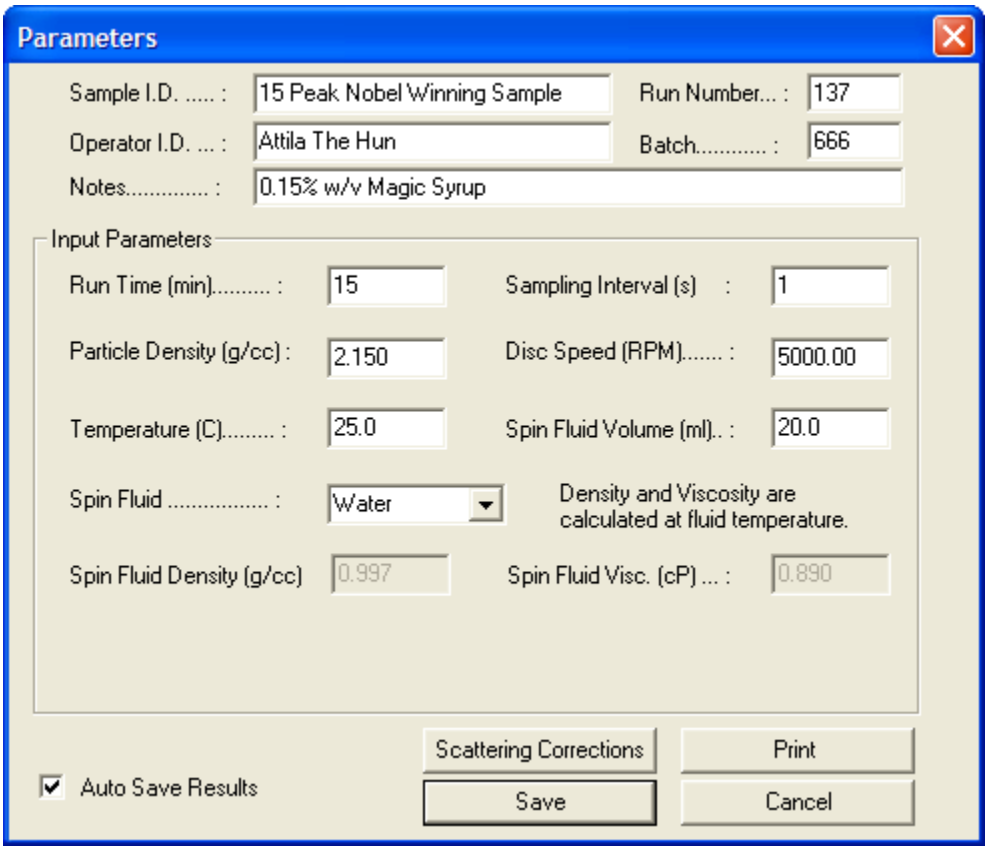

Figure IV-4: Selections in the Parameters window.

It is generally a good idea to check the **Auto Save Results** box. When this is done, the data is automatically saved into the folder currently open in the database. Since it is always faster to delete unwanted runs than it is to do runs over again, we recommend leaving this box checked.

Scattering Corrections Window

When you click the command button labeled **Scattering Corrections**, you will see a window similar to Figure IV-5.

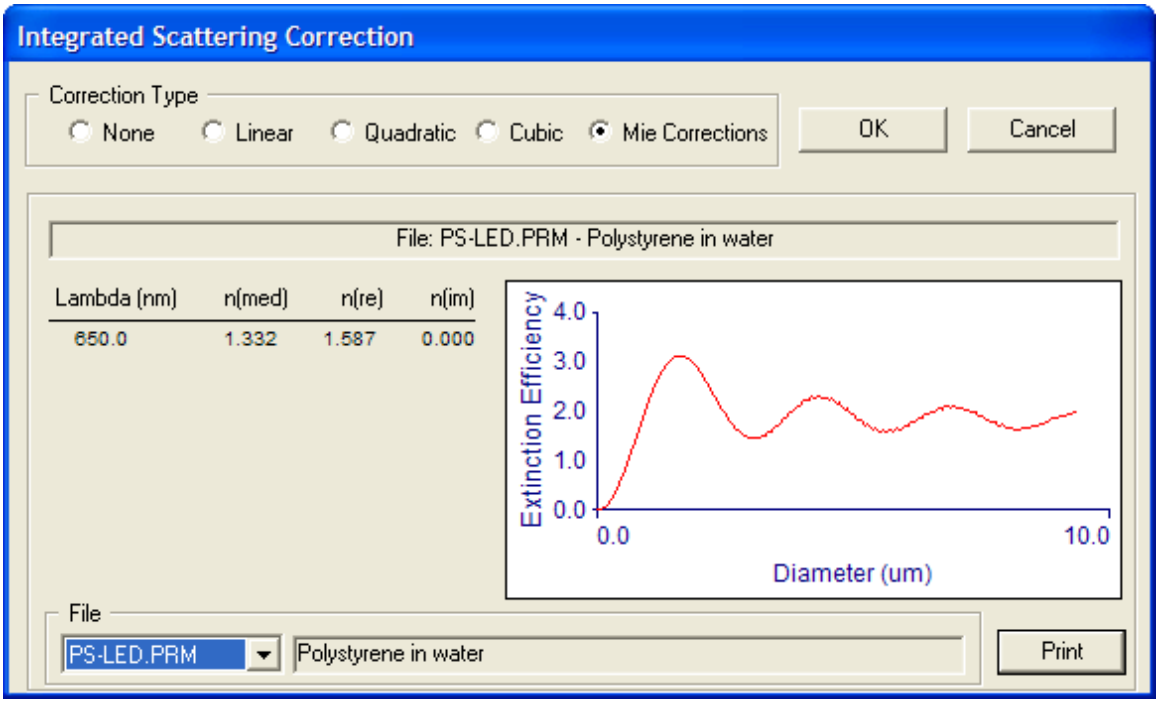

Figure IV-5: Scattering Corrections window with Mie selected.

In this window select Q_{ext}. As discussed in the section on theory, always use the full Mie correction for the most accurate results. Use the others only for comparison to legacy data. These include Q_{ext} varying as D^0 (None), D^1, D^2, or D^3.

The full Mie correction is shown for polystyrene in water at the wavelength of the BI-DCP, 650 nm. At that wavelength, the refractive index of the medium (water) is 1.332 and that for the polystyrene is 1.587. This is the real part that corresponds to the bending of light. The imaginary part, n(im), is zero corresponding to the fact that this latex is white and does not absorb light at 650 nm, a visible (reddish) wavelength.

In the region of the extinction efficiency curve, Q_{ext} vs. particle diameter, from zero to approximately 1.6 micron, the curve is rising. The first peak is at 1.6 micron. The shape of this curve is similar to that for many low-density, non-absorbing particles; however, the position of the peaks varies significantly with the ratio of particle/liquid refractive index.

Use the pull down list box to select from several common particle/liquid combinations where the refractive indices have already been taken from literature values. It is shown in Section VII: Data Analysis how to create custom Mie scattering corrections and add them to the pull down list box.

Click **OK** to return to the **Parameters** window. To save the changes and exit the Parameters window, you must click on the **Save** button. NOTE: If you click on **Cancel,** none of the values entered will be saved. Previously entered values will be used.

Normal View Window

When you have finished a measurement, the normal window view is displayed. An example, loaded from the database, is shown here in Figure IV-6.

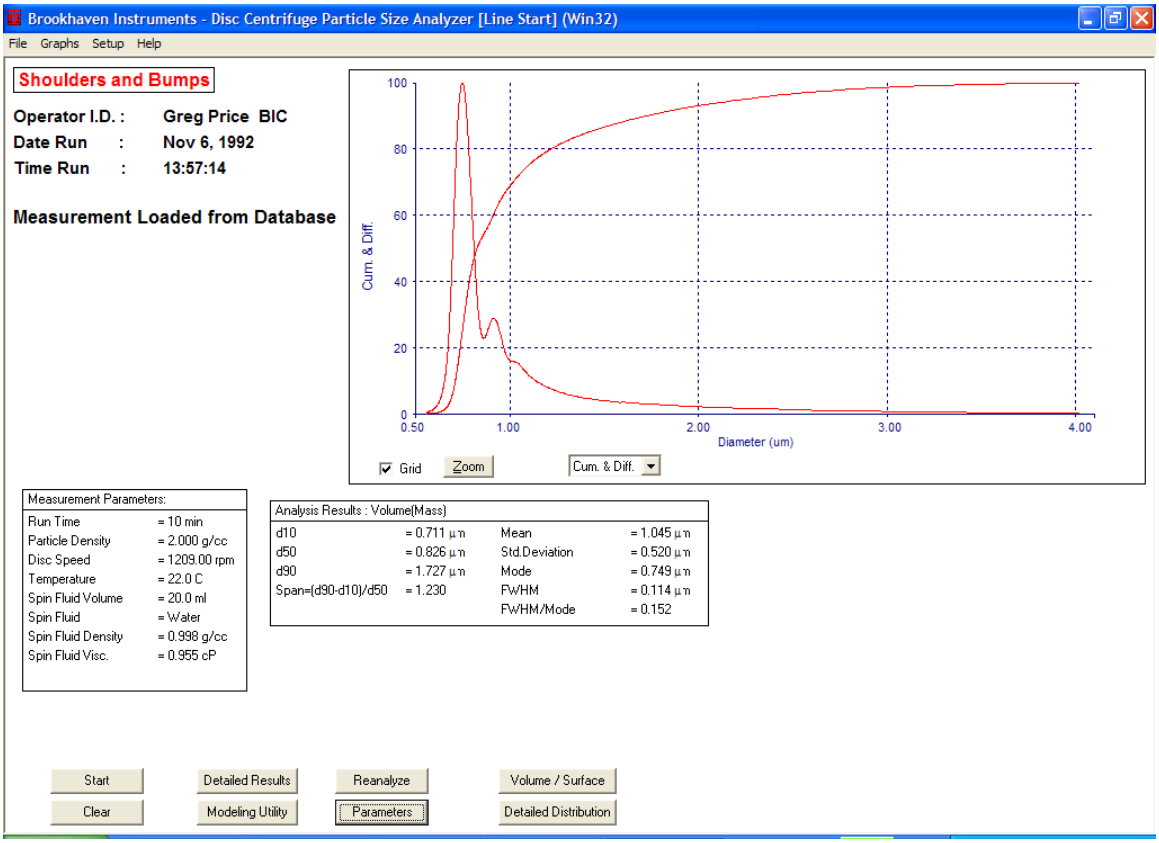

Figure IV-6: Normal window view.

Sample and operator ID and labels are given in the upper left of the screen. The graph here shows the differential and cumulative distributions weighted by volume. You can toggle through volume-, surface area- and number-weighted results by clicking on the button initially labeled **Volume/Surface**. Its name will change to indicate what the next view when clicked is. Correspondingly, the **Analysis Results** will also cycle through the three different weightings.

Measurement conditions and parameters are shown in the box to the left.

Click **Reanalyze** if you want to make any corrections except for run time and rotational speed that remain unchangeable after a run. You can, however, see the effect of varying the particle density or light scattering correction. This will help you to determine how robust the answers are.

The grid can be removed and replaced by checking the appropriate box beneath the graph. Likewise, the display can be cycled through raw data (signal vs time), differential distribution, cumulative distribution, or both as shown here.

Detailed Results Window

To obtain more detailed results, click the command button labeled **Detailed Results**. See Figure IV-7 for as an example.

