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Formation of Iron(III) Thiocyanate - Stopped Flow

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1 Abstract

The purpose of this laboratory is to determine the equilibrium constant and the forward and reverse rate constants for the formation of Iron(III) Thiocyanate.

2 Introduction

The reaction of Iron(III) with thiocyanate ion in aqueous solution is a classical metal ion substitution reaction that has been has been extensively investigated, and its pathway to formation of the dark red Iron(III)-thiocyanato complex (Fig. 1) are well understood. Using appropriate techniques, the reactant concentrations can be adjusted to give half-times between milliseconds to seconds, making it suitable to a stopped-flow spectrophotometric study. Since the proton transfer steps (via K_{a1} and K_{a2}) are diffusion controlled, and so much faster than those involving either complex formation or decay, only one process is observed on this time scale.

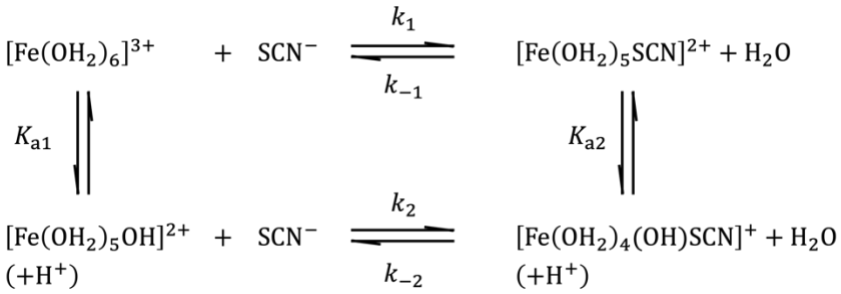

Figure 1. Reversible formation of Iron(III)-thiocyanato complexes.

Experimentally, the pseudo-first-order kinetics are followed, hence the resulting absorbance–time traces are correspondingly simple to analyze. The rate constants k_1, k_{-1}, k_2, and k_{-2} may be determined when combining the known values of K_{a1} and K_{a2} with the primary kinetic data. Also, the kinetic results can also define the formation constant of the Iron(III)–thiocyanato complex ($K_f = k_1/k_{-1}$). Additionally, since the reactants are basically colorless and the products are strongly colored, the absorbance data obtained in the kinetic experiments can be used for a more direct spectrophotometric evaluation of K_f.

To obtaining the rate law of this reversible reaction, we simplify the kinetic analysis by making the following changes to the nomenclature:

$$[Fe(OH_2)_6]^{3+} = [Fe] \qquad [Fe(OH_2)_5OH]^{2+} = [FeOH]$$

$$[Fe(OH_2)_4OHSCN]^{2+} = [Fe(OH)SCN] \qquad [Fe(OH_2)_5SCN]^{2+} = [FeSCN]$$

Thus, the rate of change of concentration of thiocyanate ion is described by

$$-\frac{d[SCN]}{dt} = k_1[Fe][SCN] + k_2[FeOH][SCN] - k_{-1}[FeSCN] - k_{-2}[Fe(OH)SCN] \qquad \text{Eq. 1}$$

Using

$$K_{a1} = \frac{[FeOH][H^+]}{[Fe][SCN]} \quad \text{and} \quad K_{a2} = \frac{[Fe(OH)SCN][H^+]}{[FeSCN]}$$

in Eq. 1, we get

$$-\frac{d[SCN]}{dt} = \left(k_1 + k_2 \frac{K_{a1}}{[H^+]}\right)[Fe][SCN] + \left(k_{-1} + k_{-2} \frac{K_{a2}}{[H^+]}\right)[FeSCN] \quad \text{Eq. 2}$$

Now let us define the forward (k_f) and reverse (k_r) rate constants as

$$k_f = k_1 + k_2 \frac{K_{a1}}{[H^+]} \quad \text{Eq. 2a}$$

$$k_r = k_{-1} + k_{-2} \frac{K_{a2}}{[H^+]} \quad \text{Eq. 2b}$$

This will allow us to simplify Eq. 2, as

$$-\frac{d[SCN]}{dt} = k_f [Fe]_T[SCN] + k_r [FeSCN] \quad \text{Eq. 3}$$

where $[Fe]_T$ represents the total concentration of Iron(III).

