

Instruction Manual for BI-SLSW Static Light Scattering Software

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Please Read

This is your instruction manual for your Brookhaven BI-SLSW Static Light Scattering Software. Please read it carefully before making measurements. The How To section describes how to install the software. You may familiarize yourself with some of the features of this software by reloading data files (Files/Database). Then choose one or more or the plots by clicking on Graphs in the main menubar. If you have any questions or suggestions, please contact Brookhaven Instruments.

This program requires Windows 3.X or higher and at least 8 Mb of RAM.

This program was designed for use with the BI-200SM motor-driven goniometer and the BI-9000AT digital autocorrelator or the BI-9025AT photon counter. Please read the goniometer alignment section in the BI-200SM manual **and** align the goniometer *before* using this software. You should consider using the BI-ISTW software to verify that the alignment is good. However, this software may also be used with a manually driven goniometer. Check with the factory for special modifications.

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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Section I: How to Use this Manual and Software

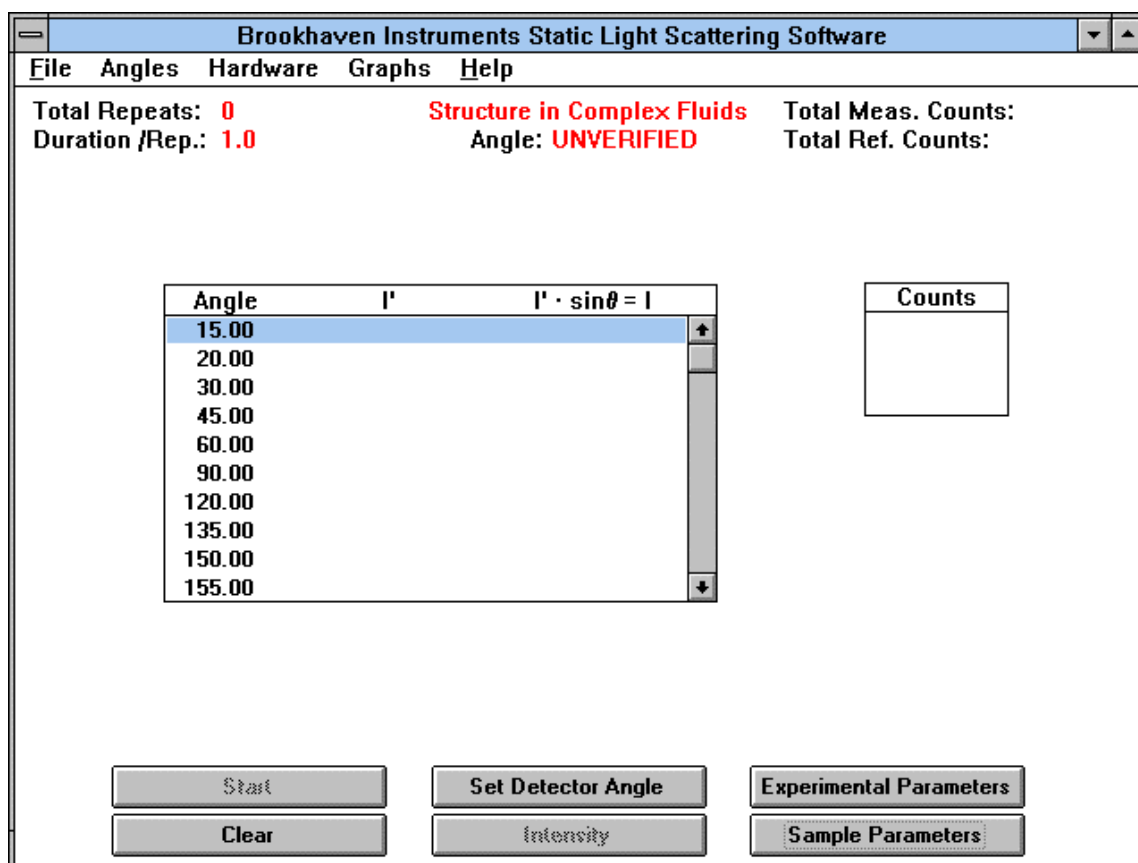
The static light scattering software is a program that will allow you to collect and analyze scattered light intensity as a function of angle from colloidal suspensions, polymer solutions, gels and other scattering systems. The program allows you to control a motorized BI-200SM goniometer, to collect and to correct measured counts as a function of angle, and to plot the results in a variety of ways. You can plot intensity or the excess intensity above that scattered from the liquid. You can choose from a variety of plots. In some of these plots, the radius of gyration, R_g , is determined. In others, the shape of the function distinguishes between a globular structure (highly branched polymers or spherical colloidal particles) and random coils or rods. In one plot, the fractal dimension can be obtained when the system studied is suitable. A couple of simple examples are given. Results can be printed, saved, and reloaded for future reference. An ASCII file can be created for use in spreadsheets and plotting programs. A stability test allows you to check the laser, detector electronics, and main power supply for stable operation.

Before proceeding, align the goniometer following the instructions in the BI-200SM manual. Check the alignment with the BI-ISTW software. Take your time. Do a thorough job. Then, follow the instructions in this manual.

To install the BI-SLSW software, place the installation disk in the floppy drive. Click on **Run** from the **File** menu. Run A:\SETUP. When finished, a BIC icon with the name Static Light Scattering Software will be added to your BIC program group, or a group with this icon and name will be added. Double click on the icon to start the program.

Section II: Setting Up the Measurement

In the Menubar of the Main Window, click on **Hardware**, **Hardware Configuration**. Click on **Motor**, if you have a motorized goniometer. Click on **Manual**, if you do not have a motorized goniometer, or if you are using this program with a motorized goniometer other than the BI-200SM. Select either zero or one **Reference Detectors**. If you have a reference detector, plug the digital signal (TTL compatible) into input B on the rear of the correlator. The scattered light and reference intensities are collected simultaneously. A ratio is formed, after correcting both for their dark count rates and for the dead-time. This ratio will account for slow drifts in the laser output and absorption, if the reference detector is attached to the beam stop in the BI-200SM and a round cell is used. This latter case is quite rare. It is more common to find a reference detector placed between the laser and the input optics of the goniometer, accounting only for a slow drift in laser power.



Click on the **Sample Parameters** command button in the lower part of the screen. Fill in the **Sample Identification**, **Operator Identification**, and **Notes** fields. The Sample ID is used in the Database section of the program for naming the files. Therefore, care should be taken in organizing files by the use of appropriate Sample IDs. Select a liquid from the pull down box or select Unspecified and then fill in the **refractive index**

for the **Sample Liquid**. Fill in the values for the **Sample Cell** (typically ~1.5) and the **Vat Liquid**. If the vat liquid is decalin (cis-trans decahydronaphthalene), the refractive index is 1.474. If you click on **Apply Reflection Corrections**, then the refractive indices are used to correct for the fact that a measurement at any angle also includes a small fraction of the intensity measured at the supplement of that angle. This is due to the light being reflected at the cell/liquid and cell/vat-liquid interfaces.