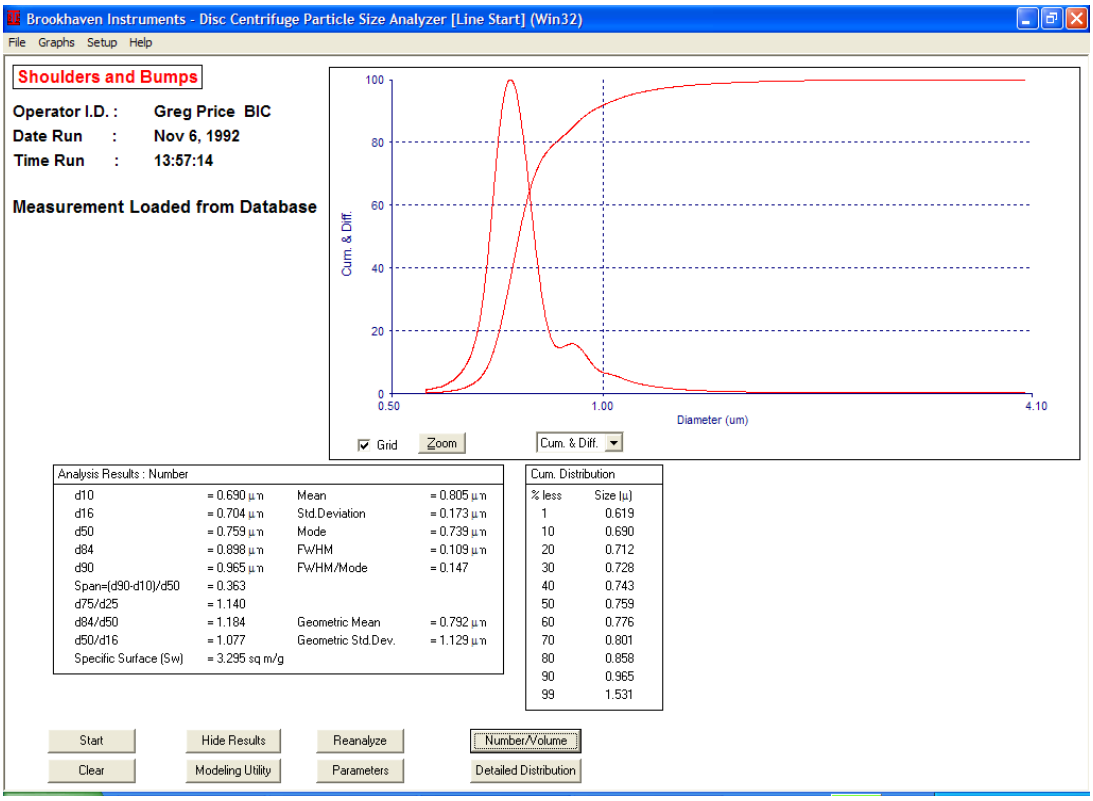

Figure IV-7: Detailed results, number weighted.

In this example, the toggle command button was used to bring the display for the graph and the tabular results to the number-weighted distribution. The diameters at various percentiles, for example the median called d_{50}, are all obtained from the cumulative distribution. Moments, such as the mean diameter, are obtained from the differential distribution.

In this view, various percentile diameters are shown such as d_{10}, d_{50}, and d_{90}. These

are the diameters at which 10%, 50%, and 90% of the particles by number are less than.

Two common measures of the width of the distribution can be determined by these percentile diameters:

- Relative span defined by $(d_{90} - d_{10})/d_{50}$
- The quartile ratio d_{75}/d_{25}, a value used by some tire companies to grade carbon blacks for use in the tread or sidewall of the tire.

Ground materials are often described by a 2-parameter, monomodal function called the Lognormal distribution. This is a Gaussian distribution on a log scale. When this is true, then the percentile ratios d_{84}/d_{50} and d_{50}/d_{16} are equal. By displaying these values, the user can determine if a particular single peak is well described by the Lognormal function or not. When it is, an estimate can be made of the Geometric Standard Deviation, one of the two Lognormal parameters. The other, the Geometric Mean Diameter can be determined from the entire data set. This is explained further in Appendix V.

In Section VII: Advanced Data Analysis, more information will be given on how to set baselines, analyze in detail bimodals, and obtain cumulative distributions at finer gradations than the 10% shown here.

Database & How To Use It

In the menu bar of the main window, click on **File** and then **Database** to examine the various data files. The view is split, as shown in Figure IV-8, into an upper window showing folders and a lower window showing files in an opened folder. Results are saved in the currently opened **Folder** as a **File** using the **Sample I. D., Date,** and **Time** as the file identifiers. Files are saved in folders using the **Save** or **Save As** under the **File** menu.

To create folders, click on **File/Database**. Click on **Create Folder**. Enter a folder name; it can be more than 8 characters; it may include spaces and punctuation. Double- click on the Folder to open it. The file folder icon *opens* when the folder is active. Single clicking on a folder selects the entire folder but does not open it. When selected, but not opened, the entire folder and its contents may be deleted, printed, or archived by clicking on **Delete Selected Folder**, **Print Selected Folder**, or **Archive Selected Folder**.

Select a single file by clicking on it. Select a string of consecutive files by clicking on the first, then, while holding down the Shift key, click on the last. Select a string of nonconsecutive files by clicking on the first, then, while holding down the Control key, click on any number of files, consecutive or not, one at a time. When selected, a single file or multiple files may be deleted, printed, or archived by clicking on **Delete Selected File(s)**, **Print Selected File(s)**, or **Archive Selected File(s)**.

Files are **archived** in a binary format in C:\Bicw32\dcplw\Data\filename.bak using the extension .bak by default. The extension .bak is automatically appended. Do not add it a second time. You may change the drive\directory, but you will then have to remember it.

If you do not change the filename, the default filename, dcplw32.bak, is used. You can archive an entire folder by selecting it, but not opening it. You can archive single files or groups of files. When archived to an existing .bak file, the selected folder or file(s) are added to it.

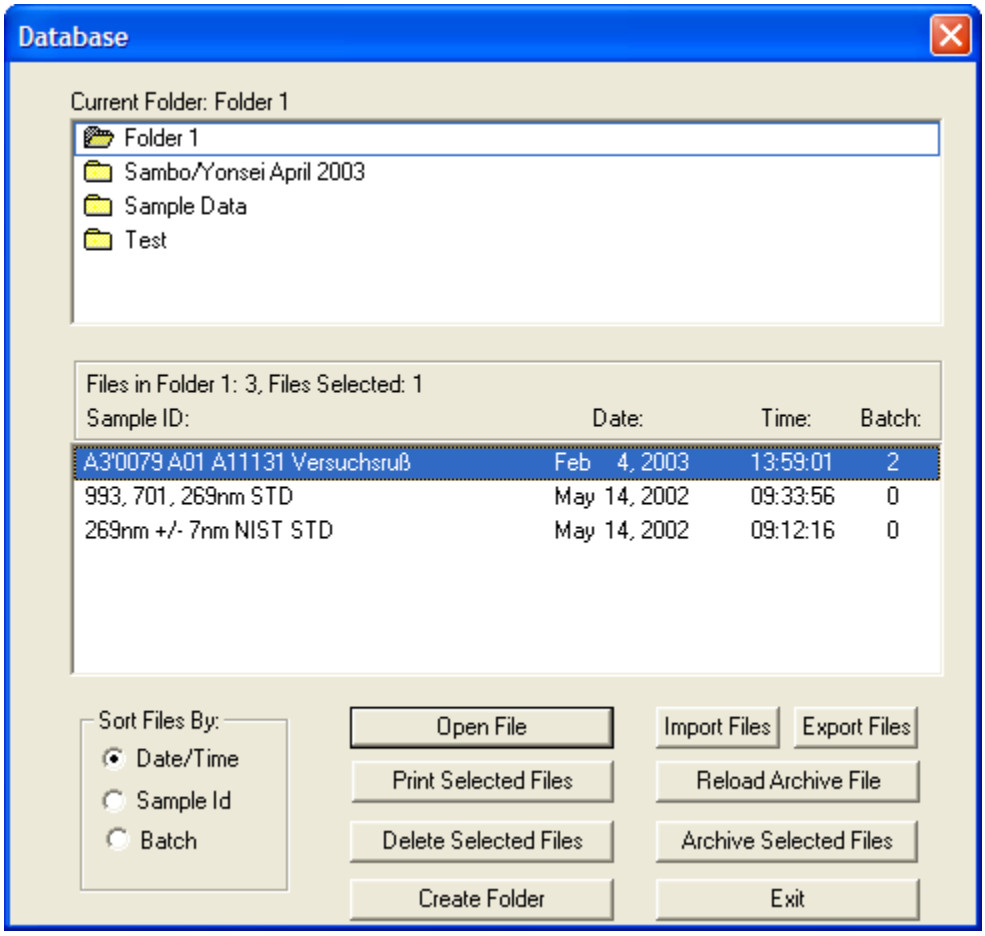

Figure IV-8: Database and its uses.

Click **Reload Archive File** when you want to reload an archived file. Click on the drive and directory where it was stored. The default path, mentioned above, is C:\Bicw32\dcplw\Data\. However, if you archived the folder\file(s) in another path, you must select that drive\directory and the correct filename. Files are reloaded and merged into the currently opened folder.

Double clicking on a file opens it. Alternatively, select the file by single clicking on it and then clicking on **Open File**. Once opened, you can reanalyze using different parameters, view, and print it. Or, you may want to use its parameters as the starting point for the next measurement.

You can create ASCII files suitable for use with spreadsheets and plotting programs. Select a file, and then click on **Export Selected File**. The format of exported files is given in Appendix IV. The raw data is voltage and time, so the ASCII files obtained from the database are for use by experts who wish to write their own data analysis program. ASCII files also have one other use. If you have an older, DOS-based BI-DCP, you can **Import** those ASCII files into this 32-bit Windows program, and then save them in the new, binary format. In this way, historic data can be viewed, managed, and reanalyzed using the latest Windows-based software.

A Special Plea from our Applications Department: Do not send ASCII files to Brookhaven for review. Do not send PDF's to Brookhaven for review. Instead, always send archived files for review. Archived files, when reloaded at Brookhaven, contain all the information associated with a particular run. And they can be used to reanalyze data. So be kind to your Brookhaven application engineer and send only archived files. Thank you.

Printing Options

The user has many choices for printouts. If any particular window has a **Print** command, then clicking it will cause the display as shown to print. This can be useful especially for the zoom window showing the baselines. Also, the tabular windows with the full cumulative distribution results allows for such individual printouts.

Generally, printouts are obtained by clicking on **File** and then on **Report Print Options**. An example is shown in Figure IV-9. Check your choices and then use the **Print Preview** command to see what you will get before clicking **Print Report**.

