# Instruction Manual for BI-ISTW Alignment & Stability Software

*Windows 9KISTW Versions 1.0 and Higher*

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# Please Read

This is your instruction manual for your Brookhaven BI-ISTW Alignment and Stability Software.  Please read it carefully before making measurements. The <u>How To</u> section describes how to install the software.  You may familiarize yourself with some of the features of this software by reloading data files (<u>F</u>iles/Database). If you have any questions or suggestions, please contact Brookhaven Instruments.

This program requires Windows 7 or higher with .NET 4.X.

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, or the latest TurboCorr. Please read the goniometer alignment section in the BI-200SM manual **and** align the goniometer according to the instructions in that manual *before* using this software. However, it 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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# Table of Contents

# Section I: How to Use this Manual and Software

The goniometer alignment software is a program that will tell you how well your goniometer is aligned. Based on the angular independent scattering from a Rayleigh scatterer such as the liquid used for index matching, 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 to emphasize the deviations from a perfect alignment. Examples are given showing what is a good result and several examples of bad results with suggestions for improving the alignment. Results can be printed, saved, and reloaded for future reference. 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 Photo Alignment manual. Take your time. Do a thorough job. Then, follow the instructions below.

We recommend using this software when first installing your BI-200SM goniometer, whenever a major change is made to it (laser change, vat removal/cleaning, for example), and once a week to check that the alignment has not changed. If the mechanics are locked down as instructed in the BI-200SM manual, and no one makes changes to the laser position or various lens/aperture adjustments, then the goniometer will remain aligned year-after-year. Experience shows, however, that small changes do occur, mostly as the result of human error. So keep people from touching the laser and the various mechanical adjustments.

To install the software, insert the flash drive into a USB port on the computer. Double click on the Application named, "9kistwSetup_vx.xx". Click "Yes" or "Allow" on the next prompt. Follow any on-screen instructions that appear. When finished, a Brookhaven Instruments Corporation icon with the name Goniometer Alignment Software will be added to your Brookhaven Instruments program group, or a group with this icon and name will be added. 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. Check or uncheck **Reference Detector**. If you have a reference detector, plug the digital signal (TTL compatible) into input B on the rear of the correlator. The scattered light intensity and the reference intensity are collected simultaneously. A ratio is formed, after correcting both for their dark count rates and for their dead-times. 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. Select "Combine 2 detectors" if equipped with CrossCorr technology.
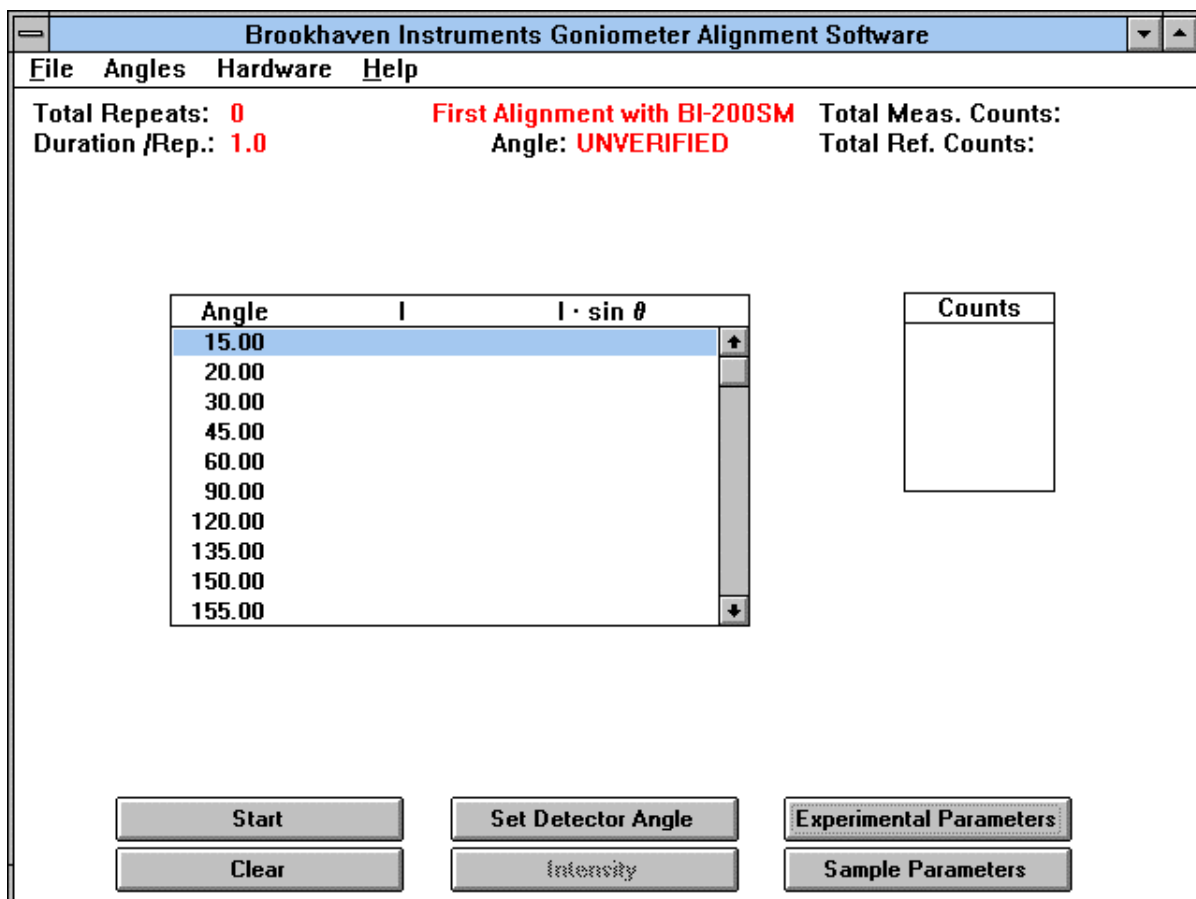