The fraction f is calculated from the refractive indices of the various interfaces involved. The fraction f is given by:

$$f \equiv f_{sl/c} + t_{sl/c}^2 f_{vl/c}$$

$$t_{sl/c} = 1 - f_{sl/c}$$

$$f_{sl/c} = \left(\frac{n_{sl} - n_c}{n_{sl} + n_c} \right)^2$$

$$f_{vl/c} = \left(\frac{n_{vl} - n_c}{n_{vl} + n_c} \right)^2$$

where $f_{sl/c}$ is the fraction reflected at the sample liquid/cell wall interface, $t_{sl/c}$ is the fraction transmitted at the sample liquid/cell wall interface, and $f_{vl/c}$ is the fraction reflected at the vat liquid/cell wall interface. These f values are calculated assuming the angle of incidence is zero and Fresnel's law applies with n_{sl} , n_c , and n_{vl} the refractive indices of the sample liquid, cell, and vat liquid, respectively.

Sample Parameters

Sample ID: Structure in Complex Fluids

Operator ID: D. Weitz

Notes: Gold Sols

Sample Liquid: Aqueous

Ref. Index of Sample Liquid: 1.336

Ref. Index of Sample Cell: 1.500

Ref. Index of Vat Liquid: 1.474

Apply reflection correction

Wavelength: 488.0 nm

Auto Save Results

OK Cancel

When the sample liquid and vat liquid are both organic liquids, with refractive indices in the range of 1.45 to 1.55, the reflection correction is typically insignificant. When the sample liquid is water (ref. index 1.33), the reflection correction is small, but worthwhile making. Because the reflection correction is small, it is not worth the effort to correct the refractive indices for wavelength or temperature. A refractive index at any wavelength in the visible portion of the spectrum is sufficient even if that wavelength is different than the one used for the scattering experiment. Likewise, unless the temperature of the measurement is many tens of degrees different than room temperature, it is not worth making a correction. Use the refractive index at room temperature.

If the supplement of the scattering angle is not present in the list of angles measured, the nearest angle measured to the supplement is used. The error introduced by this is a second order correction to a small, first order reflection correction, and is, therefore, insignificant.

The application of the reflection correction is described in numbered paragraph 8 under the section entitled **Making a Measurement**.

Enter the **Wavelength** of the laser.

Click on **Autosave Results** to automatically save the final measurements. Otherwise, to save results for later recall, click on File and either Save or Save As. Data are saved in a binary format, as files in the open Folder. The Folder/File database is explained later.

Click the **OK** command button to save the changes and exit the Sample Parameters window. NOTE: If you click on **Cancel**, none of the values entered will be accepted. Previously entered values will be used.

Manually set the goniometer arm to 90° . Click the **Set Detector Angle** command button and enter the angle as 90° .

Click on the **Experimental Parameters** command button in the lower part of the screen. Block the light to the PMT by turning the neutral density filter wheel to the closed, C, position on the BI-200SM. Enter 10 seconds in the **Duration/Repeat** field. Click on the **Dark Count Rate** command button. The dark count rate is the total photons counted divided by the duration in seconds. The units are counts/second, abbreviated cps. Click the **Close** command button and notice that the measured dark count rate is automatically transferred to the appropriate field. Since dark count rates are normally small, the fluctuations are large. Therefore, counting for ten seconds yields smaller fluctuations, and it is easier to estimate the true dark count rate.

[If you use a reference detector, block the laser light and any other source of light reaching the reference detector before making the dark count rate measurements. The B input signal, assumed here to correspond to the B dark counts, is also automatically

measured and transferred to the appropriate field when executing the sequence Dark Count Rate, Close as above.

If room light contributes significantly to the dark counts registered at the reference detector, consider two options: either block the room light, or, if constant and small compared to the total reference counts, use the sum of the reference dark counts and room light as the apparent dark count rate of the reference detector.]

Experimental Parameters

'A' Dark Count Rate: cps

'B' Dark Count Rate: cps

Duration / Repeat: seconds

Number of Repeats:

Dust Rejection Ratio:

Pinhole Size

1 mm

2 mm

3 mm

Polarization Analyzer

None

Vertical

Horizontal

Interference Filter

In

Out

Select an appropriate Duration/Repeat. Select values in increments of 0.1 seconds up to a maximum of 10 seconds. One second is common, but not necessarily optimum. Photon counting follows Poisson statistics: the standard deviation of the distribution of repeated measurements equals the square root of the average. Here the measurements refer to the Total Measured Counts or, in the case of a reference detector, the Total Reference Counts. The intensity is the Total Counts divided by the duration (units of counts/second, cps, or kilocounts/second, kcps, or megacounts/second, Mcps). To repeat: total measured counts follow Poisson statistics; count rates --counts/second-- do not.

As a result of the square root relationship, the relative error (std. dev. divided by the mean) is: 1% for 10,000 total counts; 0.32% for 100,000 total counts; and 0.1% for 1,000,000 total counts. Aim for 100,000 total counts. If this can be done in one second by increasing the incident laser power or selecting a larger pinhole (1, 2, or 3 mm), do it. If not, increase the duration/repeat. This will result in an increase in the total experiment duration; it will also increase the probability that a measurement will be ruined by dust. With weak scatterers and low laser power, it may be better to accept 50,000 or 20,000 or even 10,000 total counts rather than increase the duration/repeat. Experience will help you judge the best alternative.

The strongest scattering will generally come from the sample at the lowest angle of interest. If you have not done so previously, move the goniometer to, and **Set Detector Angle** at, the lowest angle. Click the **Intensity** command button in the main screen or from within the Experimental Parameters window. The Total Measured Counts are shown in the upper part of the main screen. Adjust the laser power, the pinhole, or the duration/repeat until a suitable total measured count is achieved as described in the previous paragraph. In any case, it is best to keep the maximum count rate less than approximately 1.5 Mcps. At all other angles, the Total Measured Counts will generally be lower and the corresponding relative error higher. [The exception is when the scatterer of interest is on the order of the wavelength and the lowest angle of interest happens to be near a minimum in the scattering pattern. In this case try a few different angles.]

From within the Experimental Parameters window, select a value from 1 to 10 for the **Number of Repeats**. This value is used to discriminate against dust as explained below. This value may be adjusted up or down, depending on the cleanliness of the sample, the duration/repeat, and the intensity of scattered light. If the sample has been well filtered, the laser power is low (< 20 mW), and the pinhole is maximum (3 mm), select 3 to 5 repeats and 1 to 5 seconds duration to achieve 10,000 to 50,000 total measured counts. If the laser power is high (> 50 mW), and the pinhole is set at 1 or 2 mm, select 5 to 10 repeats and 1 second duration to achieve 100,000 total measured counts.