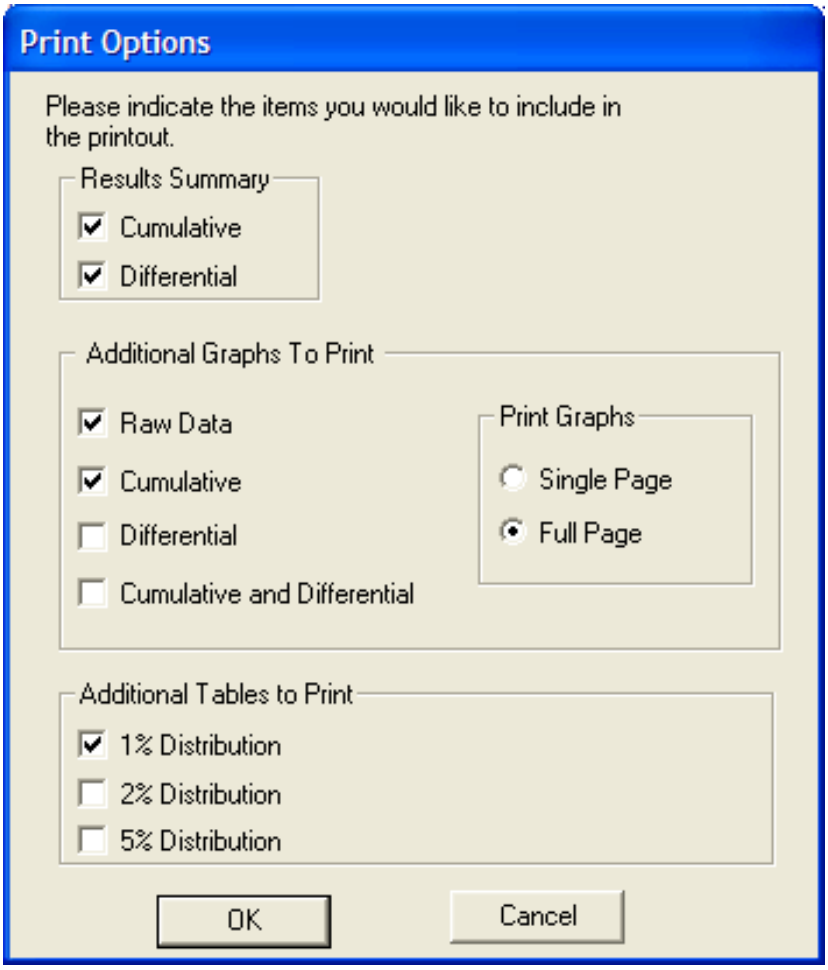

Figure IV-9: Print options window.

Section V: Sample & Gradient Preparation

The procedures described below contain some general information useful for every type of analysis. These procedures are not all embracing. They should be considered as guidelines. The actual procedures used will vary depending upon a number of factors. Among these are composition and type of suspending medium, amount of spin fluid, etc. Novices should make their initial measurements on relatively narrow size distributions that are well characterized. Do not make the common error of practicing with broad unknown size distributions until you have practiced with a standard. Narrow standards are also very useful for testing, from time-to-time, the integrity of the gradient, an especially useful procedure when performing serial injections. In addition, narrow standards can be used to test the internal temperature of a spin fluid, since the actual temperature will influence the calculated size through the viscosity.

Repeatability should be your first goal. And repeatability should be on the order of 1% or 2% on the Mean and Median (d_{50}) using the LIST mode. Use the modeling program to guide you in deciding run conditions for your samples.

Items You Need to Make Measurements

You will need the following items for sample preparation, to make a good gradient, and for cleaning the disc:

- A source of DI water or other pure solvents (for use with BI-DSCR solvent resistant disc) for spin fluids. Start with at least a 1 litre in order to make many runs. If the modeling utility indicates that you need to increase the viscosity for an aqueous-based spin fluid, you will need either pure ethylene glycol or glycerin.
- If you decide to use sucrose in water to increase the viscosity of water, use reagent grade sucrose and dry it before weighting to make accurate concentrations so the viscosity and density used are accurate.
- A litre of reagent grade methanol (MeOH, CH_3OH) for use in making gradients for some types of systems. Especially useful for polystyrene (PS) measurements.
- 250 mL bottle of Dodecane ($C_{12}H_{26}$) for preventing evaporative cooling with aqueous-based systems. May be used with some other solvents as long as Dodecane is not miscible and is less dense than spin fluid.
- 20 cc to 30 cc Syringe with Luer-lock, preferably glass, but can be plastic. Use for injection of spin fluid. Requires markings such that injected volume from 10 mL to 25 mL is good to +/- 0.2 mL or better.
- 30 cc Syringe with regular tip, preferably glass, but can be plastic (see below for caution about swelling of rubber plunger tips on plastic syringes in contact with dodecane). Use for cleaning of disc.
- 2 cc Syringe with Luer-lock, must be glass, for use in injecting dodecane or other liquid to prevent evaporative cooling. Should have markings for estimating down to 0.1 cc.

- 2 or 3 cc Syringe with Luer-lock, preferably glass, but can be plastic for injection of MeOH or other buffer liquid for use in making the gradient. Should have markings for estimating down to 0.2 cc.
- 2 cc Syringe with Luer-lock, glass for use with solvent-based samples, plastic for use with aqueous-based samples. Should have markings for estimating down to 0.2 cc.
- 4, 16-gauge, 4" long (10 cm) needles for use with Luer-lock syringes. One each for the MeOH or other buffer liquid, spin fluid, dodecane, and cleaning out the disc. To prevent mistakes, use color-coded tape to identify which syringe and needle is used with which type of liquid. NOTE: Some experts prefer a 14-guage needle for spin fluid delivery and an 18-gauge needle for delivery of sample, buffer liquid and dodecane.
- 3" (7.5 cm) of flexible rubber tubing to be attached to the 30 cc syringe for cleaning the disc. Cut a 45^{o} slice off one end to prevent it from attaching suction-like to the bottom of the disc when trying to suck out the spin fluid.
- Lots of small dilution/sample vials with screw caps. We recommend 25 cc dilution vials
- 40 W sonic bath with stand to keep dilution vials from falling below fill levels. If you have particles that adhere strongly, you may need a 100 W sonic probe with degasser cycle and duty cycle capability.
- (993 +/- 21) nm Duke Scientific Polystyrene NIST-traceable standard. See www.dukescientific.com, Catalogue 4009A or equivalent. Used for validation and also for checking integrity of gradient with serial injections.

To assist you with making measurements, the following items or the nearest equivalents are supplied with each BI-DCP:

DCP Syringe Kit

- **30 cc glass syringe with Luer-lock tip with 6" (150 mm) flexible rubber tubing for cleaning removing liquids from discs.**
- **20 cc glass syringe with Luer-lock tip**
- **2, 3 cc plastic syringes with Luer-lock tips. Do not use with dodecane and most solvents.**
- **2 cc glass syringe with Luer-lock tip. Use for dodecane.**
- **14-gauge needle, 4" long. Use for injecting spin fluids**
- **2, 18-gauge needles, 4" long. Use for sample and buffer liquid and sample injections.**

General Comments

The spin fluid and buffer liquid you choose must be compatible with the particles and disc as well as miscible with each other to form a good gradient. For example, with

organic pigments that might dissolve in alcohol, using MeOH (methanol) or EtOH (ethanol) for the buffer liquid or as part of the suspending medium can slowly dissolve the particles, shifting the size distribution ever smaller with time. Some alcohols will change the attractive forces between latexes suspended in water such that they aggregate, shifting the size distribution ever larger. Strong acids and bases, chlorinated solvents, acetone, toluene and other non-polar solvents are not compatible with the standard PMMA disc and will cause either immediate damage or slowly destroy its mechanical integrity. Check for solvent compatibility before using solvents for the first time.

Sample Preparation: General Comments

Some samples begin as dry powders; others are already in suspension.

If the sample starts as a dry powder, then proper sample preparation involves wetting the entire surface of each particle, forming a stable dispersion, and breaking apart unwanted aggregates. A stable dispersion must only be stable long enough to be measured. Thus, dispersing agents may differ from those used on products whose shelf life is much, much longer than the timescale needed for particle size determination in the lab.

Wetting and spreading are usually accomplished by a wetting agent, sometimes in combination with a small amount of a liquid with a lower surface tension than the final suspension liquid. Lists of wetting agents are available[3]. Wetting agents are supposed to lower the interfacial angle so liquid can spread over the particle surface.

Some wetting agents are simple phosphate- or sulfate-containing inorganic molecules like sodium hexametaphosphate (NaHMP) or tetrasodium pyrophosphate (TSPP). And some wetting agents are surfactants. In too high a concentration they form micellar particles. Although these particles are small (typically < 10 nm) and, as a percent of the total sample weight, usually insignificant, their presence can cause particles to aggregate in a process known as depletion flocculation. Wetting agents are generally used at low concentrations, say 0.02-0.05% wt/vol.

Once dry particles are wetted, if they are aggregated, you may want to break them down into primary aggregates, if the goal of the study is to study primary particles. Primary aggregates are face-face crystallites that are nearly impossible to breakdown further. Normally energy is applied to the sample to break up aggregates. Sometimes this energy is very little: gentle swirling and shaking. And sometimes the energy is a lot: ultrasonic probe. The energy should be enough for the aggregates to break apart, but not so much as to increase particle-to-particle collisions that promote aggregation. Short bursts of energy from an ultrasonic bath or probe are best. A good dispersion does not settle, aggregate, or otherwise change noticeably during the measurement time.

[3] T. Allen, 3rd ed. 1981, 4th ed. 1990, 5th ed. 1997, 'Particle Size Measurement", Chapman and Hall, publishers. See chapter on Dispersion of Powders.

Sometimes a wetting agent acts also as a dispersing agent such. Sometimes they do not, and for further dispersing after the aggregates have been broken apart, a dispersing agent is required. Dispersing agents include things like Triton X-100 (a polyethylene oxide polymer), sodium dodecyl sulphate (a surfactant) and dozens of others that can be found in McCutcheon's famous catalogues[4].

While stabilizing agents, also known as long-term stabilizing agents, constitute the third leg of sample preparation—wetting and dispersing agents constituting the first and second legs—for industrial products with long shelf lives, for particle sizing determination we are rarely concerned with times much longer than a few hours or a day. Stabilizing agents are often longer chain entities such as polymers.

Sample Preparation: Nominal 1 micron Polystyrene (PS) Latex in Water

A particularly good sample for many purposes is the Duke Scientific, NIST-traceable PS standard, catalogue number 4009A[5]. It is (993 +/- 21) nm, meaning this mean value is known to ± 2%, from 971 to 1,014 nm. It comes in a 15 mL squeeze bottle at a concentration of 1% wt/vol. This sample should be used to verify the instrument is working properly. It can be used to check periodically the integrity of a gradient during serial injection. It the answer is within spec, after temperature correction if any required, and the shape of the raw data is symmetric, then the gradient is still good. Obviously, you can only use this technique if the spin fluid and gradient are compatible with aqueous suspensions. And, last, by noting the answers for the 993 nm Duke standard before and after a longer run, one can bracket the temperature in the spin fluid and choose an average value.

To prepare this PS sample, add 3 mL of DI water into a 20 mL vial with screw cap. Add 3 drops of the Duke 993 nm. Mix gently by hand until the sample is homogeneously dispersed. Add 1 drop of MeOH to the suspension. Mix gently by hand.

If you add too much MeOH, the sample can aggregate and you will see particles sinking to the bottom of the vial. Since the minimum average visible size is around 30 μ, there are probably lots of aggregates larger than 993 nm but still too small to see. Assuming aggregates are not so large that they disappear by sedimentation below the beam, doublets and triplets will show up in the raw data. If baseline separated from the main peak, during analysis they can ignored by excluding them with the manual setting of the baseline. However, it is better if they are not there at all. Thus, do not add too much alcohol.

A rough approximation is that 40 drops from the squeeze bottle equals one mL.

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[4] McCutcheon's Volume 1, Emulsifiers & Detergents, has a large section on surfactants. Volume 2, Functional Materials, has sections on dispersants. Web address www.gomc.com, then click on McCutcheon's Publications.

[5] Go to www.dukescientific.com. Click on Products, then Standards & Validation Materials. Look at the 4000 series.

Thus, 3 drops of latex in 4 mL (3 mL DI + 1 mL MeOH) is a dilution from 1% (opaque) down to approximately 3/160 x 1% ≅ 0.02% wt/vol. In this case, given the density of PS latex is so close to 1 g/cm^3, the units of concentration could also be given as vol/vol or even wt/wt.

This particular concentration will yield an acceptable signal:noise ratio. You can use two or three times as much latex and also get a good signal. For other samples, it might be better to prepare a different concentration. If the concentration is too high, the signal will saturate at 2.5 volts. Depending on the value of the baseline, typically 0.2 to 0.3 volts, if the signal saturates, you have to reduce the concentration. An approximation for a starting concentration is that the value should be around 0.5% vol/vol.