Click on the **Sample Parameters** command button in the lower part of the screen. Fill in the **Sample Identification**, **Operator Identification**, and **Notes** fields. The

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.  Fill in the **refractive index** values for the **Sample Liquid**, **Sample Cell**, and **Vat Liquid**. The default values shown on the next page assume that the sample and vat liquid are the same: decalin (cis-trans decahydronaphthalene), refractive index 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:

$$\mathbf{f} \equiv \mathbf{f}_{sl/c} + \mathbf{t}_{sl/c}^{2}\,\mathbf{f}_{vl/c}$$

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

$$\mathbf{f}_{sl/c} = \left(\frac{\mathbf{n}_{sl} - \mathbf{n}_{c}}{\mathbf{n}_{sl} + \mathbf{n}_{c}}\right)^{2}$$

$$\mathbf{f}_{vl/c} = \left(\frac{\mathbf{n}_{vl} - \mathbf{n}_{c}}{\mathbf{n}_{vl} + \mathbf{n}_{c}}\right)^{2}$$

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.

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. [NOTE: Due to the weak scattering of water, it is not recommended for use when aligning the goniometer.  If the vat liquid does not provide sufficient scattering --typically due to a low power laser-- use a clean cell filled with multipli-filtered toluene.] 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**.

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$^o$. Click the **Set Detector Angle** command button and enter the angle as 90$^o$.

Click on the **Experimental Parameters** command button in the lower part of the screen. Block the light to the detector 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.]

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 weakest scattering will come from a pure liquid without particles or polymers and at 90°. The strongest scattering will occur at the extreme angles. If you have not done so previously, move the goniometer to, and **Set Detector Angle** at, 90°. 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. At all other angles, the Total Measured Counts will be higher and the corresponding relative error lower.

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 scattering liquid 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, organic liquid such as the vat liquid (for example, cis-trans decahydronaphthalene, also known as decalin) used as the scattering media for alignment

purposes, enter 1.33 for the **Dust Rejection Ratio**. Values from 1 to 10 are allowed: small numbers are best for clean liquids; somewhat larger numbers (up to 2 or 3) may be used if dust is difficult to remove. NOTE: Using larger numbers may result in less than optimum alignment, but may be necessary if dust cannot be removed.

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.

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 10 angles ranging from 15$^o$ to 155$^o$, a good selection for checking the alignment. 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$^o$ and 155$^o$. 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 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. The new list will include the first and last angles you entered, with an equal increment 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, a list of linearly spaced angles is created using an increment equal to (First - Last)/(List Size - 1).

At least 5 and no more than 100 angles are allowed. Click OK.

## Edit Measurement Angle List  ✕

**Angle (degrees)**

1. 15.00
2. 20.00
3. 30.00
4. 45.00
5. 60.00
6. 90.00
7. 120.00
8. 135.00
9. 150.00
10. 155.00

List Size: 10

Add Angle

Angle [          ]

Delete Angle 1

Delete All

Insert

Increment  5.00

Apply Increment

Set List Range

Load List      Default List      OK

Save List As...      Cancel

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 one 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.

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\9KISTW\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

Using the set of default angles, click on the **Start** command button to initiate a measurement. With a motorized BI-200SM, the arm will move to the extreme angle in the list, the one closest to the current position. If $90^{o}$ is the current position, the arm will move to $155^{o}$. With a manual goniometer, or one not under control of the BI-9000AT correlator/TurboCorr, a window will appear instructing you to move the arm to $155^{o}$.

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, for example 5.

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 is 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 (i.e. filtering the vat liquid, perhaps changing the filter).

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.]*

The average is divided by the duration to form the average, uncorrected count rate (an intensity).

5. From the average uncorrected intensity the dark count rate is subtracted. This is the measured, average intensity corrected for dark count rate.