With a well-filtered sample enter 1.33 for the **Dust Rejection Ratio**. Values from 1 to 10 are allowed: small numbers are best for clean samples [less dust]; somewhat larger numbers (up to 2 or 3) may be used if dust is difficult to remove. NOTE: Using larger numbers may reduce accuracy, especially at low angles, but may be necessary if dust cannot be removed. When fitting the data, look for abnormally high and erratic intensities at the lower angles. Delete them if necessary during fitting.

Fill in the remaining 3 boxes of information. None of the values are used in any subsequent calculation, yet they are valuable pieces of information when reviewing the results. Select the **Pinhole Size** corresponding to the pinhole set on the detector optics. If you do not have the optional polarization analyzer attached to the front of the detector optic, the most common case, select *none* in the **Polarization Analyzer** box. If you have an analyzer, set it to accept vertical polarization to match the vertical polarization of the laser and so indicate in this box. To block room light use the snout provided with the BI-200SM and rotate the interference wheel until the filter number matches the wavelength of the laser used. Click on **Interference Filter "In"**.

Click the **OK** command button to save the changes and exit the Experimental Parameters window. NOTE: If you click on **Cancel**, none of the values entered will be accepted. Previously entered values will be used.

Section III: Making a List of Measurement Angles

Click **Angles** in the Menubar at the top of the screen. Click **Edit Measurement Angles List**. For the alignment test click the **Default List** command button. This results in 15, equally spaced angles ranging from 15° to 155° , a good selection for many initial measurements. Click on **OK** to implement the list and return to the main screen. If you click on **Cancel**, the last list, not the Default List, will be used in the main screen for measurements.

A list of measurement angles may be created in a number of ways from within the Edit Measurement Angles List window.

Click on the **Delete All** command button. Notice the flashing vertical cursor in the remaining edit box in the list of angles. Enter an angle between 9° and 155° . Click in the edit box labeled **Angle**. Enter an angle. Click on the **Add Angle** command button. Notice the angle is added to the list. Repeat the procedure to add more angles. The minimum allowed list contains five angles.

To add a single angle to a list of displayed angles, enter the new angle in the edit box labeled **Angle** and then click on the **Add Angle** command button. To change any angle in a list, click on it in the list and type over it. To delete an angle in a list, click on it and then click on the **Delete Angle** command button. Angles are automatically rearranged from lowest to highest.

Click on the **Increment** box and enter an increment in degrees. Click on any angle in the list. Click on **Insert Increment**. The new angle is inserted and the list size increases by one. If the increment is larger than the difference between the current angle in the list and the next higher, only half the increment is added.

Click on the **Increment** box and enter an increment in degrees. Click on any angle in the list. Click on **Apply Increment**. The increment is applied from the current angle. The list size remains constant; however, the values of the angles after the current are different, with the increment applied consecutively.

To delete any angle, click on it. Then click on **Delete Angle**. Notice the List Size is decreased by one.

Edit Measurement Angle List

Angle (degrees)

1.	15.00
2.	25.00
3.	35.00
4.	45.00
5.	55.00
6.	65.00
7.	75.00
8.	85.00
9.	95.00
10.	105.00

List Size: 15

Add Angle

Angle

Delete Angle 1

Delete All

Insert

Increment 10.00

Apply Increment

Set List Range

Load List Default List OK

Save List As... Cancel

Click the **Set List Range** command button. Enter the **First** and **Last Angle**. Click on *either* the **Increment Between Angles** or the **Number of Angles in the List**. If you selected **Increment Between Angles**, then enter the **Increment** in degrees. The new list will include the first and last angles you entered, with an equal increment starting from the first angle. The difference between the last angle and the one preceding it may not be equal to the increment entered. For example, if you entered 15° to 155° by 15°, the list will include 15°, 30°, ..., 120°, 135°, 150°, 155°.

If you selected **Number of Angles**, you may select equal spacing by angle, by q , by q^2 , or by $\ln q$. Here q is the magnitude of the scattering wave vector, and it is explained further in the section entitled **SLS Plots**. A list of angles is created, from the first to the last with appropriate spacing. The spacing is calculated as $(\text{First} - \text{Last})/(\text{List}$

Size - 1), where First and Last are either values corresponding to angle, or q , or q^2 , or $\ln q$. From the equal spacing in q , or in q^2 , or in $\ln q$, the corresponding angle is calculated in order to compile the list of angles for the measurement.

At least 5 and no more than 500 angles are allowed. Click OK

After creating a specialized list of angles, click on **Save List As** and enter a filename up to 8 characters. The extension "ang" is automatically appended if you do not enter it. Click on OK.

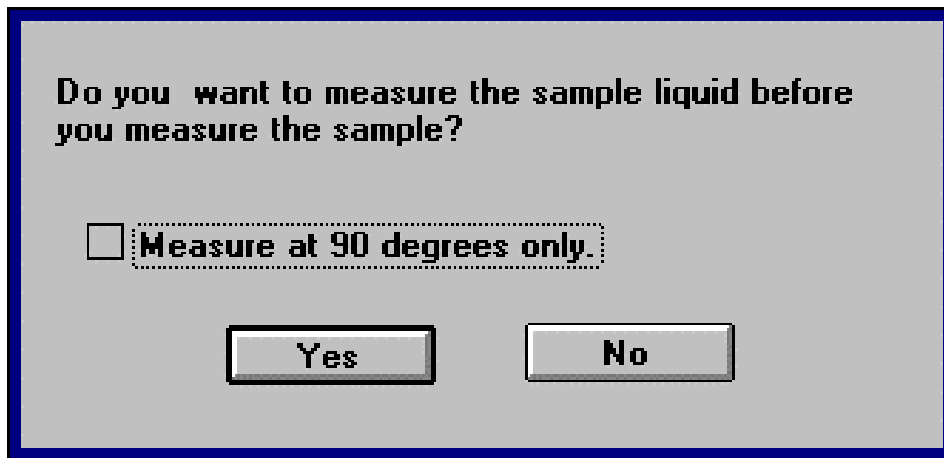
[NOTE: To delete a file containing a list of angles, do so through the operating system. Open C:\BICW\9KSLSW\DATA, locate the filename, and delete it.]

Click on **Load List** to reload a list of angles. Click on the filename of the list of angles. Click on OK. The angles in that list is now loaded.

CAUTION: Click on **OK** to implement the selected list of angles and return to the main screen. If you click on **Cancel**, the last list, not the selected list, will be used in the main screen for measurements.