If the concentration is too high, even before saturation, you can get hindered settling. This will look a little like plug flow in the disc, resulting in a tailing effect in the raw data. If the concentration is too low, the signal:noise ratio is such that it may be hard to tell the difference between a real peak and noise.

A little practice with an unknown sample will help in determining a good compromise. If in doubt, start with 0.5% vol/vol. If you are use to wt/vol units for concentration, simply multiple this figure in vol/vol by the particle density. For example, with 4.2 g/cm^3 as the density of a TiO_2 sample, one would start with about 2% wt/vol or 20 mg/mL.

Sample Preparation: Carbon Black in Water

Because the typical carbon sample can vary from 10 nm to 300 nm, the surface interactions are very large, often leading to aggregation. Therefore, to make a well suspended sample of just the primary aggregates (a good example of a fractal particle), a lot more effort is required.

First, to wet the particles, 10 mg of carbon black are added to 2 mL of 100% EtOH in a 20 mL, screw-cap, dilution vial. The suspension is sonicated for 5 minutes in a 30 W ultrasonic bath at 50% power. Allow the sample to cool to room temperature. Using an ice-water mixture will hasten the process and take only a few minutes. Second, to begin the dispersing process, while sonicating in the bath again, very slowly add 6 mL of 0.1% vol/vol Triton X-100. Do not add this solution rapidly. If you do, you may trap particles in a gel-like networked structure. So add no faster than 2 mL/minute while constantly agitating the suspension.

Third, using a 250 W probe at 40% power and 50% duty cycle, sonicate the sample for 10 minutes. To prevent the liquid from boiling away, you have to surround the vial by an ice-water bath. Fourth, use a pipette to withdraw the 8 mL suspension, taking care not to collect any undispersed particles sticking to the walls of the vial. Empty the contents of the syringe into a clean, 20 mL, screw-cap vial.

Fifth, de-gas the suspension for five minutes using the de-gas mode of a sonic bath.

The degas mode is not a constant mode, but one that is intermittent. And finally allow the capped suspension to warm up to room temperature before using it.

This is an involved procedure that requires an ultrasonic bath with a degas mode and an ultrasonic probe with variable duty cycle. While some variations on this procedure are allowable, if you do not wet and then disperse the sample properly, you will detect large aggregates in the early part of the raw data measurement. These are indicative of a relatively few, large, agglomerates (aggregates of aggregates) that have not been properly broken up and coated with the Triton X-100 that acts as a dispersing agent. If you do not cool the sample at various steps, the liquid will boil away.

If you are not sure if any particular sample has been prepared properly, add more time to one or more of the sonication steps and then see if the size has shifted lower. If it has, then your original procedure was not sufficient. With a good preparation, the sample will not aggregate for a very long time, allowing the overlay of measurements made months apart.

Gradients

A long time ago in the history of particle sizing by centrifugation it was discovered that injecting a sample into a spinning liquid too often resulted in hydrodynamic instability: For a variety of reasons, including mechanical ones (viscosity and density differences), as well as thermal, particles did not follow Stokes' Law and sediment under laminar conditions. It was discovered that if a series of liquids of ever decreasing density were layered on top of the spin fluid, that the mechanical reasons for instability were rare. Eventually, it was found that one could use a small volume of a single, so-called buffer liquid to form a gradient with the spin fluid and achieve hydrodynamic stability conditions.

Today there are a number of simple methods for forming this gradient and one will be presented here. Remember: This buffer is required for good and repeatable separation of particles. A good gradient can be used multiple times using serial injections, simply remembering to increase the spin fluid volume in the software to account for the increased distance the particle travels.

Here is a table of typical spin fluids with corresponding buffer liquids that together form the gradient:

Spin Fluid	Buffer Liquid

Water	Methanol
Water	Ethanol
Sucrose Solutions, 1-50% wt/wt	Water or less concentrated sucrose solutions
Ethylene Glycol	Water
MethylEthylKetone	Dodecane

Clearly, the spin fluid must be chemically compatible with the buffer liquid and it must be miscible. Furthermore, the buffer liquid must be less dense and less viscous than the spin fluid. There are lots of pairs that are suitable. Start with choosing a suitable spin fluid for the particles and select the buffer liquid accordingly.

Forming An Internal Gradient: Water/MeOH Example

Assemble the liquids: spin fluid (15 to 25 mL, typically), buffer liquid (0.2 mL, typically), and the evaporative cooling liquid, often dodecane (0.1 mL typically).

Depending on the liquid, select the appropriate syringe. For example, a plastic syringe with a rubber cone on the end of the plunger while acceptable for water, is unacceptable for use with MeOH or dodecane, both of which swell rubber. So for these liquids, select glass syringes. Also, since you use small volumes of these liquids, use a 1, 2 or 3 mL syringe, something with markings every 0.1 or 0.25 mL so you can easily judge the small volumes required.

It is here assumed that you have already used the Modeling Utility and know what rotational speed you will use and what Spin Fluid volume you will inject. It is also assumed that the disc cavity is clean and dry. Folded paper towels pushed to the bottom of the internal cavity while rotating by hand the disc is a useful way to dry the disc, but only after all particles and liquids have been removed and rinsed away.

Prepare a small syringe with an 18-gauge needle 4 inches (10 cm) long. Suck up a tiny amount, no more than 0.1 mL of dodecane, and lay the syringe aside. Do the same with another syringe but using this time 0.2 mL of 100% MeOH. Lay it aside as well. Assuming you have determined that 15 mL of water is the spin fluid (perhaps with a small amount of dispersing agent used in the sample preparation), fill a 20 to 30 mL syringe using a 14-gauge needle 4 inches (10 cm) long with a little over 15 mL. Lay it aside.

The next steps need to be followed exactly so as to form a good gradient.

With the disc stopped, inject the 0.2 mL of the MeOH into the dry disc. Invert the spin fluid syringe and gently expel bubbles and excess liquid until the plunger reaches exactly the 15.0 mL mark. With just a little pressure against the side of the plunger to prevent leakage out of the needle, insert the needle into the injection port BUT DO NOT INJECT the spin fluid. Press the MOTOR button on the DCP. WAIT the second or two until it reaches speed. THEN smoothly and briskly inject the spin fluid, taking no longer

than approximately three seconds to empty the syringe.

Immediately inject the 0.1 mL of dodecane. WAIT at least five minutes to establish mechanical and thermal equilibrium. This is important: Do not inject a sample and initiate measurement for at least five minutes after setting up the gradient. When properly set, a gradient can be used for many hours and cleaned only once. To check its integrity, one can inject narrow, known standards or reference materials that, at the speed selected (you can't change speed once the gradient is made), will rapidly transit the spin fluid. If the gradient is still good, the signal will be narrow, symmetric and result in the same answer as before.

Injection of the sample follows and is discussed in Section VI on making a measurement.

Section VI: How to Make a Measurement

Please review Section V to ensure you know how to make a suitable sample, how to select a spin fluid and compatible buffer liquid, and how to model and thereby estimate a suitable rotational speed and injection volume. Also, please review Section V on how to make a gradient. Establishing a good gradient is the key to making a good measurement using the DCP.

Remember: After a measurement, you can recalculate changing the particle density, the liquid's density and viscosity, reset the baseline, changed the look of the graphs, even change the light scattering correction. But you can't change the gradient, the speed of the measurement, the spin fluid volume, or the sample preparation. So pay attention to these details *before* you make a measurement.

RUNNING A SAMPLE

NOTE: It is recommended that the instrument be switched on 20 minutes prior to use in order to obtain stable operating conditions. If, from experience, you know that by the end of a long, high-speed run, the liquid in the disc will be at 28 ^{o}C, then warm up the spin fluid, the buffer liquid, the sample dispersion to this temperature to within one or two degrees. If you are not sure if a run will significantly raise the temperature of the liquids spinning in the disc, do a trial run with just the spin fluid. Use a duration that is at least as long as the expected measurement time from the modeling utility.

Any time spent practicing will be paid back with good results.

1. Prepare samples as described in Section V.
2. Prepare the gradient as described in Section V.
3. Setup the run conditions in the Parameters window. Here is a typical set of run conditions for a one micron polystyrene narrow standard in water:

Measurement conditions:

Run Time:	5 minutes
Disc Speed:	4,000 rpm
Spin Fluid:	Water
Spin Fluid Volume:	15.0 mL
Particle Density:	1.051 g/cm^3
Temperature:	Enter 23 ^{o}C.
Liquid Density:	0.997 g/cm^3, automatically calculated
Liquid Viscosity:	0.993 cP, automatically calculated
Buffer Liquid:	Internal gradient using 0.2 mL, 100% MeOH
Evap. Barrier Liquid:	0.1 mL, 100% dodecane

4. When ready, use a 1 or 2 mL syringe with a 4 inch (10 cm) long, 16- or 18-guage needle to inject briskly about 0.2 mL of the suspension.

5. Immediately press the START button on the DCP or click the START button on the screen. This establishes t = 0, and if you are efficient, you can press or click start while in the middle of the injection. Thus, the error in the start time should be no greater than 1 second, possibly a fraction of a second. For runs of a few minutes or more, such an error is insignificant as long as there is at least ten to twenty seconds of reasonably flat baseline before the signal starts to rise.

Monitoring the Run

Observe the sample in the disc. Use the built-in strobe to freeze the motion of the disc. You should be able to observe a clearing of the liquid near the surface. In the case of a mixture of narrow peaks, you can see the rings corresponding to different sizes. For broad distributions, you cannot see individual rings; however, you can see the leading edge as it moves towards the perimeter of the disc, and the trailing edge as it clears the meniscus.

While the sample is running it should be observed, periodically, for any unusual behavior, such as turbulence or mixing. This can be seen as a swirling motion of the liquid when the strobe is on. Or, one might observe the leading edge of the sample suddenly dash towards the perimeter of the disc, filling the entire disc with an apparently homogeneous suspension.

Observe the monitor to ensure that the data collected is a smooth curve (taking the inherent noise in the detector signal into account). When streaming occurs the signal often remains abnormally high for a long time indicating the sample has been homogenized and is not following Stokes' Law.

Having set the duration in the Parameters window, the run will automatically stop on completion. If the run appears to be going badly—steaming explained below as explained below—you can stop the run manually by pressing the Motor key on the DCP and clicking on the Stop button in the program to terminate data collection.

Steaming can occur for a variety of reasons. Ultimately, streaming is caused by non-laminar flow conditions. Without a proper gradient, the injected particles may enter the liquid at too high a speed causing turbulence and streaming. Thermal gradients can invert the hotter layer below the colder layer nearer the meniscus and mix the sample causing streaming. And, if particles attain too high a velocity, they can cause turbulence and mixing.

A proper gradient reduces the chance of streaming due to the entrance velocity of particles. Preheating the liquids and waiting for thermal equilibrium before injecting the sample reduces the chances of thermal problems. Using a more viscous and dense spin fluid, and a lower rotational speed, reduces the chance of turbulence due to excessive velocities inside the spin fluid.

DO NOT OPEN the analyzer door while a sample is running. A cutoff switch will stop the motor and require a new setup.

Stopping the Run

The duration of the run is the same as the Run Time entered in the Parameters window. Data collection will automatically stop when this time has elapsed and the data are saved. This is the normal completion mode.

The disc will continue to spin until the MOTOR button on the analyzer is pressed. That is, data collection, and disc rotation are separate functions. It is this feature that allows for serial injections.

NOTE: Once the disc stops, immediately clean it. Do not go on break, to lunch, or to watch a soccer game. Clean the disc. Dirty discs with embedded particles are a major cause of problems with subsequent measurements.

Cleaning the Disc

Except for serial injections, you need to start with a clean, dry disc.