6. The measured, average intensity corrected for dark count rate, $I_m$, is further corrected for the dead time, $\tau_d$, to produce the true count rate as follows: $I_t = I_m/(1-\tau_d I_m)$. For the BI-9000AT, $\tau_d$ 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.

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

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

Here f is the combined reflection correction discussed in the **Setting Up the 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.

8. To form the intensity scattered per unit volume, one has to account for the different volumes observed at different scattering angles. Focusing of a $TEM_{001}$ 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 $\theta$.

[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, and to this software, for determining alignment.]

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 <u>only</u> 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 $\theta$:

    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 few minutes required to test alignment. 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 more useful. To test the stability of your laser and goniometer, use the stability test.

# Section V: Interpretation of $I\sin(\theta)$ Measurements

By definition, a Rayleigh scatterer is one that scatters light (per particle) independent of angle. Particles very much smaller than the wavelength of light are Rayleigh scatterers. Compared to the wavelength, the particle acts like a point dipole, and point dipoles display no angular dependence in their scattering pattern. There is no better, or more convenient, Rayleigh scatterer than a liquid molecule (also a particle) such as toluene or decalin, provided it scatterers sufficient light given the laser power and cleanliness of the liquid.

Therefore, if the goniometer is well aligned, a plot of $I'\sin(\theta)$ vs. $\theta$ for a liquid should be a flat, horizontal line. Deviations, above random error, signify either misalignment, excessive dust, scratches on the vat or cell walls, or a source of light reaching the detector from a position other than the scattering volume. Such a source of unwanted light is called flare light. It may arise from smudges on the entrance window of the vat, a poorly positioned beam stop, a poorly positioned aperture that is clipping the laser beam, or impurities in the vat or cell walls that scatter light excessively.

To amplify the possible errors, the results of two different normalizations are shown:

$$I' \cdot \sin(\theta) / \langle I' \cdot \sin(\theta) \rangle - 1 \quad \text{vs.} \quad \theta$$

$$\text{or}$$

$$I' \cdot \sin(\theta) / I'_{90} - 1 \quad \text{vs.} \quad \theta$$

In the first case, the normalization is to the average of all the $I'\sin(\theta)$ values. In the second case, the normalization is to the value at $90^0$. Each has an advantage.

With a perfect alignment, either method of plotting would result in a horizontal line with zero magnitude. Due to statistical errors, even a perfectly good alignment shows random values centered around zero.

The example below shows a very good $I'\sin(\theta)$ result: the line is flat with no single value greater than +/- 1% above the average of all the others. You may review this result by clicking **File**, then **Database**, then double clicking on the **folder** labeled **Sample Alignment Data** and finally double clicking on the **file** labeled **Very Good Results**.
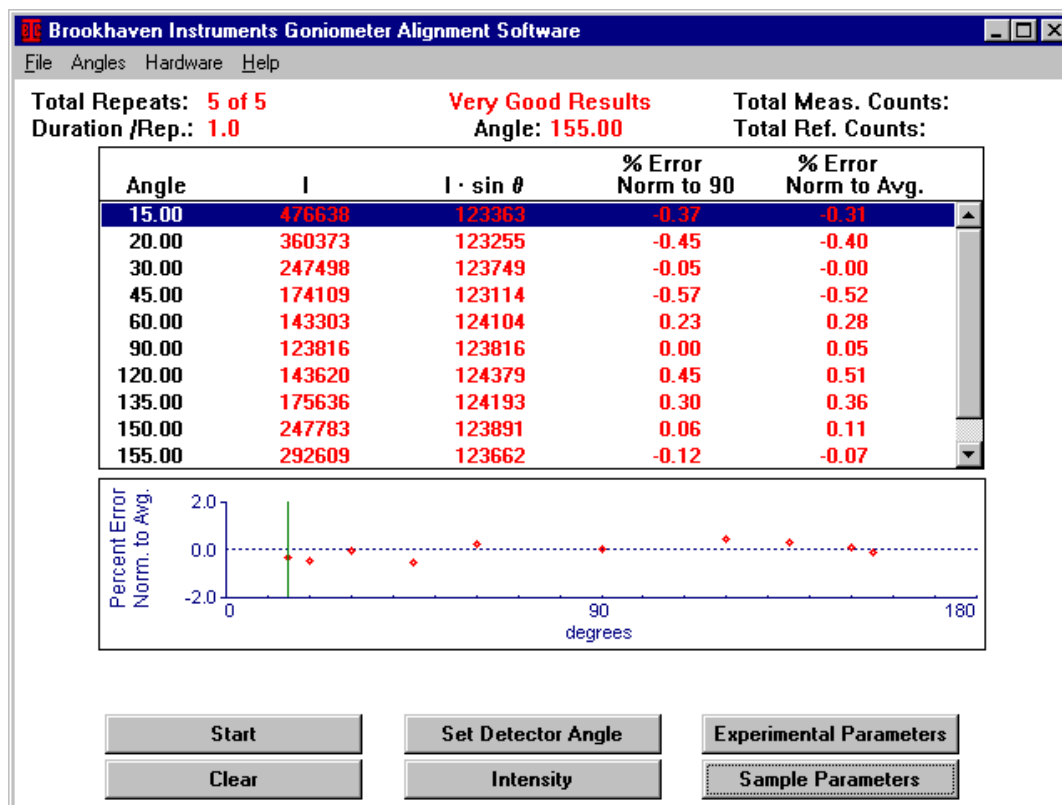
Not all results will be this good. During alignment, however, do everything you can to achieve a result like this. It may mean that the index matching vat has to be removed and soaked overnight in mild laboratory detergent while a Teflon-coated stir bar is gently agitating the soapy solution. It may mean that the vat will have to be rotated a very slight amount so the entering laser beam misses a minute imperfection in the glass. It may mean that the output mirror of the laser, as well as the focusing/steering lens in the BI-200SM, must be cleaned carefully. Or it may mean that you will repeat the various alignment procedures several times until the final results are optimal.