At any given time, t, the concentration of thiocyanate ion, $[SCN]$, may be expressed in terms of a displacement, x, from the equilibrium concentration, $[SCN]_{eq}$. In other words,

$$[SCN] = [SCN]_{eq} + x \quad \text{Eq. 4}$$

A similar result can be found for the bound concentration of thiocyanate ion, $[FeSCN]$, using the stoichiometry of the reaction:

$$[FeSCN] = [FeSCN]_{eq} + x \quad \text{Eq. 5}$$

At equilibrium $-d[SCN]/dt = 0$, so $k_f [Fe][SCN] = k_r [FeSCN]$. Using Eq. 4 and Eq. 5 into Eq. 3 leads to

$$-\frac{dx}{dt} = (k_f [Fe]_T + k_r) \cdot x \quad \text{Eq. 6}$$

Now Eq. 6 and Eq. e can be combined to obtain

$$\frac{d[FeSCN]}{dt} = (k_f [Fe]_T + k_r) \cdot \left([FeSCN]_{eq} - [FeSCN]\right) \quad \text{Eq. 7}$$

Rearranging terms and integrating, Eq. 7 leads to:

$$\ln \frac{[FeSCN]_{eq}}{[FeSCN]_{eq} - [FeSCN]} = (k_f[Fe]_T + k_r) \cdot t \quad \text{Eq. 8}$$

Since FeSCN is the main absorbing species we can use Beer's Law to describe its absorbance

$$A = \varepsilon_{FeSCN} \cdot [FeSCN] \cdot \ell \quad \text{Eq. 9}$$

Which, replacing in Eq. 8, leads to

$$\ln \frac{A_{eq}}{A_{eq} - A} = (k_f[Fe]_T + k_r) \cdot t \quad \text{Eq. 10}$$

where A_{eq} represents the absorbance of the system at equilibrium.

Plotting $\ln\left(A_{\mathrm{eq}}/(A_{\mathrm{eq}}-A)\right)$ vs. t shows a linear relation between them, where $(k_{\mathrm{f}}[\mathrm{Fe}]_{\mathrm{T}}+k_{\mathrm{r}})$ is the slope. This quantity is defined as the observed first-order rate constant, k_{obs}. In other words,

$$k_{\mathrm{obs}} = k_{\mathrm{f}}\,[\mathrm{Fe}]_{\mathrm{T}} + k_{\mathrm{r}}$$

Or, using Eq. 2a and 2b

$$k_{\mathrm{obs}} = \left(k_1 + k_2\frac{\mathrm{K_{a1}}}{[\mathrm{H^+}]}\right)[\mathrm{Fe}]_{\mathrm{T}} + k_{-1} + k_{-2}\frac{K_{\mathrm{a2}}}{[\mathrm{H^+}]} \qquad \text{Eq. 11}$$

3 Experimental Details

Distilled water is used in all preparations. The following stock solutions should be prepared in advance

1. 1.00 M $\mathrm{HClO_4}$, from dilution of a standardized concentrated solution of perchloric acid to $1.00\ \mathrm{dm^3}$.
2. A standardized ferric ion solution –ca. 0.2 M Iron(III)– prepared from $\mathrm{Fe(ClO_4)_3}\cdot x\ \mathrm{H_2O}$ and made up to be exactly 0.400 M in $\mathrm{HClO_4}$. This corresponds to about 25 g of $\mathrm{Fe(ClO_4)_3}\cdot x\ \mathrm{H_2O}$ dissolved in 1.00 M $\mathrm{HClO_4}$ $(100.0\ \mathrm{cm^3})$ with dilution to $250.0\ \mathrm{cm^3}$. Because the water content of solid ferric perchlorate is variable, it is not a simple matter to make up the solution to a particular Iron(III) concentration. If analysis shows it to lie in the range 0.17 to 0.23 M no adjustment is necessary.
3. 2.00 M $\mathrm{NaClO_4}$ prepared by dissolving $\mathrm{NaClO_4}\cdot\mathrm{H_2O}$ (280.92 g) in water and diluting to $1.00\ \mathrm{dm^3}$.
4. A solution approximately 1.5×10^{-4} M in NaSCN and 1.00 M in $\mathrm{NaClO_4}$.