If the suspension tends to spill out when the disc is stopped, gently pull slightly forward as you push up on the metal cylinder holding the thermistor in front of the disc opening. Then press the CUT button on the DCP's keypad. In the LCD window, you will see three choices. Enter the #1 on the DCP's keypad to retract the head. Wipe up any excess liquid and particles.

Use the large syringe or other siphoning arrangement, with flexible tubing attached, to withdraw the suspension from the disc. The tubing should be long enough to reach down to the bottom of the disc cavity. Cut the end of the tubing at 45^{o} to prevent this end from becoming stuck via suction on the bottom of the disc.

If you use a rubber-tipped plunger on a plastic syringe, note that dodecane, an oil, can quickly swell and freeze the movement of the plunger. To prevent this, inject a milliliter of soapy water into the disc and press the Mix button on the DCP's keypad to emulsify the dodecane. Press Mix again to stop the action. Alternatively, use a glass syringe to remove the spin fluid, buffer liquid, dodecane, and particles.

Now inject 10 – 15 ml of a dilute soap solution into the disc cavity. Press the MIX button on the analyzer. For samples that tend to coat the disc walls, let the cleaning action continue for as long as it takes to remove coated particles. Press Mix again to stop the action. This should remove residual particles. Remove the liquid and repeat this rinsing procedure until the disc cavity is clean.

The final rinse should be with deionized water. Dry the disc cavity with a paper towel folded such that it can be pushed into the cavity and ride along its inner perimeter.

The disc is made of a relatively hard plastic, but it can be scratched, so use non-abrasive paper towels. Clean the disc thoroughly and carefully.

NEVER LET A SAMPLE DRY IN THE CAVITY. Remove liquid and particles immediately after the disc stops. Allowing liquid to evaporate will almost certainly result in particles stuck to the walls of the disc. If you do not properly maintain the cleanliness of the disc, your results will suffer over time.

Cleaning does not take long, perhaps a few minutes in most cases. However, if you are running the same samples over and over, to save time in preparing gradients and in cleaning the disc, consider serial injections. In this case, you must establish a good gradient and from time-to-time test it by injecting a narrowly dispersed standard. The gradient is still useable if the shape of the raw curve is still symmetric and the result within expected limits. Just remember to increase the Spin Fluid Volume by the small amount of each previous injection.

Section VII: Advanced Data Analysis

Setting the Baseline Manually

From the main window, please click on **Zoom** to enter the window shown in Figure VII-1. In this window you can display the raw data curve as shown below or the cumulative distribution, the differential distribution, or both distributions by using the pull down list box in the middle of the right side of the window. With the raw data curve displayed as shown here, the time, diameter, and signal voltage are displayed corresponding to the location of the cursor. The cursor can be moved left and right either by clicking the **Left** and **Right** buttons or by clicking at any point in the graph.

The graph scales can be changed by clicking on the **Manual** button and entering the desired X and Y ranges. Then click anywhere on the graph to enable the changes.

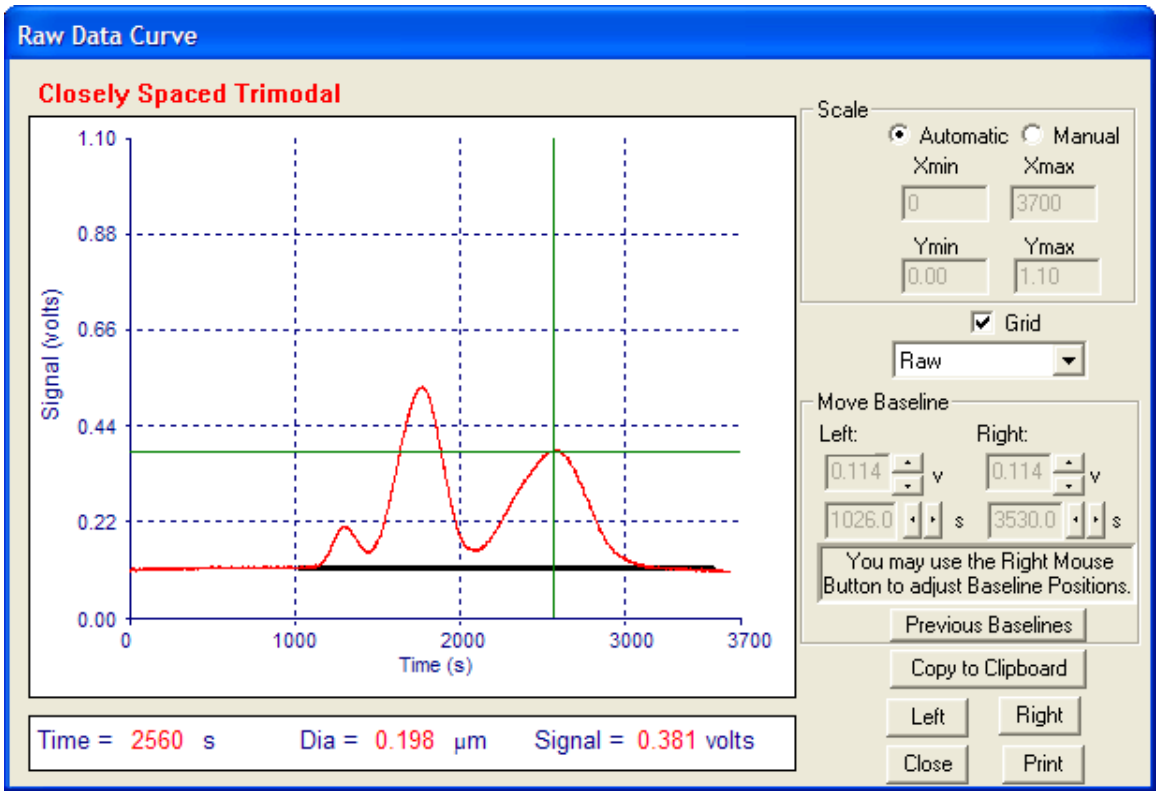

Figure VII-1: Zoom window for setting baselines manually and for reading data points individually.

The baseline, shown in a heavy, dark color on the screen, is automatically set to cover all the features obtained in the run. You may wish to reset the baseline to examine just one peak or a group of peaks or you may want to see the variation in the size results by using your own judgment in placing the baseline.

To change the baseline positions, click on **Left** and **Right** up/down arrows to adjust the appropriate y-axis value for the voltage. Click on the **Left** and **Right** left/right arrows

to adjust the appropriate x-axis value for the time in seconds. Alternatively, use the right mouse button to drag up/down and left/right one side of the baseline. Then repeat for the other side.

If you do not like the baseline and think the original was better, click **Previous Baseline**. Once the graph scales and the baseline are set by the user, click on the **Close** button to exit the window. Any settings changed in the **Zoom** window are reflected in the main window. Specifically, if the baseline was changed, then the user is asked to verify the change. Once verified, results are recalculated with the new baseline. Again, when changing to a different data set, the user is asked once again to verify the changed baseline.

If you want to overlay (discussed below) the same raw data analyzed with different baselines, or using a different particle density, or with a different light scattering correction, you can do it provided you have saved changes under a new name. It is also useful to give it a new Sample ID to make it easier to distinguish in the file folders. After making changes, click on **File/Save As** and give it a new filename. You can tell the raw data is the same because the date and time stamps in the database are identical.

Detailed Distribution View

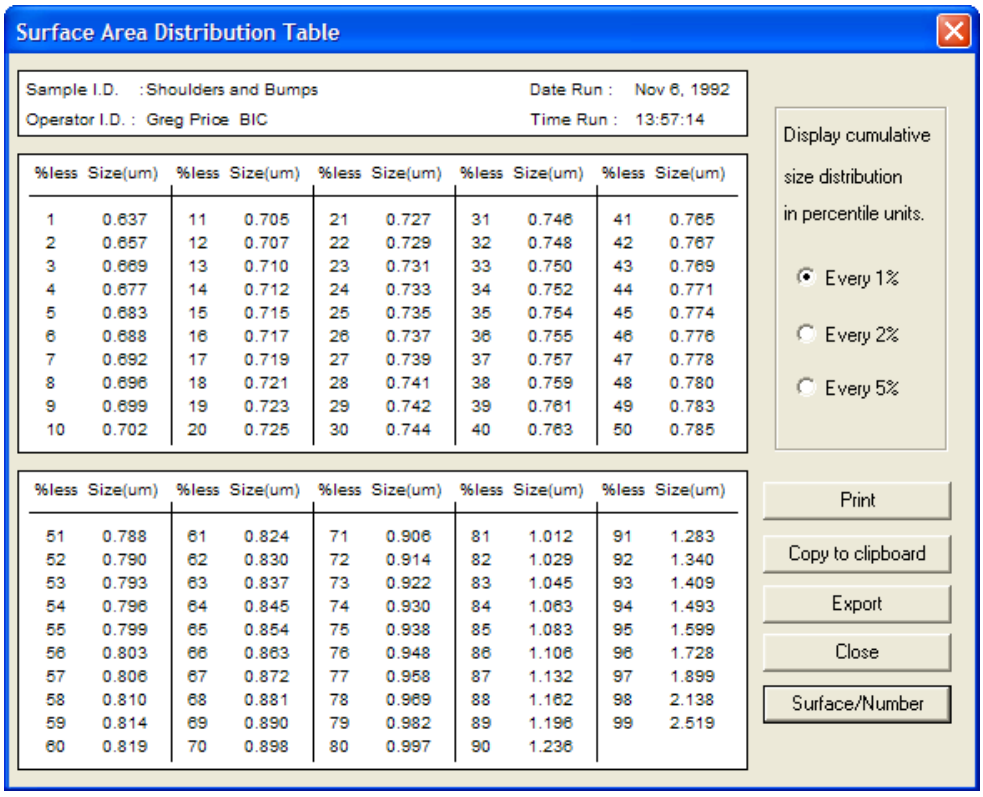

Figure VII-2: Cumulative Distribution tables

From the main window click **Detailed Distribution**. An example is shown in Figure VII-2. Check the 1%, 2%, or 5% view. Remember: The 10% view is standard and

appears when you click **Detailed Results** from the main window. You can toggle from volume to surface to number by clicking on the bottom right command key. You can print the window or select it for printing later from the **File/Report Print Options** menu options. To obtain a copy for inclusion in another document, click on **Copy to Clipboard**. To obtain an ASCII file that can be imported into a spreadsheet and used for plotting from your favorite program, click on **Export**. This will produce an ASCII text file with header information (run parameters, several calculated results) and a 3-column, comma delimited values consisting of size in microns, differential distribution value, cumulative distribution value.

Specialty Graphs

From the main window, please click on **Graphs**. There are four choices as shown in Figure VII-3.

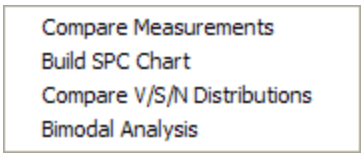

Figure VII-3: Advanced analysis using graph choices.

If you click on **Compare Measurements**, your next screen view is of the database. Open the folder that contains files you want to compare. Select up to 6 files. Then click on **OK**. The selected files are overlaid in the **Zoom** window. Select the view as raw, differential, cumulative or both. Select the scale as **Linear** or **Log**. Select manual scale and supply appropriate x-min and x-max values. Use the cursor to read specific values and the **Next Curve** command button to rotate through the selected curves. Use the **Copy to Clipboard** feature to obtain results for inclusion in other programs.

If you click on **Build SPC Chart**, your next screen view is of the database. Open the folder that contains files you want to compare. Select as many as you want. Then click **OK**. A statistical process control chart appears. The individual files are listed by Sample ID, date, time and a fourth column from your choice (from a pull down list box) of d_{50}, Mean, Mode, and FWHM (full width at half maximum, a measure of a single peak's width). Below this fourth column is the mean and standard error of the various values in the fourth column. [The standard error is the standard deviation divided by the square root of the number of measurements. Equal weighting is assumed.]