The next example, **Interior Mode**, shows an acceptable result *except* the value at $30^{\circ}$. This may be the result of flare light. Try twisting the beam stop. Try blocking some of the extraneous light using black, electricians tape. The amount of flare light that comes from the laser varies from laser to laser, model to model, and manufacturer to manufacturer. There are no constant rules to follow. Look for flare light around the entrance to the vat with the room lights off.

The flare light may be caused from room light or from window light. Block the window light with curtains or black paper. Attach the black, plastic snout to the detector optic after doing the initial alignment. The snout blocks most extraneous room and window light.

An interior peak or valley in the curve may be the result of a smudge or dust on the exterior of the vat: clean it using lens paper dipped in reagent grade methanol. If that doesn't work, try acetone followed by reagent grade methanol. (Lens paper is special paper designed for cleaning microscope lenses and other optical instruments. It is not regular tissue or lab paper, which may scratch optical surfaces.) If that doesn't work, you will have to remove the vat and soak it overnight in mild laboratory detergent as described above. After cleaning, keep your fingers off the surfaces where light enters or exits. Clean the nylon screws that hold the vat in place. Clean the inside of the black metal pot that holds the vat. Do not allow the nylon screws to touch the vat until *after* it is in place. With these precautions, you minimize the chance that smudges or dirt on the vat, arising from the tips of the nylon screws or from the inside wall of the black metal pot, will affect the measurements.
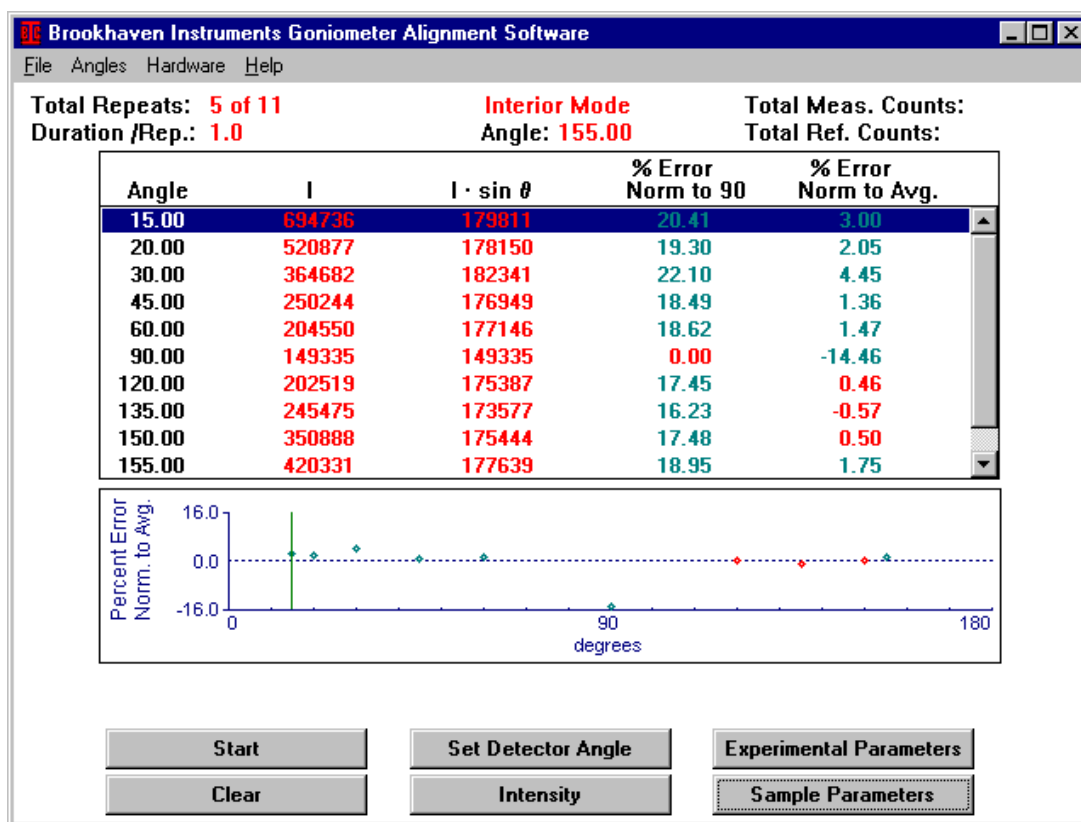