Solution Name	$\mathbf{0.2\ M\ Fe(ClO_4)_3}$ & $\mathbf{0.40\ M\ HClO_4}$ $(\mathbf{cm^3})$	$\mathbf{1.0\ M\ HClO_4}$ $(\mathbf{cm^3})$	$\mathbf{2.0\ M\ NaClO_4}$ $(\mathbf{cm^3})$
A1	0.25	1.90	3.85
A2	0.50	1.80	3.70
A3	1.00	1.60	3.40
A4	1.50	1.40	3.10
A5	2.00	1.20	2.80
B1	0.25	3.90	2.85
B2	0.50	3.80	2.70
B3	1.00	3.60	2.40
B4	1.50	3.40	2.10
B5	2.00	3.20	1.80
C1	0.25	5.90	1.85
C2	0.50	5.80	1.70
C3	1.00	5.60	1.40
C4	1.50	5.40	1.10
C5	2.00	5.20	0.80

Table 1. Stock solution volumes for preparation of Iron(III) reagents. Each reagent is made up to a volume of 10.00 $\mathrm{cm^3}$ with water.

4 Procedure

1. Follow the reaction progression by monitoring the reactant spectroscopically. The absorbance is proportional to the concentration of $[\mathrm{FeSCN}]$.
2. Since these are ionic reactions, the ionic strength depends not only on concentrations but on the $[\mathrm{H}^+]$, so the rate constants will be measured as a function of acidity. For reaction A the concentration is 0.10 M, for reaction B is 0.20 M, and for C it is 0.30 M.
3. The change in absorbance is observed on each reaction and designated as the quantity ΔA. Also measure k_{obs}.
4. Obtain values for k_{f} and k_{r} by plotting k_{obs} vs $[\mathrm{Fe}]_{\mathrm{T}}$ and fitting it with a linear trend line, according to Eq. 11.
5. Now obtain values for k_1 and k_2 by plotting k_{f} vs $K_{\mathrm{a1}}/[\mathrm{H}^+]$ and fitting it with a linear trend line, according to Eq. 2a. Also, obtain values for k_{-1} and k_{-2} by plotting k_{r} vs $K_{\mathrm{a2}}/[\mathrm{H}^+]$ and fitting it with a linear trend line, according to Eq. 2b. Use the literature values for $K_{\mathrm{a1}} = 2.04 \times 10^{-3}\mathrm{M}$ and $K_{\mathrm{a2}} = 6.5 \times 10^{-5}\mathrm{M}$.

5 Device and program configuration

1. Make sure the regulator behind the sampling handling unit is at 4 bars and on the N_2 gas tank is at 100 psi.
2. In the **load position**, screw two syringes with clean water. Then pull down on the brown pistons and make sure there are no air bubbles inside the drive syringes (where water was displaced). Then set it to the **drive position**.
3. Open the **Pro-Data SX** program on the computer. Click the **Drive** icon so it displaces old water into the flow circuit. Click the **Drive** icon 5 more times.
4. Enter the following parameters:

   Wavelength: 450 nm

   Time base: Time=0.125 s, Point=10,000

   Trigger: External

   Baseline: check Auto HV

   Click the Set icon after all parameters have been set
5. With clean water in the flow circuit and cell, click the **Reference** icon (in the Baseline panel). The reading for **Absorbance** at the top should read **0 AU**.
6. Switch the drive valves to **load position** on machine, then raise the drive syringes and remove the water syringes. Place the new drive syringes with the reagents onto the sample handling unit. Lower the brown piston until they reach the drive ram (both should be touching the drive ram). Set the drive valves to the **drive position**.
7. In the program, click the **Drive** icon to displace water in circuit with reagents. Click the **Drive** icon 5 more times.
8. Click the **Acquire** icon to perform and collect absorbance data. The graph will appear with **time** on x −axis and **absorbance** on y −axis.
9. Repeat steps 2 and 3 before using other reagents.