The values in the SPC chart are plotted vs. a constant increment to spread them out. The Mean is initially defined to be the CTL, the control value. The UCL, the upper control limit, is initially defined as CTL + 3 x Standard Error; and the LCL, the lower control limit, is initially defined as CTL – 3 x Standard Error. The user can change CTL, UCL, or LCL simply by typing in different values.

The plot is then used to determine any values out of control. The percent above and

below the limits are shown. The results can be printed or copied to a clipboard.

The SPC feature is useful for maintaining quality control on often measured samples of what should be the same material. Out of spec samples can easily be spotted in this way. The SPC feature is useful for batch-to-batch characterization, ageing studies, or spotting changes caused by processing conditions.

If you click on **Compare V/S/N Measurements**, your next screen view is of the database. Open the folder that contains the file for which you want to overlay the **V**olume/**S**urface Area/**N**umber distributions. Click **OK**. See Figure VII-4, for example.

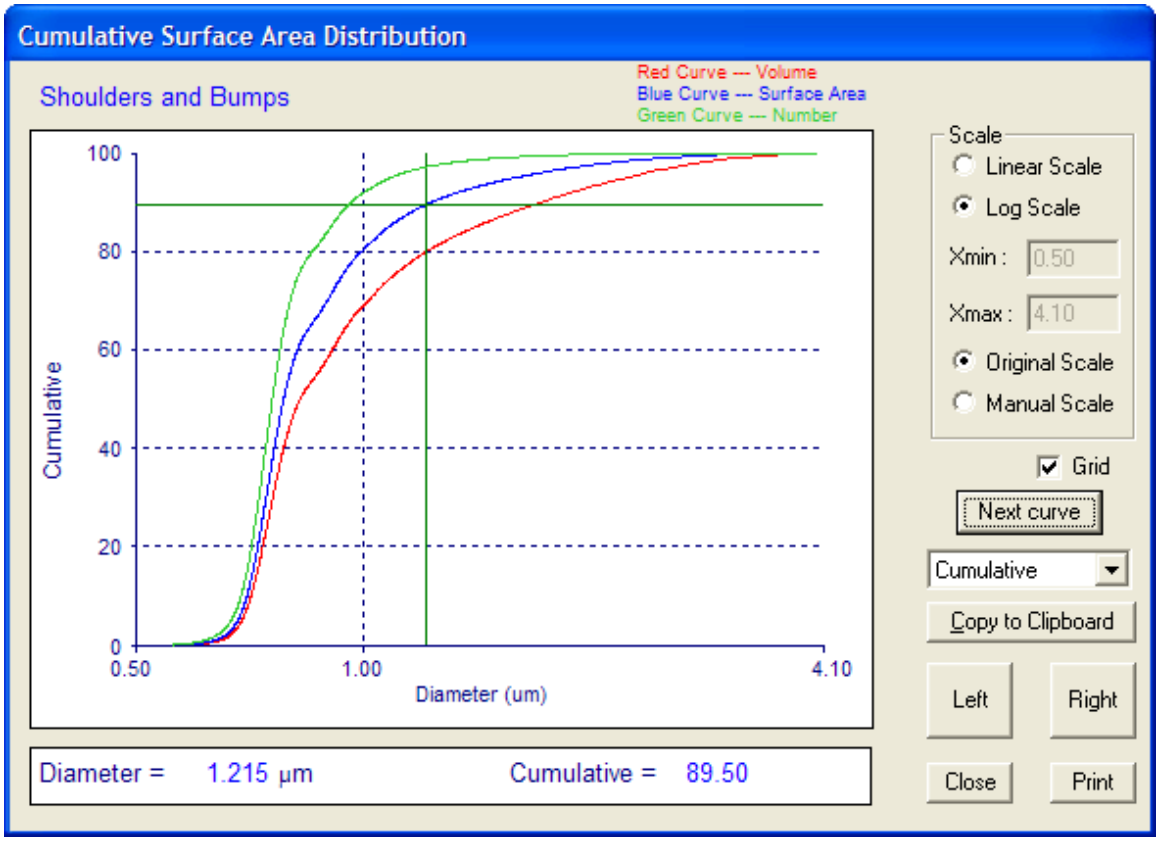

Figure VII-4: Comparing the volume, surface area, and number distributions.

You can display the data using a linear or log scale. You can manually change the x-min and x-max values or work with the automatically chosen, original scale. You can add or delete a grid, whose vertical values depend on the range of the x-axis. By toggling **Next curve**, you can rotate through the three plots with the cursor value of diameter, cumulative percent, and relative differential value (or both) changing appropriately. You can, of course, move the cursor to the left or right or click anywhere on the graph.

In this simple example, for a somewhat broad distribution, as expected the cumulative distribution by volume is shifted to higher sizes, the distribution by number is shifted to lower sizes, and the distribution by surface area is in the middle. For very

narrow distributions, all three curves lie on top of each other.

If you click on **Bimodal Analysis**, your next screen view is of the database. Open the folder that contains the file for which you want to do a bimodal analysis. If you select either a monomodal file or one with more than two modes, this particular feature is less useful. Figure VII-5 shows an example using polyvinyl chloride (PVC), a type of sample for which this bimodal analysis feature was developed.

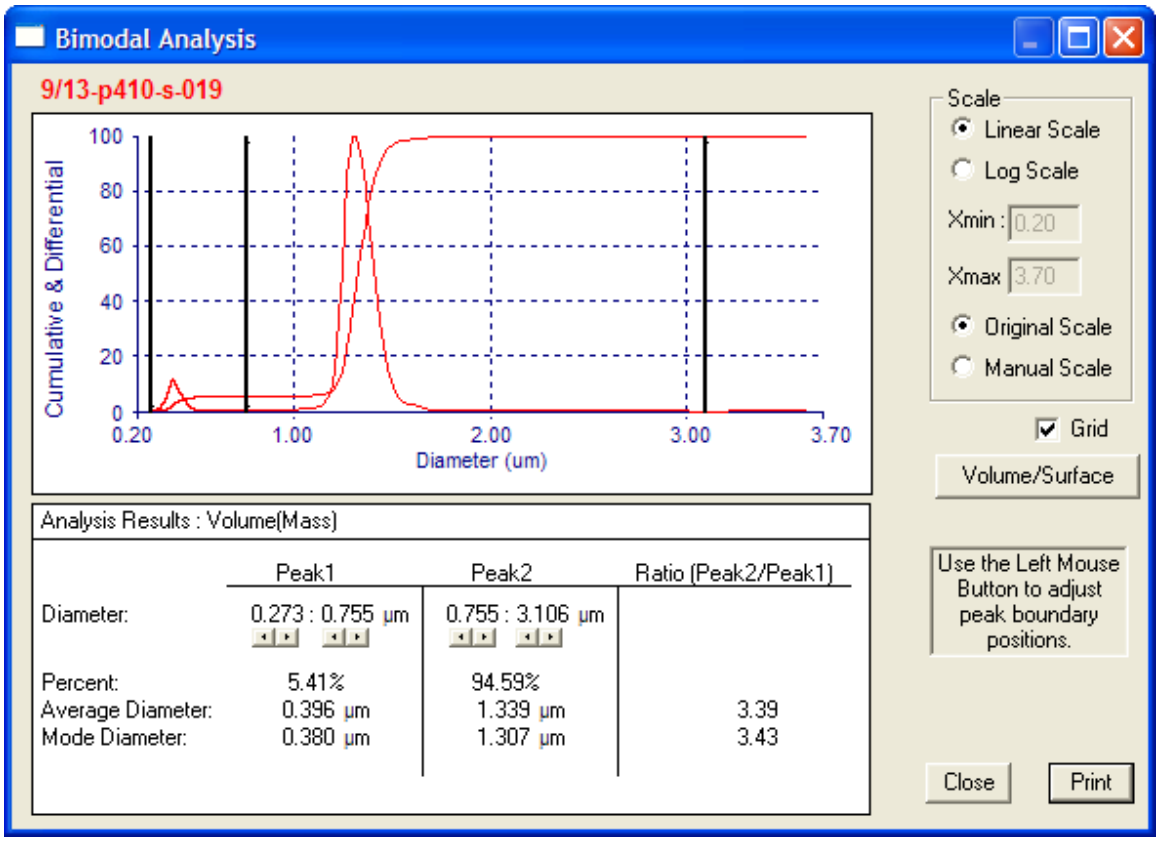

Figure VII-5: Bimodal Analysis feature.

Two sets of boundary limits are placed automatically around each peak. In this particular example, the upper position for Peak 1's boundary is in the same position as the lower position for Peak 2's boundary, both at 755 nm. The upper position for Peak 2's boundary, 3.106 micron, is a bit high and could be placed manually lower to see if it significantly affects the results. You can move any of the four boundaries by clicking on their respective left/right arrows, or you can hold down the left mouse button as you drag any of the four boundaries to the left or right. Release the button when you are satisfied.

For any given position of the boundaries, the mean, mode and percent in each peak are calculated as is the ratio of the means and modes. By toggling through Volume/Surface, Surface/Number, and Number/Volume these various values are displayed for the volume, surface area, and number distributions respectively. Figure VII-5 shows the volume distribution results as shown in the label for the tabular results.

Custom Mie Scattering Corrections

A light scattering correction is required to transform the raw, turbidity-weighted data into, first, a volume-weighted differential distribution as discussed in Section II: Theory. The exact, spherical Mie scattering theory requires the refractive index of the particle and liquid at the wavelength used as well as the particle size obtained from the timed sedimentation run. The use of the Mie correction and various legacy alternatives was discussed in Section IV: Software Overview. Several common pairs of particle/liquid are given in the pull down list box accessed as shown again here in Figure VII-6.

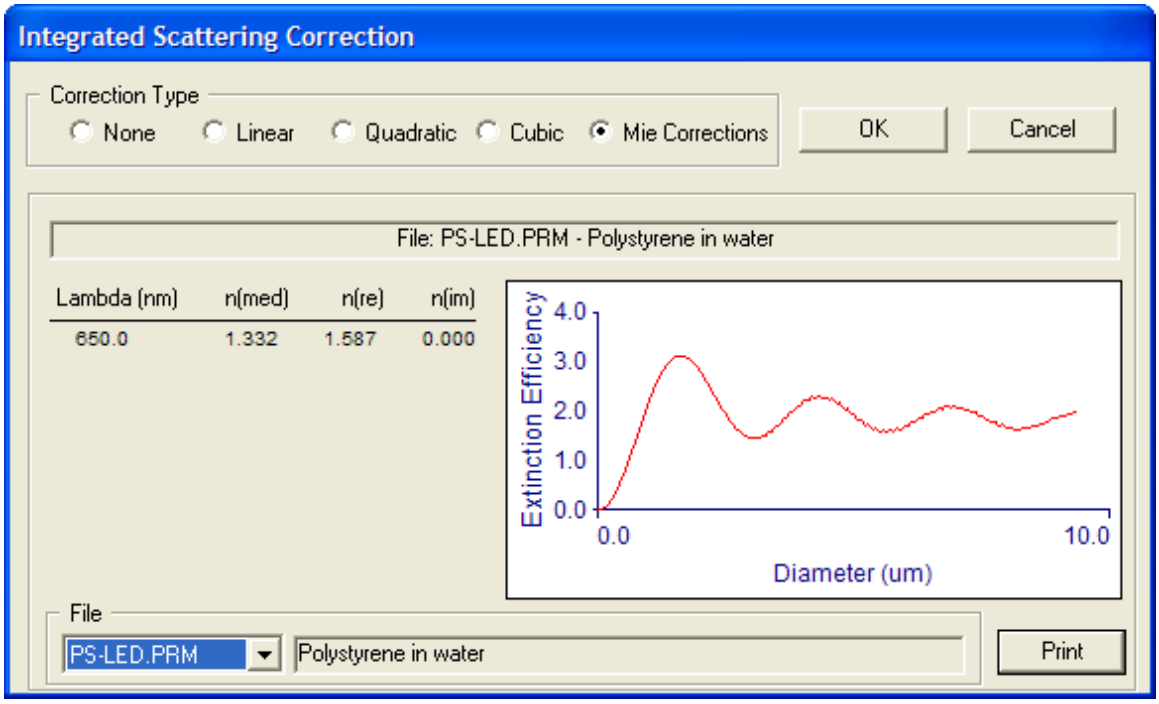

Figure VII-6: Selecting a Mie scattering correction.