If all efforts fail to remove an interior peak or valley, make measurements at angles two degrees on either side of the offending angle. Do this both to check the alignment and when making dynamic and static light scattering measurements. Eventually, replace the vat or find the cause of the problem. In the meantime, perfectly good measurements can be made by ignoring the problem angle(s).

The next example, **Dishbowl**, shows a curve, roughly symmetric about $90^0$ with an error of only a few percent at the extremes. Some dish bowls can be flattened by changing **slightly** the vertical adjustment on the focusing/steering lens assembly. This suggests that the beam was not parallel to the optical table and the adjustment --try one

way then the other, checking each by making an $I\sin(\theta)$ measurement-- is making it more parallel.
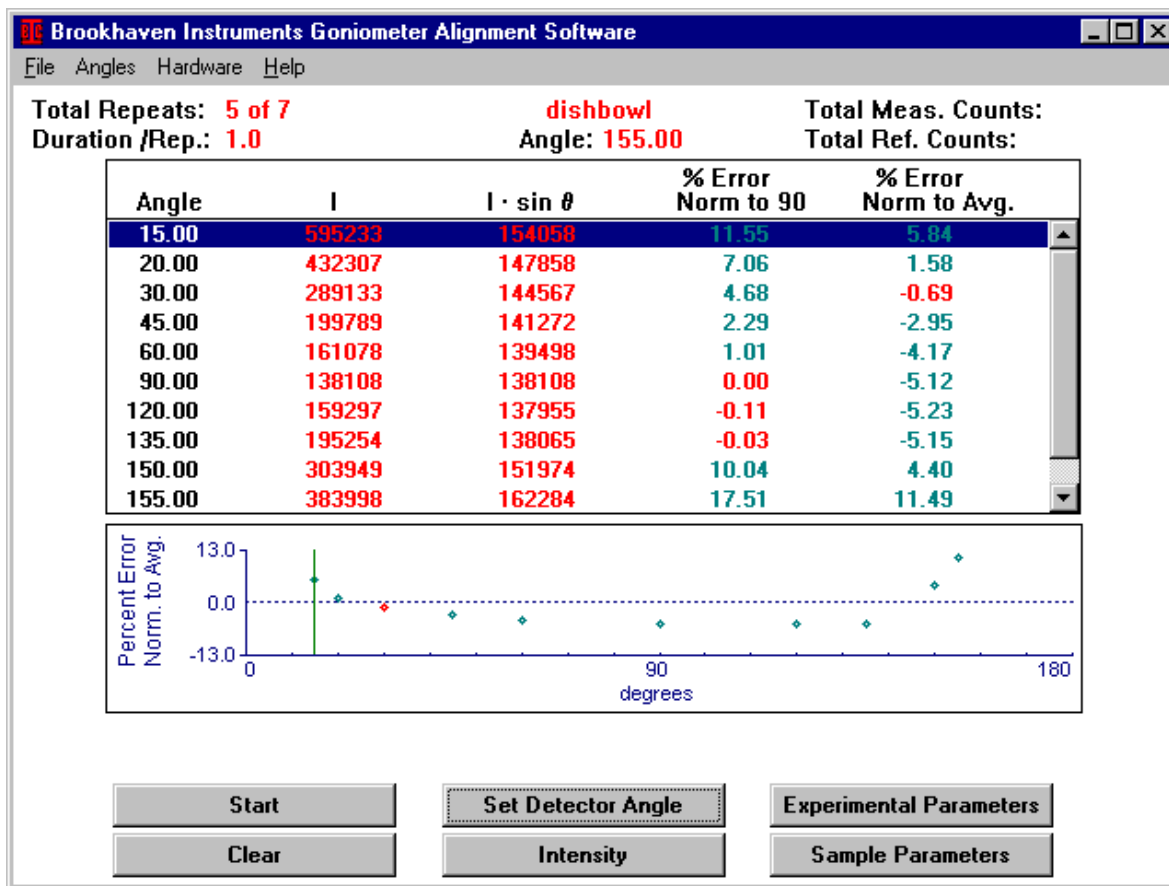


A dramatic example of the symmetric, positive dish bowl occurs if the polarization of the laser is horizontal instead of the required vertical. Here the deviations at the extreme angles can be 30% and higher. The effect is the result of dipole scattering. Dipoles do not scatter along their polarization axis. Thus, a horizontally polarized light will not excite scattering in an isotropic scatterer at 90$^o$. Most liquid molecules are not isotropic; they are anisotropic scatterers. As a result the scattering at 90$^o$ will not be zero but it will be a minimum and the dish bowl will be symmetric, positive and quite large in magnitude. All this can be quantitatively predicted from the angle of polarization, the scattering angle, and the depolarization ratio of the scatterer.