Section IV: Making a Measurement

Choose a set of angles or use the set of default angles. Click on the **Start** command button to initiate a measurement. You will be asked if you want to measure the liquid without the sample. Click on yes if you want to plot the excess intensity [sample minus liquid intensity]. Click on no if the scattering from the liquid is much lower than that from the sample. Sometimes it is difficult to clean the liquid, especially water, and the low angle values are erratic and high. In this case, either answer no, or click the box for measuring the liquid at 90°. A set of liquid values will be calculated from the 90° value. With a motorized BI-200SM, the arm will move to the lowest angle in the list. With a manual goniometer, or one not under control of the BI-9000AT correlator, a window will appear instructing you to move the arm to the lowest angle.



At each angle, the following sequence will occur.

1. In the **Counts** box the total measured counts, raw, uncorrected counts, will appear and repeat measurements will follow up to the limit set by the Number of Repeats, 5 for example.
2. Dust discrimination is achieved using a software algorithm and is based on Poisson and Gaussian statistics as follows. The average and standard deviation of the set of N values are calculated as well as the square root of the average. The standard deviation is based on Gaussian statistics. Whereas, the square root of the average yields a standard deviation based on Poisson statistics. A dust event will increase the total measured counts during the duration. Assuming most measurements are not affected by dust, this increase only modestly affects the average and the Poisson standard deviation calculated from the average. But it increases significantly the Gaussian standard deviation.
3. The ratio of the Gaussian and Poisson standard deviations is formed. If this number is greater than or equal to the Dust Rejection Ratio, the largest of the total measured

counts in the set of N is rejected and another one is collected. The calculation is repeated with this new set of values. The rejection criterion is applied again, and, if necessary, the highest value is again rejected. The procedure is repeated until either a set of N values is found that satisfy the criterion, or a total of 3N measurements have been made. If after 3N measurements have been made, the remaining set of N values do not satisfy the criterion, the highest value is rejected and the remaining N-1 are tested against the dust rejection criterion. This procedure is repeated until the criterion is satisfied or the last, representing the lowest, total measured count remains.

4. This average is displayed in the upper right hand corner of the main screen under the heading Total Measured Counts.

[NOTE: With clean liquids, N values can normally be found to satisfy the criterion. At low angles, where dust scatters most, rejections will occur. If most of the measurements reach the limit of 3N measurements, consider aborting the run and cleaning the sample.

This software criterion for rejecting residual dust works well when only a small amount of dust particles remain. It is no substitute for the mechanical removal of dust by filtration (most commonly) or, *under special circumstances, centrifugation.*]

5. The average is divided by the duration to form the average, uncorrected count rate (an intensity).
6. From the average uncorrected intensity the dark count rate is subtracted. This is the measured, average intensity corrected for dark count rate.
7. The measured, average intensity corrected for dark count rate, I_m , is further corrected for the dead time, τ_d , to produce the true count rate as follows: $I_t = I_m / (1 - \tau_d I_m)$. For the BI-9000AT, τ_d is 25 ns.

The true count rate is always larger than the measured, since a finite dead time means that no more than one pulse can be registered in a given interval. For dark count rates, and for low count rates in general, this correction is insignificant. At 10,000 cps the result is only 3 cps, an insignificant 0.03% correction. At 100,000 cps the result is 250 cps, a small 0.25% correction. At 1,000,000 cps the result is 25,640 cps, a significant 2.6% correction.

8. The true count rate is finally corrected for reflection where

$$I(\theta) = [I_r(\theta) - f \cdot I_r(180 - \theta)] / (1 - f^2)$$

Here f is the combined reflection correction discussed in the **Making a Measurement** section, the paragraph discussing the **Sample Parameters**.

This average, corrected value is transferred to the column labeled I' in the floating window in the middle of the main screen. It represents the intensity scattered by all the particles or molecules in the scattering volume as observed by the detector optics.

9. To form the intensity scattered per unit volume, one has to account for the different volumes observed at different scattering angles. Focusing of a TEM₀₀₁ laser beam produces a hyperbola of revolution; however, with a long focal length lens, such as that used in the BI-200SM goniometer, the shape is cylindrical, at least over a millimetre or two around the center of rotation. Therefore, at any angle the length of the cylinder is larger by $1/\sin(\theta)$. Thus, to compare the intensity per unit volume at various angles, the average, corrected value is *multiplied* by $\sin(\theta)$. The last column in the floating window shows a list of $I'\sin(\theta)$ as a function of θ .

[The effect is the same as looking at a railroad track through a hollow cylinder. Starting with the axis of the cylinder perpendicular to the track, rotate around a fixed point on the track. The length of the track seen varies as $1/\sin(\theta)$. In fact, this effect has given its name to the procedure in Brookhaven's alignment software.]

Note: If you have designated a **reference detector**, the calculations are modified slightly as follows.

1. Pairs of Total Measured Counts and Total Reference Counts are collected simultaneously.
2. The dust rejection criterion is applied only to the Total Measured Counts. If rejected, the corresponding reference count is also rejected, and more pairs of measurements are made up to the limit of 3N pairs.
3. The Total Measured and Reference Counts are divided by the duration, producing intensities in counts/second.
4. The dark count rate is subtracted and the dead time correction applied to each one of the pair.
5. The reflection correction is applied only to the scattered intensity, not the corresponding reference intensity.
6. The ratio of corrected scattered intensity divided by corrected reference intensity is determined for the pairs, up to N, of those remaining after the dust rejection criterion was applied.
7. The average of the ratios is taken and multiplied by $\sin(\theta)$.

8. In the floating window in the middle of the screen, the following values are displayed at each angle θ :
 - a. The average of the corrected scattered intensities
 - b. The calculated (see below) average of the corrected reference intensities
 - c. The average of the corrected ratios as described in step 7.
 - d. The average of the corrected ratios as described in step 7 multiplied by $\sin(\theta)$.

The calculated average of the corrected reference intensities is obtained by dividing the average of the corrected scattered intensities by the average of the corrected ratios. It is the ratios that are important if the reference detector is of any value; however, the program also displays the average corrected intensities and reference intensities in order to determine the general magnitude of these values when data is later recalled.

Note: One can turn the reference detector normalization on and off. For most modern lasers, the stability is very good over the several minutes required for many measurements. However, for older lasers, or in labs where the room temperature may change a few degrees over the time it takes to make a measurement, the reference detector can account for the drift in laser power that is related to slow temperature drifts or uncompensated power supply drifts. In SLS measurements that may take tens of minutes or longer, the normalization provided by a reference detector may prove even more useful. To test the stability of your laser and goniometer, use the stability test.

Section V: SLS Plots

Static light scattering yields information on structure: size and shape of molecules and colloids; fractal dimensions of irregularly shaped particles; structure in liquids, especially complex fluids. However, there are usually limitations and the reader is well advised to consult the literature. The simple fits shown here, by themselves, may be misleading, and the user is forewarned.