The selected file here is polystyrene in water. [LED is the light emitting diode with wavelength 650 nm.]. In order to generate custom extinction efficiency files, one must first start with a parameter file with the extension .PRM. It is then modified and placed in C:\Bicw32\DcpScatt. When accessed the first time from within the BI-DCPLW program, the scattering correction files (.SCT files) are generated and kept for future use.

The first step is to generate a new .PRM with exactly, repeat, exactly the same spacing used with other .PRM files. Therefore, double click on any .PRM file in C:\Bicw32\DcpScatt. An example is shown in Figure VII-7.

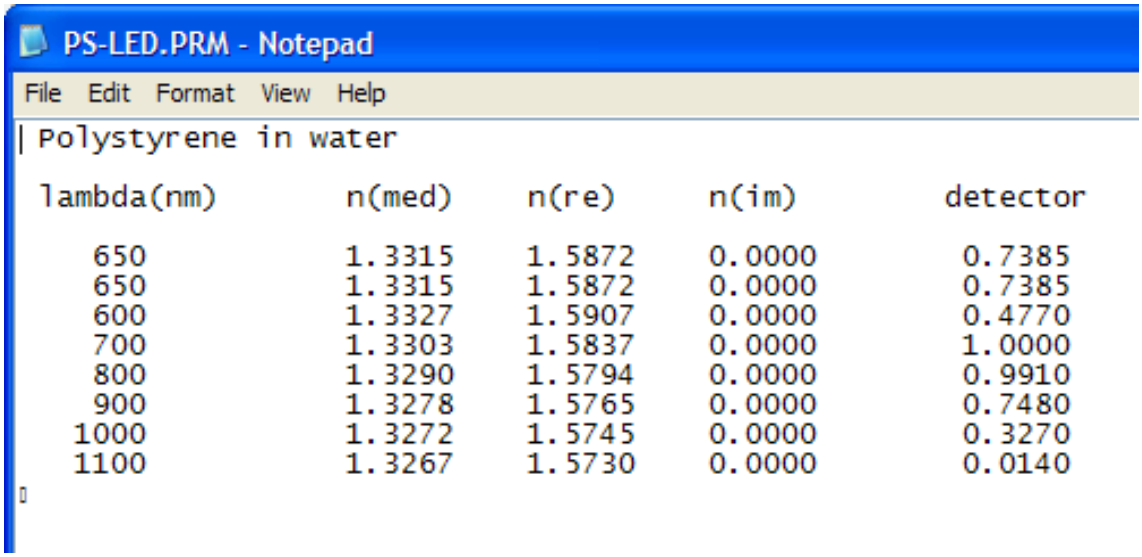

Figure VII-7: A PRM file in C:\Bicw32\DcpScatt.

Notice that the refractive index of the liquid medium, n(med), the real part of the refractive index of the particle, n(re), and the imaginary part of the refractive index of the particle, n(im) are given to exactly four places past the decimal point. When editing an existing PRM to create a new one, maintain the same number of figures past the decimal point and exactly the same spacing. This means adding two zeros to 1.58 to obtain 1.5800.

The accuracy of the final size distributions does not require anything more than approximately two figures past the decimal point. For water and for polystyrene extra figures are known and were used. However, it is not required. For particles that do not absorb in the visible (in particular at 650 nm), the n(im) is zero. Such particles look white or clear.

If you don't have refractive index values at 650 nm, use the values you do have in the visible. Quite often the wavelength given in tabulations of refractive index is the sodium D-line at 589.3 nm since this was used historically in Abbe refractometers. The wavelength dependence of refractive index values is such that the differences between 589.3 nm and 650 nm can be ignored. Of course, if you have the data, or can interpolate from two measurements in the visible (n varies as A + B/wavelength^2), do so.

These PRM files maintain the legacy structure from a time when the light source was a tungsten-halogen lamp with a distribution of wavelengths and a sensitivity that peaked around 700 nm. For that reason, the PRM files contain a 'detector' column and values at wavelengths other than 650 nm. This does not matter as long as the wavelength in the second row equals 650 nm. When this happens, the only values of interest are those in the first row and first four columns: wavelength, n(med), n(re), and n(im).

After changing these values, edit the top line to give the file a memorable

description. This description shows up in the bottom line of Figure VII-6. When you save the file, you must give it a new name, no longer than 8 characters. The extension .prm will be automatically attached. Then copy this PRM file into C:\Bicw32\DcpScatt.

To test your custom PRM file, run the BI-DCPLW program. Click **Parameters, Scattering Corrections, Mie Corrections**, and then use the pull down list box to locate the file name you gave to the new PRM file. If you maintained the exact spacing of the file, then an SCT file is created and the Extinction Efficiency vs. Particle Diameter from that file is displayed in the graph. If the graph does not appear, look again at the PRM file and compare it to one that works.

If the spin fluid has the same composition as one that is already used in a PRM file, it is convenient to use that PRM file as the template for creating a custom one. Alternatively, if an existing PRM file has the n(re) and/or n(im) for the particle of interest, it may be convenient to use that as the template for a new PRM file.

Appendix I: Removing and Replacing Discs

The BI-DCP is shipped with its measurement disc removed. This is done to protect it during transportation. Once the instrument has been unpacked the measurement disc must be attached before any analyses may take place. The user is encouraged to carefully inspect the new disc to ensure that its surface is free of any defects and/or scratches. Any defects must be reported back to BIC immediately so that we may correct the problem. Please note that sections of the circumference of the disc may have been drilled out. There may also be small amounts of a gray epoxy on the outside rim of the disk. ***Do not remove this material*** as it is used to balance the disc.

Once the disc has been removed from its shipping box and inspected for defects it is ready to be attached to the BI-DCP. Follow the directions below. Please remember that attaching the disc for the first time is difficult and new users can be expected to make several attempts at it before succeeding. Once the user gets some experience, however, the procedure becomes much easier.

Attaching the disc:

1. Turn the BI-DCP on.
2. Inspect the measurement disc to be attached to ensure that both of its hub screws are present and loosened enough so as not to protrude into the keyway slot inside the discs hub.
3. Press the **CUT** button on the front panel of the BI-DCP. This will bring up a user selection screen on the front LCD panel.
4. Press the number **1** on the front panel to retract the measurement head.
5. Inspect the axial of the motor. It will have a notch running through its end. This is called the **keyway** and it holds a rectangular metal pin called a **key**. The key slips into the keyway in the axial of the motor and into an identical keyway that is cut into the hub of the measurement disc. It is responsible for keeping the disc from slipping off during the measurement. Two lock down screws located directly over the disc keyway secure the key in place and lock the disc to the motor axial.
6. Position the motor axial so that the keyway slot points directly upwards. Place the key into the motor axial keyway. Make sure that the key is fully inserted into the keyway and that its tip is flush with or sticks out slightly from the end of the motor axial.
7. Open the small square door located directly over the disc chamber on the BI-DCP. Look down into the chamber through the opening and locate the motor axial. You should be able to identify the key and the keyway in the axial. Reach down into the disc chamber with the supplied disc (Allen) wrench. Use the wrench to hold the key in place while you push the disc onto the axial.
8. Reach over with your free hand and pick up the measurement disc which is to be attached. Hold the disc by its face so that the discs hub sticks out. Rotate the disc, if necessary, so that when you place it on the motor axial the keyway located inside

of the disc is lined up with the key which is already inserted into the motors keyway.

9. Hold the key in place with the Allen wrench so that while you push the disc onto the motor axial it is not allowed to slip out. Many users accidentally allow the key to slide out of the keyway while attempting to attach the disc. Make sure, by looking through the open section on the top of the BI-DCP that the key is staying securely in place while the disc is inserted. Take great care not to allow the key to slide back in the axial keyway or the key will not perform its function and the disc may spin free of the disc.
10. Press the disc firmly against the motor axial. Tighten the two lock down screws located on the top of the disc hub. This is accomplished by reaching down through the disc chamber door with the supplied Allen wrench and tightening the screws until they cannot be turned any further. Make sure that the screws are firmly in place or they may come loose during a measurement.
11. The disc is considered well attached when the following criteria are met:
    - The key is securely fixed inside of both the motor and the disc keyways.
    - The disc hub is pressed firmly against the end of the motor axial. This is assured pressing firmly on the disc's center after it has been attached.
    - The measurement head is free to travel over the disc surface. This is tested by placing a small section of paper flush on the surface of the measurement disc and ensuring that the plane of the paper does not extend into the measurement head.
    - The two lock down screws located on the disc hub are firmly screwed down on the key.
12. To make sure that the disc is inserted all the way into the motor axial the user is encouraged to gently place a section of paper over the forward facing plane of the disc. The plane of the paper should easily extend between the detector head and the measurement disc. If the disc is not attached fully the paper will not slide behind the detector head. **DO NOT go to step 14 before ensuring that the disc is fully fastened to the motor axial. Failure to do so can cause permanent damage to the disc and to the BI-DCP unit.**
13. Press **CUT** on the front panel of the BI-DCP to bring the user selection screen back up on the front LCD panel.
14. Press **2** to restore the head to its previously aligned position (if the user simply removed and cleaned the disc) or press **3** to realign the system (if the user has placed a new disc on the instrument which has a different volumetric dimensions.

The measurement disc has now been properly attached. Should the user wish to remove the disc simply follow the directions printed below:

Removal of the measurement disc:

1. Turn the BI-DCP on.
2. Press **CUT** button on the front panel of the BI-DCP. This will bring up a user selection screen on the front LCD panel.
3. Press the number **1** on the front panel to retract the measurement head.

4. Open the small square door located directly over the disc chamber on the BI-DCP. Look down into the chamber through the opening and locate the motor axial. You should be able to identify the key and the keyway in the axial.
5. Reach into the disc chamber through the front door and rotate the measurement disc until the two lock down screws located on the discs hub are pointing directly upwards.
6. Reach down into the disc chamber with the supplied disc removal tool Allen wrench. Find the lock down screws with the wrench and loosen them to the point that they turn with little effort. Do not take the screws all the way out of the disc hub or they may be lost.
7. Reach into the disc chamber through the front door and take hold of the measurement disc. Gently but firmly, pull the disc off of the motor axial. Take great care not to pull too hard on the disc. After the disc becomes free turn it slightly to allow it through the door. If the user pulls too hard it will cause the disc to rapidly come free and to possibly hit the front door enclosure which would damage the disc and possibly the instrument itself.
8. Remove the key from the disc keyway if it is found to remain inside upon taking the disc off of the instrument. Place the key in a secure place so that is it not lost.
9. The removed measurement disc should be handled with extreme care to avoid scratching its surface. Discs, when to attached to the instrument, should be either wrapped in protective material and stored in a safe location or, for short periods, placed with its hub down and face pointing upward in a safe location.