If the vertical polarization of the laser is within +/- 5$^o$, the effect is insignificant: less than 0.4% in toluene at 15$^o$ and 165$^o$ scattering angles. In fact, while this effect is rare, it has happened in two, special cases: when using a cylindrical laser and not paying attention to the marking for vertical polarization; and when a laser is purchased from an outside source and the polarization is horizontal. For a cylindrical laser the solution is trivial: rotate the laser until the polarization is vertical. For the case of a laser that was designed for horizontal polarization output, a polarization rotator is required.
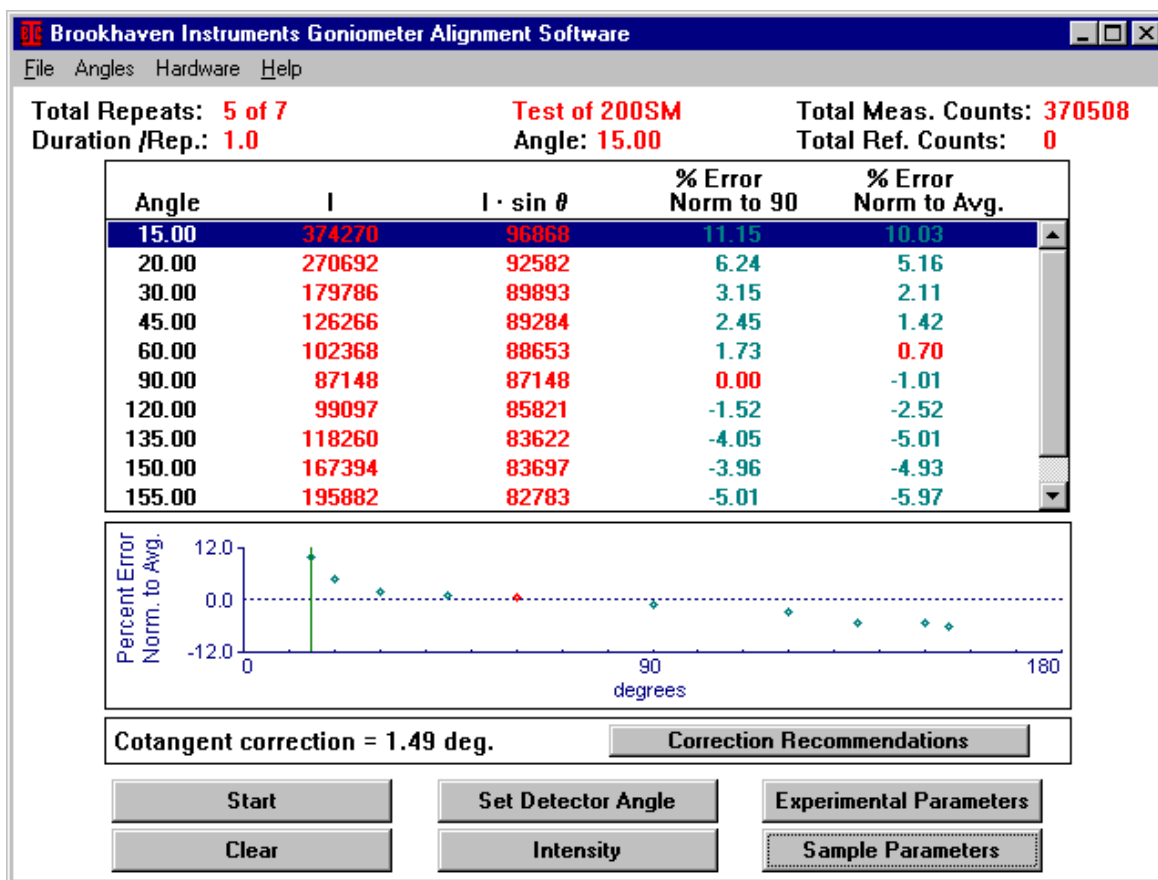
The next example, **Cotangent Correction**, is by far the most common. The results, when normalized not to the average of $I'\sin(\theta)$, but rather to $I'_{90}$, look like an S-shaped curve, symmetric about $90^\circ$, lying on its side. It may show positive deviations below $90^\circ$ and negative above (reverse S), or negative deviations below $90^\circ$ and positive above (normal S). In either case the curve, if symmetric, resembles the function $\varepsilon \cot(\theta)$ vs. $\theta$, where $\varepsilon$ could be positive or negative.