In SLS the independent variable is q , the magnitude of the scattering wave vector is given by:

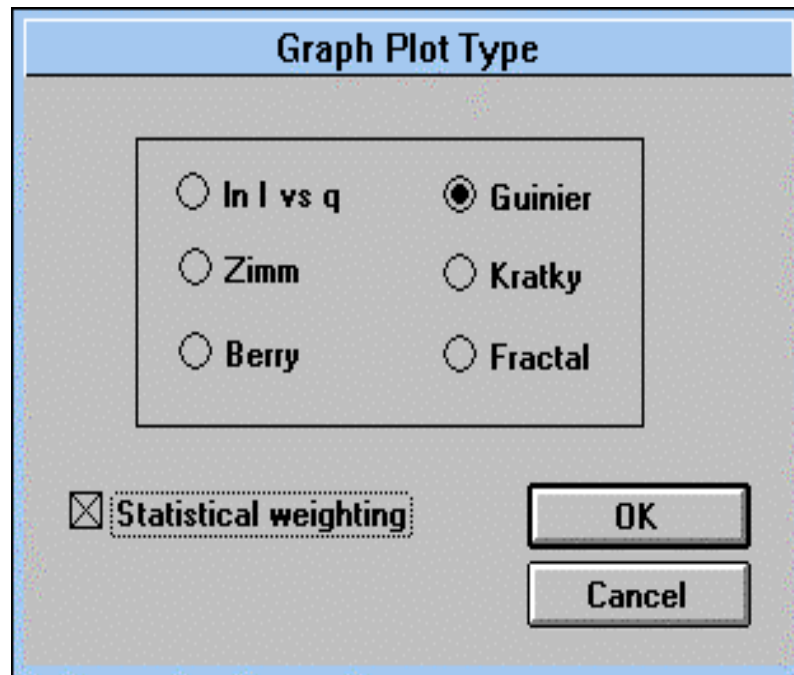
$$q = \frac{4\pi n_l}{\lambda_o} \sin(\theta / 2)$$

where n_l is the refractive index of the liquid, the continuous media, and λ_o is the wavelength of the light source in vacuo.

Typical laser wavelengths used in the visible include 488.0, 514.5, 532.0, 632.8, and diode laser values up to about 720 nm. Though such lasers with high wavelengths are not recommended for use with photomultipliers where the quantum efficiency (sensitivity) is very poor. Typical refractive indices vary from a low value of 1.33 (water and methanol) up to 1.6 (some halogenated solvents). The typical angular variation is from approximately 15° to 155° . The variation in q is from approximately 0.00345 nm^{-1} to 0.0258 nm^{-1} using a HeNe laser (λ_o) in water, a little less than a decade of variation. [Note: q is a function of wavelength and angle. Although one could vary the wavelength, and this has been done with a Krypton laser, it is the variation in angle that typically leads to the variation in q .]

When probing structure the length scale of the probe is q^{-1} . Using the above example, the scale ranges from $\sim 39 \text{ nm}$ to $\sim 290 \text{ nm}$. While one can probe systems whose length scale is smaller than $\sim 39 \text{ nm}$ using SLS, it becomes increasingly difficult to do so with any sensitivity. [The length scale is here defined as the longest dimension. For a sphere this is the diameter. The radius is half, about 20 nm for the above case. The R_g is smaller again, about 15 nm in this case.] Many interesting phenomena are outside this range and other probes (small angle x-ray and neutron scattering) yield either complementary or better information. Keep this in mind when interpreting data. [Note: Using DLS, dynamic light scattering, one can probe systems with sizes considerably smaller than 39 nm .]

The current plots available are obtained by clicking **Graphs** in the Menubar of the Main Window.



The first plot is the most general, Intensity vs. q , where the expected variation in I is large and a log plot is chosen as a convenience in scaling. With structure on the order of the wavelength, large variations in intensity are expected and a Mie scattering pattern, with minima and maxima, are expected. Fitting this type of data is beyond the scope of this software package, yet data can be collected and exported for use with user-supplied fitting routines.

NOTE: In this section on the interpretation of SLS plots the intensity I of scattered light or I_{ex} , the excess intensity of scattered light, has already been corrected for the change in the number of particles seen as a function of angle. That is, it has already been multiplied by $\sin(\theta)$ to account for differences in scattering volume as a function of angle. Thus, in all equations and in all plots, I and I_{ex} are equal to $I' \cdot \sin(\theta)$ or $I'_{ex} \cdot \sin(\theta)$.

In advanced texts on this subject it is the z-average particle scattering factor $P_z(q)$ that contains the variation of intensity with q after correction for $\sin(\theta)$. $P_z(q)$ is also called the form factor or the intraparticle structure factor. It contains information on the structure or form of the particles. At higher concentrations, when interparticle interactions are important, there is another term called the static structure factor or the interparticle structure factor, $S(q)$, which contains information on the distribution of the particles in the liquid. [There is also a dynamic structure factor, accessible using dynamic light scattering.] The intensity $I(q)$ is, for randomly oriented, monodisperse particles, a product of $P_z(q)$ and $S(q)$. For the dilute systems considered here, $S(q)$ is constant. Again, for convenience, we

refer here just to intensities. It is up to the user to account for the more complex cases.

Guinier (see Guinier & Fournet, *Small Angle Scattering of X-rays*, Wiley Interscience, 1955) proposed the following simple variation for large and globular structures:

$$I_{ex}(q) = C \cdot \exp(-R_g^2 q^2 / 3)$$

Plotting $\ln(I_{ex})^{-1}$ vs. q^2 yields a straight line *when a Guinier plot is appropriate*. From the slope R_g , the radius of gyration, can be determined. R_g is given by:

$$R_g^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i}$$

Here m_i is the *ith* mass element of the scatterer and r_i is the distance from the center of gravity to the *ith* element. The interesting thing about this definition is that it is independent of the shape of the scatterer, although to interpret the measured R_g further requires a model. For spherical scatterers $R_g^2 = 3/5 R^2$ where R is the radius of the sphere and for long, thin rods $R_g^2 = L^2/12$ where L is the length of the rod. For other shapes consult specialized texts (Burchard, *Static and Dynamic Light Scattering from Branched Polymers and Biopolymers*, in *Advances in Polymer Science, Vol. 48, Light Scattering From Polymers*, table 3, pages 74-75, Springer-Verlag, New York, 1983).

Please note that R_g is also and more properly called the root-mean-square radius. Unfortunately, the vast majority of texts and publications use the term radius of gyration or root-mean radius of gyration, and it is difficult to break the habit. [Witness: molecular weight vs. relative molar mass.] In addition, for a polydisperse system, $R_g = \langle R_g^2 \rangle_z^{1/2}$, the z-average, root-mean-square radius. Z-averaging is a result of intensity-weighting, and has some interesting consequences which will not be explored further. Contrast this with the weight-averaging of the molecular weight also obtained from light scattering.