6 Shutting Down the Machine

1. Switch to the **load position** and raise the brown pistons. Then put syringes with clean water and pull-on brown pistons.
2. Set the drive valves to the **drive position** and in the program click the **Drive** icon. Click the **Drive** icon 5 more times.
3. Turn off the lamp power supply unit and close the valve on the gas tank. Turn off the electronics unit SX.

7 References

1. Hoag, C. M. Simple and Inexpensive Computer Interface to a Durrum Stopped-Flow Apparatus Tested Using the Iron(III)−Thiocyanate Reaction. J. Chem. Educ. 2005, 82 (12), 1823−1825.
2. Clark, C. R. A Stopped-Flow Kinetics Experiment for Advanced Undergraduate Laboratories: Formation of Iron(III) Thiocyanate. J. Chem. Educ. 1997, 74 (10), 1214−1217.
3. Tonomura, B.; Kakatani, H.; Ohnishi, M.; Yamaguci-Ito, J.;Hiromi, K. Test Reactions for a Stopped-Flow Apparatus. Anal.Biochem. 1978, 84, 370−383.

8 Appendix: Pro-Data SX

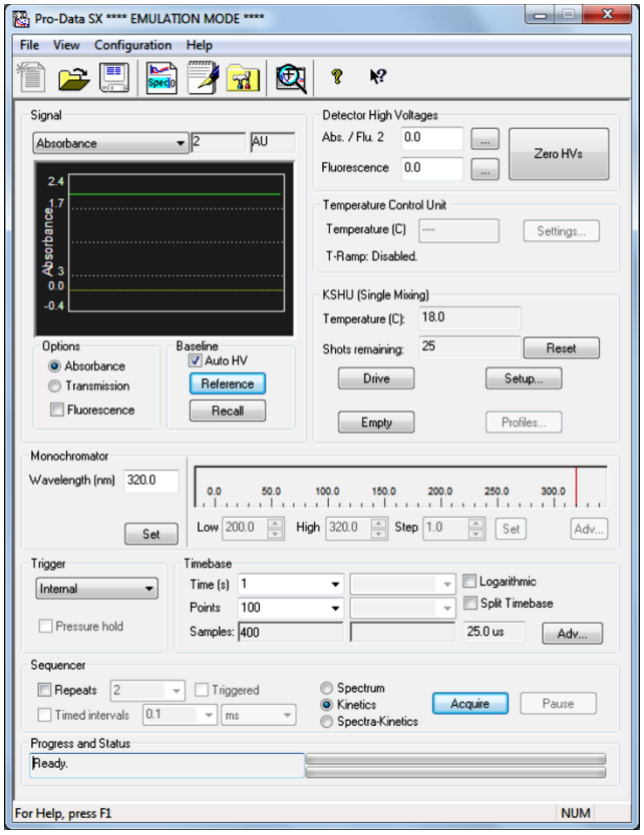

Figure 2. Pro-Data SX main panel.

8.1 The Monochromator Panel

8.1.1 General

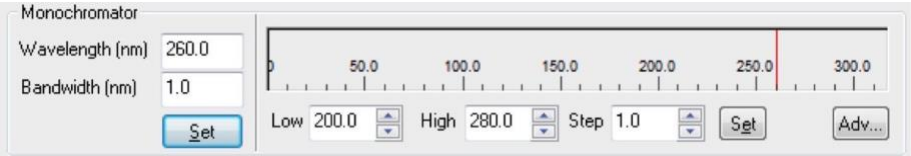

Figure 3 the Monochromator panel

- The **Monochromator** panel (Figure 3) provides access to the parameters that control the operation of the SX monochromator. Here you may set the scan range and step-size for your experiment; you can also move the monochromator to a specific wavelength.
- To drive the monochromator to a specific wavelength, use the **Wavelength (nm)** edit box and click the **Set** button below the box; to set the bandwidth, use the **Bandwidth (nm)** edit box and click the same **Set** button. Setting wavelength and bandwidth can be done simultaneously with a single click.
- To set the wavelength range for a scan, use the **Low** and **High** edit boxes to set the lower and upper wavelength limits; use the **Step** edit box to set the step-size; all units are nanometers. Click on the **Set** button to the right of these boxes to confirm these parameters. Note the monochromator always scans from high to low wavelength.
- To save the current monochromator parameters as the default ones, click on the **Adv...** button, which displays the **Monochromator Scan Setup - Advanced** dialog box (Figure 4) and click on **Save As Default.** Click **OK** to take you back to the Pro-Data SCP.