A common reason for this to occur is the following: the measured angle $\theta_m$ does not equal the true angle $\theta_t$. There is a difference between the mechanically defined zero angle as read on the verniers and the true, optical zero angle as defined by the laser beam.

Defining $\varepsilon$, the angular error, by $\theta_m = \theta_t + \varepsilon$, and expanding $\sin(\theta_m) = \sin(\theta_t + \varepsilon)$ assuming $\varepsilon$ is small, leads to the following approximation:

$$I' \cdot \sin(\theta_m) / I'_{90} - 1 \approx \varepsilon \cdot \cot(\theta_m)$$

Thus, normalizing to $90^\circ$ allows one to see more clearly if the cotangent correction applies.

**Brookhaven Instruments Goniometer Alignment Software**

File  Angles  Hardware  Help

Total Repeats: 5 of 7     Test of 200SM     Total Meas. Counts: 370508
Duration /Rep.: 1.0     Angle: 15.00     Total Ref. Counts: 0

| Angle | I | I · sin θ | % Error Norm to 90 | % Error Norm to Avg. |
|-------|-----|-----------|---------------------|----------------------|
| 15.00 | 374270 | 96868 | 11.15 | 10.03 |
| 20.00 | 270692 | 92582 | 6.24 | 5.16 |
| 30.00 | 179786 | 89893 | 3.15 | 2.11 |
| 45.00 | 126266 | 89284 | 2.45 | 1.42 |
| 60.00 | 102368 | 88653 | 1.73 | 0.70 |
| 90.00 | 87148 | 87148 | 0.00 | -1.01 |
| 120.00 | 99097 | 85821 | -1.52 | -2.52 |
| 135.00 | 118260 | 83622 | -4.05 | -5.01 |
| 150.00 | 167394 | 83697 | -3.96 | -4.93 |
| 155.00 | 195882 | 82783 | -5.01 | -5.97 |

Percent Error Norm. to Avg. — 12.0 / 0.0 / -12.0 — 0 ... 90 ... 180 — degrees

Cotangent correction = 1.49 deg.     Correction Recommendations

Start     Set Detector Angle     Experimental Parameters
Clear     Intensity     Sample Parameters

With the software as provided, if there is a significant, symmetric deviation about $90^\circ$, then the user is offered the opportunity to either apply the correction or not. If applied, $\varepsilon$ is automatically calculated using an equally weighted, linear least-squares fit of

all the points not deleted. Points may be temporarily deleted by double clicking on them. This can be useful if there is an interior peak or flare at the extreme angles which may mask the S-shaped nature of the curve.

NOTES: Applying the cotangent correction to any S-shaped curve almost always improves the next $I'\sin(\theta)$ measurement, even if the curve is not symmetric about $90^{\circ}$. It may take more than one application of the cotangent correction to get the full benefit, especially if the initial $\varepsilon$ is greater than $0.5^{\circ}$.

After applying the cotangent correction, follow the instructions for setting the true angle and making the next measurement. When successfully completed, both verniers should be adjusted mechanically to agree with the correct angle as shown on the screen.

As a final note, consider that many molecular weight measurements, especially in aqueous solutions, are made over the classic angular range from $30^{\circ}$ to $150^{\circ}$. This is a range over which most alignment procedures produce good results. At the extremes, especially at low angles, it is sometimes harder to align. At the low angles flare from the main beam and residual dust are the biggest problems.

# Section VI:  Stability Test

Occasionally, alignment is not the problem; stability is. 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 the $I\sin(\theta)$ results to be good.