For smaller particles and molecules, the partial Zimm and partial Berry plots are useful in the determination of R_g . The word “partial” used here signifies that only the angular variation is considered, not the concentration variation that is required for the determination of the weight-average molecular weight of polymers in dilute solution. For that use the BI-ZPW software. Here, these plots are exclusively for determination of R_g .

The partial Zimm plot stems from the following approximate formula:

$$1 / I_{ex}(q) = C(1 + R_g^2 \cdot q^2 / 3)$$

Here R_g is determined from the slope and the intercept of a plot of $1/I_{ex}(q)$ vs. q^2 .

Zimm and partial Zimm plots are appropriate when the third virial coefficient is negligible. Virial coefficients describe the interaction between scatterers and are beyond the scope of this discussion. However, when the polymer concentration is too high or when the interactions are strong (polyelectrolytes at low salt concentration, for example), an approximation suggested by Berry (*J.Chem.Phys.*, 44, 4550 (1966)) may be used.

The partial Berry plot follows from the following equation:

$$\left(1 / I_{\text{ex}}(q)\right)^{1/2} = C\left(1 + R_g^2 \cdot q^2 / 6\right)$$

Here R_g is determined from the slope and the intercept of a plot of $(1/I_{\text{ex}}(q))^{1/2}$ vs. q^2 . Note the 1/6 instead of 1/3. This arises naturally when taking the square root of the term in parenthesis in the Zimm plot, assuming $(R_g \cdot q)^2/3$ is small compared to 1.

For branched polymers information on the extent of branching may be obtained from the shape of the Kratky plot, where $q^2 I_{\text{ex}}(q)$ vs. q is plotted. Highly branched polymers display a distinct maximum and unbranched polymers do not. However, polydispersity also affects the shape of the plots, and the user should be careful in interpreting the shape of the plot without additional information. For more information consult Burchard, *Macromolecules*, 10, 919 (1977).

Some interesting colloidal particles result from the aggregation of smaller subunits. The structures obtained display a variety of irregular shapes, some more open than others, including branching. The openness of the aggregates is described by a noninteger number called the fractal dimension, d_f : the larger the fractal dimension, the more compact the structure and the lower the fractal number, the more open the structure.

The determination of the fractal dimension is appropriate when the size of the subunit, R_0 (radius of an assumed spherical monomer), and the radius of gyration of the aggregate, R_g , satisfy the following criteria:

$$R_0 < q^{-1} < R_g$$

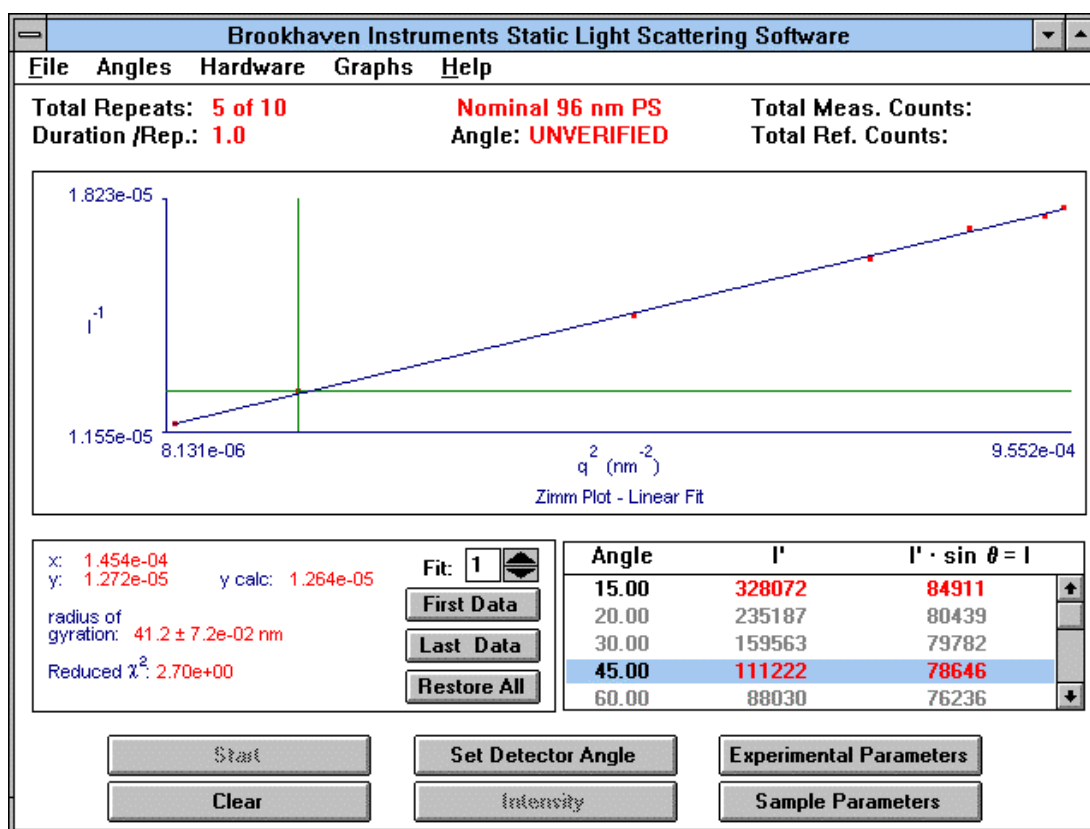
Fractal dimensions also indicate how the aggregate was formed: limiting, ideal cases are diffusion-limited, cluster-cluster aggregation (DLCCA or DLCA) and reaction-limited, cluster-cluster aggregation (RLCCA or RLCA). See Carpineti, Ferri and Giglio, *Physical Review A*, 42, 7347, (1990) for more information.

When a determination of the fractal dimension is appropriate, the following equation is applied:

$$I_{\text{ex}}(q) = C \cdot q^{-d_f}$$

The fractal dimension is obtained as the slope of $\ln I_{\text{ex}}(q)$ vs. $\ln(q)$. Ln-Ln plots are notorious for yielding seemingly straight lines. However, the reader is warned that such plots do not always yield straight lines over a sufficient $\ln(q)$ space for the resulting slope to be usefully interpreted as the fractal dimension.

For those plots for which either R_g or d_f may be determined (Guinier, partial Zimm and Berry, Fractal), the software automatically fits a polynomial to all the points chosen for fitting. This may be all the data taken or a subset. Individual points may be eliminated by clicking on them in a displayed list or by selecting all the points above or below the current cursor position in the plot. An example is shown below for a partial Zimm plot of a nominal 96 nm (diameter) spherical latex.