Appendix II: Detector Alignment Procedure for the BI-DCP

Overview:

In order to calculate particle diameter from Stokes' Law, the geometry of the disc must be known. This was done at the factory. In addition, the exact position of the detector must be known in order to calculate the distance through which particles move. This requires alignment of the head with a known amount of liquid in the spinning disc.

Here is an overview of what happens during the alignment procedure. Exactly 5.00 mL of water is injected into a clean, dry disc. The disc is spun. The signal output from the LED source is monitored as the head is moved right (in air, low signal) to left (towards and through the meniscus of the liquid) until the meniscus is detected (a maximum in signal). A small correction is made for the finite width of the detector slit.

Since the screw mechanism for moving the head has a little play, always move it in one direction when making final determinations.

The CUT button on the front panel of the BI-DCP is used to bring up a menu. The CUT button is also subsequently used to move the head from right to left. The BOOST button is used to move the head from left to right. While there is an automatic menu choice for determination of the proper alignment, scratched or dirty discs can result in the wrong alignment. You can check by noting if the red LED light, looking through a clean disc, is symmetric about the detector slit when alignment is achieved.

Procedure:

1. Turn on and warm up the BI-DCP. This takes approximately 5 to 10 minutes. The disc should not be rotating.

2. Suck out any particles or liquid using the syringe with the rubber tubing attached, the one with the 45^{o} cut on the end to prevent the tube from puckering on the bottom of the disc. If the disc is dirty, add a little soap to water and slosh it around until it is clean. Finally, dry the disc completely using folded, paper towels.

3. Use a 5.00 mL, Class A pipette. DO NOT USE a syringe. DO NOT USE a burette. If you use an automated pipette, make sure to calibrate it with a known weight of water and use the density at the measurement temperature to calibrate the pipette. Class A pipettes have accuracies listed at 20 ^{o}C of typically +/- 0.01 mL. Take notice if you have a TC (to contain, meaning you have to blow out the last drop) or TD (to deliver, meaning you do not have to blow out the last drop). Deliver exactly 5.00 mL of DI water into the clean, dry disc, making sure to get all the water into the disc. Leave the door in front of the disc open.

4. Press the CUT button to bring up the menu. Using the keypad, press 3 to enter the alignment mode. Press 1 to select a manual alignment. The disc should start

spinning at 1,000 rpm. The head moves to its home position. This corresponds to step position zero that should be displayed on the LCD. The voltage should also be displayed and recorded manually. Voltages between 0.2 to 0.7 volts are acceptable.

5. Press and hold down the CUT button. The head moves to the left. Look for the dark shadow cast from the meniscus as the detector slit moves towards it from the right. Release the CUT button before the meniscus's shadow is coincident with the detector slit. Write down the voltage and step number. The voltage should be approximately the same as it was before. The step position might be approximately 200.

6. Now record the voltage and step position while moving one step at a time by pressing the CUT button. As you approach the meniscus, the voltage will increase. Eventually it reaches a maximum. Typically, the maximum is in the range of 2.0 to 2.25 volts and the step position is approximately 230. Discs vary slightly as do source/detector sensitivities, so these are approximate values. The saturation voltage is 2.50 volts. If you get this value, you have moved too far to the left.

7. In fact, to determine a maximum, you have to move beyond it and notice a decrease in the voltage. DO NOT move back and forth across the apparent maximum using the CUT and BOOST in single or double steps. This will cause an error due to play in the screw threads. If in doubt, or to verify the maximum now that it has been located approximately, use the BOOST button to move to the right at least 10 or 20 steps. Then use the CUT button, recording the voltages at each step to verify where the maximum is.

8. When you have found the step position corresponding to the maximum, subtract five steps to account for the slit width. The result is the correct alignment position. Use the BOOST button to move to the right at least 10 steps below the correct position. Then use the CUT button to move to the correct alignment position.

9. Once you have reached the correct alignment position, press the MOTOR button on the front panel of the BI-DCP. The alignment program is exited and the correct alignment position is recorded by the firmware. The instrument is now aligned. Verify using a standard as described in the manual.

Appendix III: Concentration Definitions and Calculations

A reasonable concentration for measurements with any sedimentation device, including the BI-DCP, is 0.005 volume fraction, also designated as 0.5% by volume. While there are some cases where a concentration of this magnitude might cause either particle-particle interactions or saturate the detector and, as a result, distortions in the final answer, this is s good initial value. If in doubt, make measurements at .1% by volume to see if there has been a systematic shift in the results. A strong scatter like TiO_2, or a strong absorber like Carbon Black, should be made initially at 0.1% concentration. If the signal is too weak, then increase the concentration.

The volume fraction ϕ is a fundamental parameter for describing concentration. The cube root of ϕ is proportional to the ratio D/L, where L is the average center-to-center interparticle distance and D is the particle size. When the volume fraction is high, the particles are close together, and concentration effects on the measured size are more likely to be important.

ϕ is defined as,

$\phi = V_p/V_s = V_p/(V_p + V_l)$ where

V_p = the total volume of all particles,
V_l = the volume of the liquid,
V_s = the total volume of the suspension (particles + liquid).

For example, assume a suspension with 1 ml of particles and 49 ml of liquid. Then $\phi = 0.02$. The concentration is 2% by volume.

{Note for Chemists: Unless a solution is ideal, the total volume is not equal to the sum of the component volumes. This is due to molecular interactions. Suspensions are not solutions. Only the surface molecules around a stable particle interact significantly, if at all, with the liquid in which it is suspended. Therefore, it is a good approximation to assume that the volumes add. One need not be concerned with partial molar volumes. }

For low concentrations $V_p << V_l$ and $\phi \approx V_p/V_l$. For high concentrations, this approximation is no longer valid.

Another common definition for concentration is the mass fraction defined as the total mass of particles divided by the total mass of suspension. Like the volume fraction, the mass fraction is a true fraction: it has no units. Unlike the volume fraction, the mass fraction is not directly related to particle-particle interactions. In addition, it is not common practice to weigh the liquid used to make a suspension. Instead, the volume of the liquid is measured. This practice gives rise to the most common definition of concentration.

Let $C = M_p/V_l$, where M_p equals the total mass of the particles. For example, if 1 g of particles is added to 50 mL of liquid, then C = 0.02 g/mL.

This is – unfortunately and illogically – often referred to as a 2% solids concentration, or 2% by weight. Notice the mixed units, g/mL. A fraction and the corresponding percent have no units, as in the case of volume or mass fraction. A further problem arises when a concentration is given only as 2%. It is not clear whether this means volume or mass fraction or C. More exacting analysts will add the units and say 2% w/v. Protein chemists refer to 1% solutions by which they mean 0.1 mg/mL. If in doubt, ask.

With the help of a little algebra, one can relate ϕ and C. Namely,

$$C = \phi \cdot \rho_p / (1 - \phi) \quad \text{or} \quad \phi = C/(C + \rho_p)$$

Where, ρ_p is the density of the particle.

For example, if a 30 g sample of particles with $\rho_p = 1.2$ g/cm^3 is suspended in 50 mL of liquid, C = (30 g)/(50 ml) = 0.6 g/mL, or 60% solids. Using the above equation to calculate ϕ, one finds 33.3% by volume.

For low concentrations, $C \approx \phi \cdot \rho_p$. This is a particularly useful approximation. For example, it was stated at the beginning that making measurements at $\phi = 0.5\%$ is a good starting point. For polyvinyl chloride, where $\rho_p = 1.38$ g/cm^3, C = 0.5% x 1.38 = 0.69%; and for TiO_2, where $\rho_p = 4.2$ g/cm^3, C= 0.5% x 4.2 = 2.1%.

In preparing samples for particle size analysis it is quite common to use wetting agents and surfactants. These should be used at very low concentrations. In addition, the density of these materials is typically close to 1g/cm^3. For these two reasons, it is normal practice to ignore completely the difference between ϕ and C.

Likewise, when preparing samples for use with the BI-90, 90Plus, FOQELS, ZetaPlus, ZetaPALS, BI-MwA and the BI-200SM (all instruments based on static and dynamic light scattering), the concentrations are typically between 10^{-5} to 10^{-2} volume fraction. At such low concentrations the difference between suspension volume, V_s, and liquid volume, V_l, is insignificant, and the difference between ϕ and C is, again, often ignored.

Ignoring the difference between ϕ and C, at low concentrations, is very common and acceptable for rough, qualitative work. It is never acceptable for quantitative work. For example, if you are not sure if the current dilution is sufficient, halve the concentration, and repeat the measurement. It is not too important to know the exact concentration or its definition, if and only if the concentration is roughly in the right range. If, however, you want to plot values against concentration or fit results to an equation in concentration, then you must be quantitative when measuring, diluting and specifying the concentrations, especially the units.

Appendix V: Distribution Statistics, Definitions and Calculations

Following are the definitions of the various distribution statistics that are calculated in the "Detailed Results" window.

d_{xx} is the diameter at the XX percentile of the cumulative undersize distribution. (For example, d_{50} is the 50^{th} percentile, also known as the median. And d_{25}, d_{50}, and d_{75} are the 25^{th}, 50^{th}, and 75^{th} percentiles, also known as the quartiles.)

Span is one measure of distribution width. We define the relative span as $(d_{90} - d_{10})/d_{50}$.

d_{84}, d_{50}, and d_{16} are used to compare a monomodal distribution to a lognormal distribution.
When $d_{84}/d_{50} = d_{50}/d_{16}$, the measured distribution, if monomodal, approximates a lognormal
distribution, at least over the range from 84% to 16%.

The mean diameter is calculated from the differential distribution as follows:

$$\text{Mean} = \frac{\sum_{i=1}^{n} d_i V_i}{\sum_{i=1}^{n} V_i} = \bar{d}_v$$

where, V_i is the volume of the particle, with diameter d_i, and n is the number of data points. Analogous definitions for distributions weighted by Number and Surface Area apply.

The Std. Deviation, also calculated from the differential distribution, is another measure of distribution width, and is defined as follows:

$$\text{Std. Deviation} = \left(\overline{d_v^2} - \overline{d_v}^2 \right)^{\frac{1}{2}}$$

where,

$$\overline{d_v^2} = \frac{\sum_{i=1}^{n} d_i^2 V_i}{\sum_{i=1}^{n} V_i}$$

The mode in the differential distribution is the diameter corresponding to the highest peak and is most important in a monomodal distribution. For multimodal distributions, use the cursor to determine the diameters at the remaining modes.

FWHM is the full width at half maximum of the highest peak in the differential distribution. It is most useful for a monomodal distribution. It is another measure of distribution width.

FWHM/Mode is a dimensionless ratio. It is a relative measure of the distribution width.

Geometric Mean Diameter is calculated as follows:

$$Geometric\ Mean\ Diameter = \frac{1}{\phi}\sqrt{\prod_{i=1}^{n} d_i^{V_i}}$$

Where , $\phi = \sum V_i$.

For a monomodal distribution that is uniquely described by the lognormal function, the modal diameter equals the geometric mean diameter.

Geometric Std. Dev. is calculated as follows:

$$\text{Geometric Std.Dev.} = \sqrt{\frac{d_{84}}{d_{50}} \times \frac{d_{50}}{d_{16}}}$$

When the Geometeric Std. Deviation = 1, the distribution is monodisperse. In this case all d_{xx} values are equal, FWHM = 0, and all mean values are equal and equal to the modal diameter.

Note: This simple method of estimating geometric standard deviation is only valid when the actual distribution is accurately described by a lognormal function. When this is true $d_{84}/d_{50} \approx d_{50}/d_{16}$, values of which are presented in the "Detailed Results" window. A more complete definition using all the data points is given in William C. Hinds[6], chapter 4, pg.85, equation 4.40.

[6] William C. Hinds, Aerosol Technology Properties, Behavior, and Measurement of Airborne Particles; Wiley-Inter-science Publications: New York, 1982.