You can check the stability at any time, even before alignment is finished. It is only necessary to warm up the laser, introduce and filter the vat liquid, and adjust the detector optics such that the total measured counts at any angle --90$^{\circ}$ 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 improving the alignment.
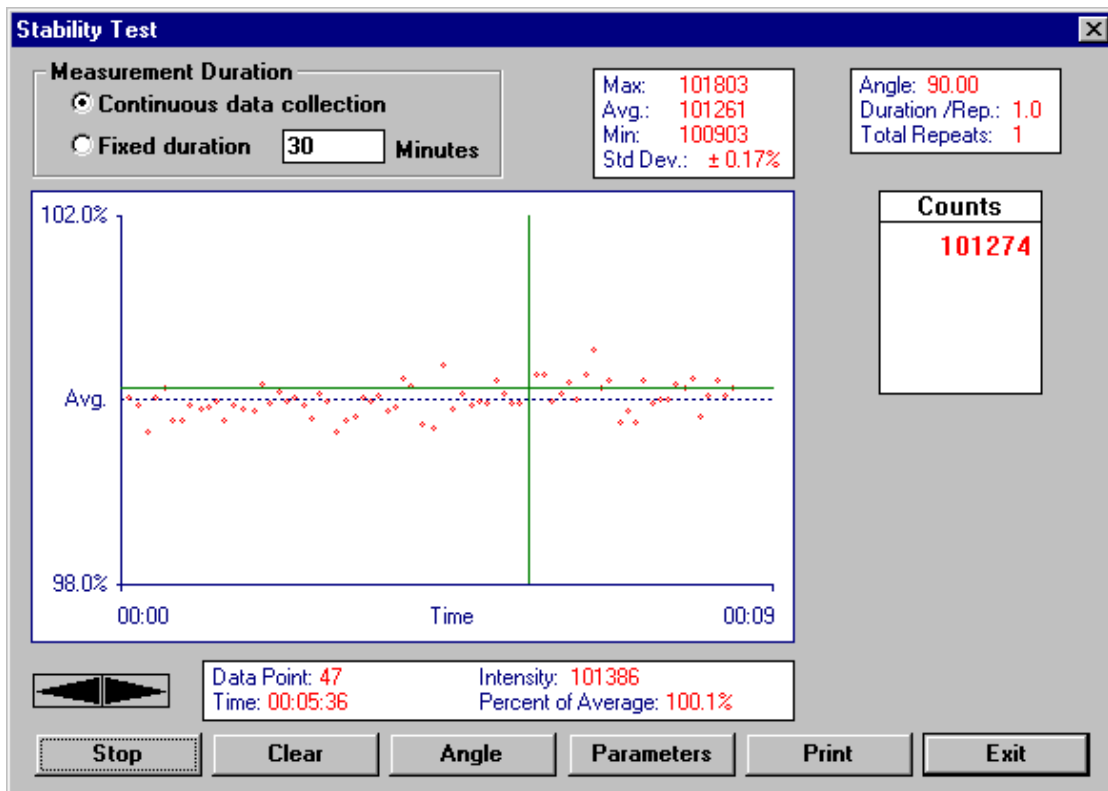


To access the stability test window, click on **Hardware**, **Stability Test**  in the Menubar of the Main Window. The experimental parameters may be changed from within this window.  The intensity will, given enough time, show some trends, perhaps cycling very slowly with room temperature. As long as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

I′sin(θ) measurements take only a few minutes to complete; molecular weight measurements may take 20 to 30 minutes. Thus, if the stability is good for an hour or more, stability is not a problem.

If the counts vs. time is flat over an hour or so, 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

        Alignment data 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**.
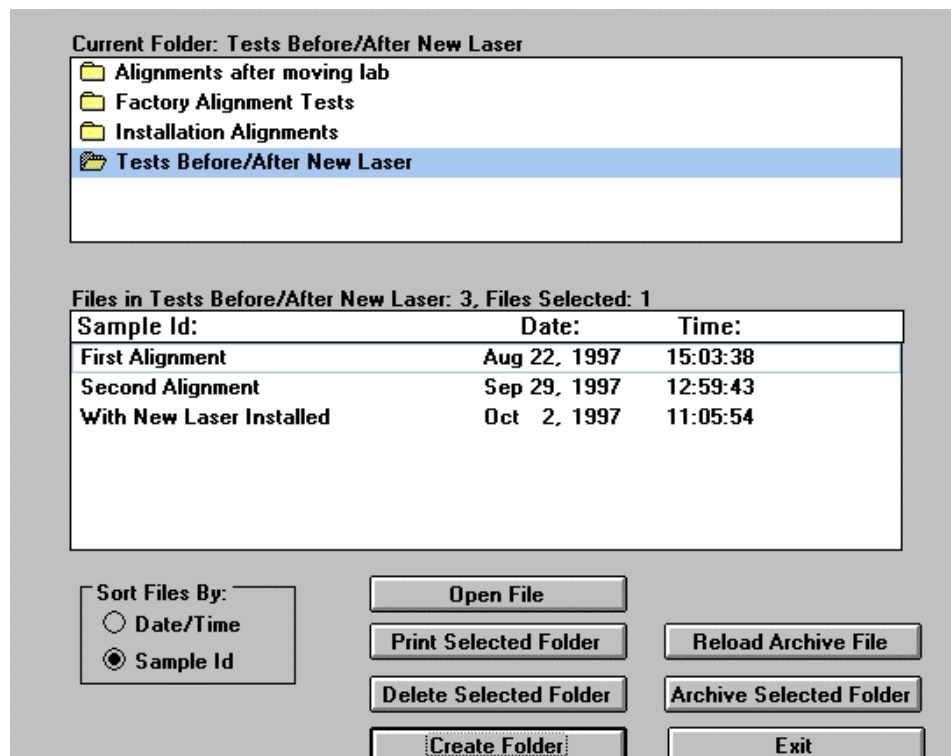


        Select a single file by clicking on it. Select a string of consecutive files by clicking on the first, then, while holding down the Shift key, click on the last. Select a string of nonconsecutive files by clicking on the first, then, while holding down the Control key, click on any number of files, consecutive 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\9kistw\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\9kistw\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**.