The best fit of the low angle data yield 41.2 ± 0.1 nm; whereas, simple theory predicts 38 nm ($R_g = (3/5)^{1/2} \cdot R$). The reduced χ^2 is 2.7, indicating the fit is reasonable after deleting a few of the data points (greyed out entries in table) that lay obviously too far from the linear fit. [Reload the data from the database and see for yourself.] Perhaps the remaining difference is due to an error in the assumed particle diameter (TEM gives 96 nm, DLS gives 98 nm); perhaps, due to a relatively small number of doublets, it is due to the z-averaging; perhaps it is due to residual errors in the remaining data points; perhaps it is due to multiple scattering and the measurements should be done again at a lower particle concentration.

When fitting you can choose the order of the fit: 1 for a linear fit, 2 quadratic, 3 cubic, 4 quartic, and 5 quintic. While fits always improve, in an RMS sense, with more parameters, they do not necessarily yield better parameters in the physical sense. We strongly recommend using just the linear and quadratic fits. Why, you ask, did we include the others? Because someone out there in light scatteringland will ask for it. Use the higher order fits with great caution.

Each fit includes either R_g or d_f and $\pm \sigma$, where the error here is the standard deviation. In addition, either the root-mean-square error is given or the reduced χ^2 (chi-squared). Both are measures of goodness-of-fit. The RMS is produced when you choose not to use the statistical weighting. This is accomplished by not clicking on the Statistical Weight box in Graph Plot Type window accessed from clicking on Graph in the main menubar. The equivalent is to assume equal weighting in which case it is impossible to calculate the reduced χ^2 . Instead, the RMS error, a measure of the error of the overall fit, is used to determine the variances and covariances in the fitted parameters.

The advantage of using weighting is that reduced χ^2 (reduced chi-square) not only is a relative measure of goodness-of-fit (lower values mean better fits as with RMS values), but that a good fit should result in a reduced χ^2 of 1 to 2. Smaller values are probably due to statistical fluctuations and not better fits, while significantly larger values indicate one of two possibilities. Either the equation chosen to fit the data is not appropriate, or the errors (systematic like flare or dust, and the random errors) are too large.

Whenever a data point is deleted (double click on the entry in the table in the row showing that angle) or undeleted (double click again on the row with the angle), a fit is changed (1, 2, ...5), or a change in the weighting is selected (Statistical Weighting or Equal Weighting), this forces a new least squares fit to the data with changes in the results.

We use a least-squares fitting routine, where, when Statistical Weighting is selected, we calculate the weights as the reciprocal of the variance in each Y-axis value. This variance must be calculated for the actual quantity plotted ($1/I$, $1/I^{1/2}$, or $\ln I$), taking into account that the variance for a counting experiment is equal to the square root of the total counts. In the table below the Y-axis variable, the X-axis variable, and the propagated statistical weight is shown for each case.

Weighted, Linear Least Squares Fitting			
<u>Type</u>	<u>Y-Axis Variable</u>	<u>X-axis variable</u>	<u>Statistical Weights</u>
Guinier	$\ln I_{ex}$	q^2	$T \cdot (I_s - I_t)^2 / (I_s + I_t)$
Fractal	$\ln I_{ex}$	$\ln q$	$T \cdot (I_s - I_t)^2 / (I_s + I_t)$
Berry	$1/(I_{ex})^{1/2}$	q^2	$4 \cdot T \cdot \sin^2 \theta \cdot (I_s - I_t)^3 / (I_s + I_t)$
Zimm	$1/I_{ex}$	q^2	$T \cdot \sin^2 \theta \cdot (I_s - I_t)^4 / (I_s + I_t)$

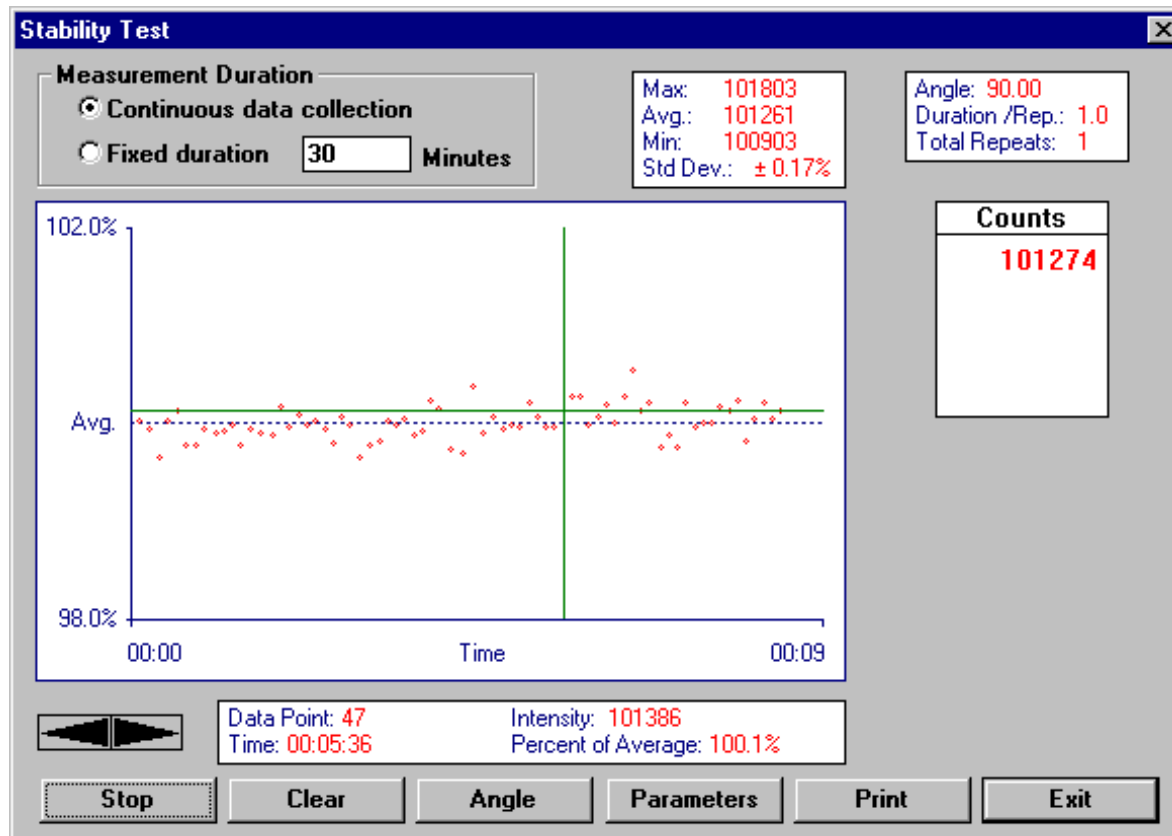
In the case of $I_{ex} = I_s - I_t$ where s stands for either solution (dissolved polymer) or suspension (colloid suspended) and l stands for the liquid without particles or polymer, the propagated weight if just I_{ex} were plotted is $T \cdot \sin^2\theta / (I_s + I_t)$. The different weightings arise from propagating the errors arising from the different functional fits [$\ln I_{ex}$, $1/(I_{ex})^{1/2}$, and $1/I_{ex}$]. The duration for counting is T and it is 0.1, 0.2...9.8, 9.9, or 10.0 seconds.