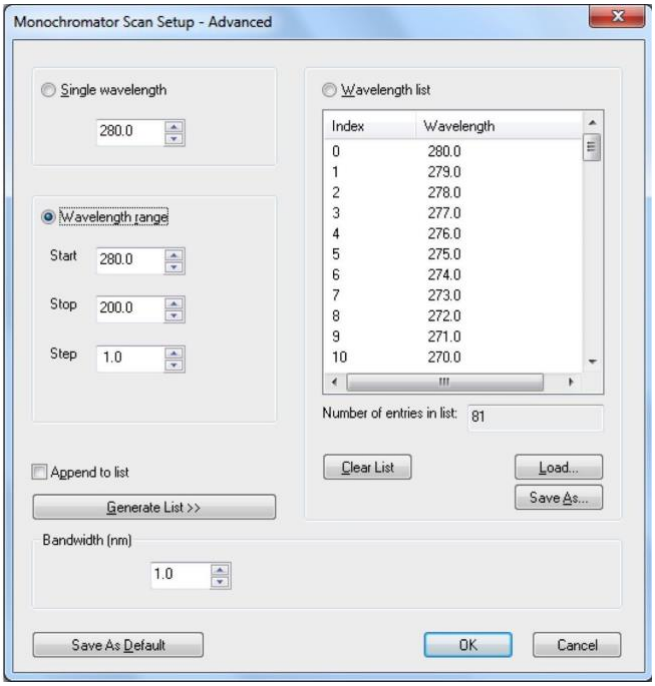

Figure 4. The Monochromator Scan Setup - Advanced dialog box

8.1.2 Advanced mono setup: discrete wavelengths

- The **Monochromator Scan Setup - Advanced** dialog box (Figure 4) can be used to set the software up to perform single wavelength scans. Such measurements are useful when following a change in property as a function of some independent variable other than wavelength - temperature, for example.
- Select **Single wavelength** and specify the wavelength in the associated edit box. Click **OK.** The dialog box will close and when you click on the **Start** button in the **Spectrum** panel of the interface, the monochromator will drive to the selected wavelength and measure the CD or other chosen property of the sample at that wavelength.
- It is also possible to create a list of discrete wavelengths. Clear the wavelength list by clicking on **Clear list** and then select **Append to list.** Now select **Single wavelength,** specify the wavelength in the edit box and click on **Generate list.** Each time you type in a wavelength and click on **Generate list**; the specified single wavelength will be appended to the list. When you are satisfied that the list of wavelengths is correct, click **OK.** When you click on **Start** in the **Spectrum** panel of the interface, the monochromator will drive to the selected wavelengths in the order they appear in the list and measure the CD or other chosen property of the sample at those discrete wavelengths.

8.1.3 Advanced mono setup: skip-scans

- A simple wavelength range can be set in the **Monochromator** panel and there is no need to use the advanced panel to set such a range. However, if you wish to carry out a more sophisticated scan, select **Wavelength range** in the **Monochromator Scan Setup - Advanced** dialog box. Then clear the wavelength list by clicking on **Clear list** and then select **Append to list.** Specify the **Start, Stop** and **Step** values for the first wavelength range and click on **Generate list.** A number of entries that correspond to your specification will appear in the list. Then enter the **Start, Stop** and **Step** values for the second range and click on **Generate list** once more. The new values will be appended to the existing values in the list. Repeat this cycle until you have completed the skip-scan list. The total number of entries in the list is recorded at the foot of the list.
- Skip-scans are in general used on samples that you know well and that you might wish to measure again in the future. Use the **Save As...** button to save the list as a .conf (configuration) file that can be retrieved using the **Load** button at a future date. This obviates the need to generate a new list every time you run the sample.