The weighted, least-squares fitting routine, using a straightforward matrix calculation, returns the intercept, the slope, the variances in each, the covariance between the two parameters, and the reduced χ^2 also designated $\chi^2 / (N-p)$ in some texts on data reduction and error analysis. Here N is the number of fitted data points and p is the number of fitted parameters. For polynomials $p = n + 1$, where n is the order of the polynomial fit. When the reduced chi-square is close to 1, the fit is good *if and only if* the data used in the fit contain only statistically weighted random errors and the equation chosen for the fit is appropriate. Values much greater than 1 indicate a poor fit. Please consult standard statistical textbooks for more information on the use of chi-square.

When we report R_g , we also report the propagated and random error from the fit. In the case of Zimm and Berry plots, the covariance as well as the variances are used to calculate the error in R_g . However, do not place undue emphasis on statistical weighting. It is less important than obtaining good data and choosing the appropriate fit. There is no substitute for making repeat measurements on fresh samples and comparing results to determine if the statistical error from a single fit, using weights determined by the measured intensities and the propagated errors, is about equal to the error from multiple determinations. If it is, you can place a great deal of confidence in the answers. If it is not, you will have to judge the quality of the data in some other way.

Section VI: Stability Test

Occasionally stability is a problem. This may arise from an unstable laser, unstable detector electronics, or a problem in the laboratory main power supply. It may occur if the mechanical parts are not secured properly, causing them to slowly move with time. If the stability is a problem, then do not expect static light scattering measurements results to be good.



You can check the stability at any time. Warm up the laser, filter the vat liquid, and adjust the detector optics such that the total measured counts at any angle --90° is convenient-- is 100,000. The statistical repeatability should be approximately +/- 0.32%, for reasons explained earlier. If there is a nonrandom trend in the counts as a function of time, a trend that is significantly larger than the statistical result, then search for the cause of the instability before spending time making static light scattering measurements.

To access the stability test window, click on **Hardware, Stability Test** in the Menubar of the Main Window. The experimental parameters may be changed from within this window. The intensity will, given enough time, show some trends, perhaps cycling very slowly with room temperature. As long as the results remain randomly flat,

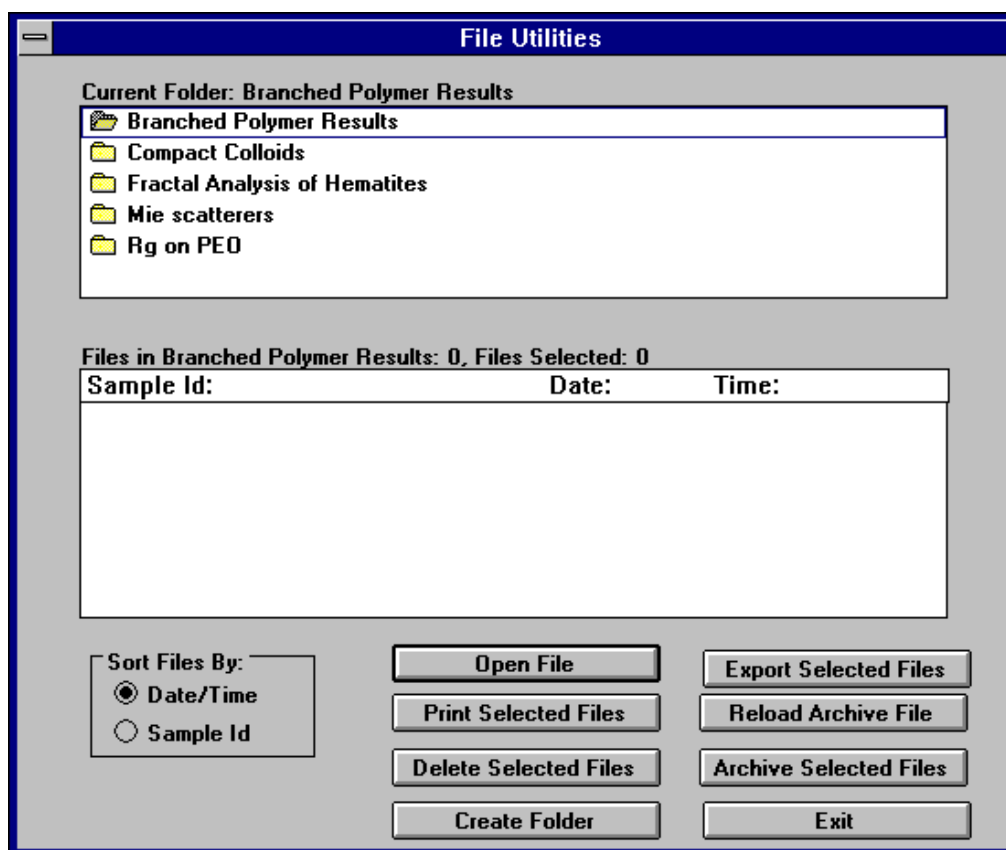
with deviations less than or not much greater than the expected statistical results, over periods of time longer than measurements you will make, the stability is sufficient.

If the intensity vs. time plot shows no obvious trends, then use the Std. Dev. in the box at the top of the Stability Test window as a measure to compare against the expected statistical result.

Section VII: Database and File Format

Results are saved in the currently opened **Folders** as **Files** using the **Sample ID**, **Date**, and **Time** as the file identifiers. Files are automatically saved when the **Auto Save Results** box, under the **Sample Parameters** command button, is checked. If not checked, you can still save folders using **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 the drive\directory path c:\bicw\9kslsw\data using the extension .bak by default. You may change the drive\directory, but you will then have to remember it. If you do not change the filename, the default filename, archive.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.

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:\bicw\9kslsw\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**.

You can create ASCII files suitable for use with spreadsheets and plotting programs. Select a file, then click on **Export Selected File**. The format of exported files is as follows:

Sample ID
 User ID
 Measurement start time
 Measurement date
 Yes/No (liquid intensity measured?), Yes/No (reflection correction applied?)
 Number of angles measured
 Angle 1, Intensity 1, Liquid Intensity 1 (only if “Yes” , liquid intensity measured)
 Angle 2, Intensity 2, Liquid Intensity 2
 .
 .
 .
 Angle N, Intensity N, Liquid Intensity N
 Wavelength
 Sample liquid refractive index
 Sample cell refractive index
 Vat liquid refractive index
 Dark count rate
 In/Out (interference filter)
 N/V/H (polarization analyzer)
 1/2/3 (pinhole size in millimetres)
 Number of repetitions
 Duration per repetition

The intensities are not the excess intensities. You will need to form those in your external program.