- With the list generated, click on **OK** to return to the SCP. When you click on **Acquire** in the **Sequencer** panel, the monochromator will drive to the wavelengths specified in the list in the order in which they appear in the list and the instrument will measure the chosen property (CD, voltage, fluorescence, etc.)

8.1.4 The Emission monochromator

- If a second (emission) monochromator is fitted to the instrument and it is selected in the Fluorescence panel, then the monochromator panel changes to allow control of both devices. The radio buttons in the panel allow selection of Emission scanning or Excitation scanning. In Emission scanning mode Mono 1 is set at a fixed wavelength using the left-hand panel and Mono 2 is scanned. In Excitation scanning mode the roles of the two monochromators are reversed.

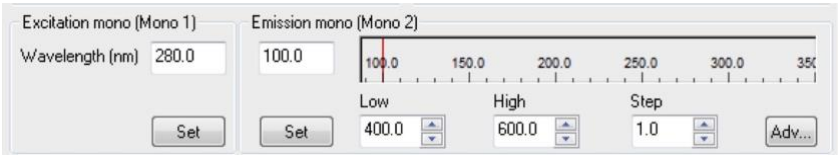

Figure 5 the Excitation Mono and Emission Mono panels

8.2 The Trigger and Timebase panels

Figure 6 the Trigger and Timebase panel

- The **Trigger** and **Timebase** panel (Figure 6) are visible when operating in Kinetics or Spectrakinetics modes. The **Trigger** drop down menu allows the selection of **Internal** trigger, **External** trigger, and **Remote** trigger.
- **Internal trigger** allows data to be collected without being preceded by a stopped flow drive and is generally used for testing purposes. **External trigger** is used for normal operation and **Remote trigger** allows an external signal to start the acquisition.
- When using external trigger, the **Pressure hold** option becomes available. This maintains the pressure applied to the drive syringes until the data acquisition is complete. If this is not selected, the pressure is released approximately 30 ms after the data acquisition is triggered. This pressure release may result in poor quality data under certain circumstances. With measurements of 2 seconds or less which have an artifact at around 30 ms, enabling the **Pressure hold** option may improve data quality. However, for measurements in excess of 5 seconds keeping the pressure applied will exert unnecessary stress on the flow circuit possibly leading to premature failure. Additionally, the pressure hold function will not provide detectable improvement in data quality over such timescales.
- The acquisition **Time** and number of data **Points** are set using the drop-down menus in the **Timebase** section. When using a photodiode array the **Points** setting will be the number of spectra acquired over the time interval (1000 max). The **Samples** box displays the number of samples which will be averaged in order to obtain each data point. Selecting the **Logarithmic** option results in the logarithmic distribution of data points over the selected acquisition time. This feature may be useful when the kinetic change being monitored has a fast initial phase, but a slower second phase. As an alternative a **Split Timebase** may be used in which data points are distributed between two linear intervals.

8.3 The Sampling panel

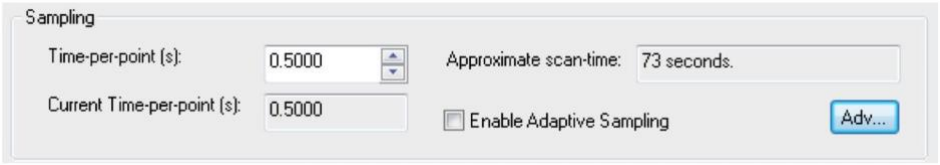

Figure 7 the Sampling panel

- The **Sampling** panel (Figure 7) replaces the **Trigger** and **Timebase** panel when operating in Spectrum mode and is used to control the sampling time for each point in a scan. Use the **Time-per-point (s)** edit box to specify the time in seconds to be spent collecting data at each point; an approximate scan-time is calculated from the product of the time-per-point and the number of points in the scan (specified in the **Monochromator** panel).
- If the **Enable Adaptive Sampling** check box is ticked, the time-per-point is varied inversely as a function of the light reaching the detector. Where the signal is weaker, more time is spent collecting data than where it is stronger. The algorithm has been developed such that it will usually take less time to measure a spectrum than at constant time-per-point.
- Clicking on the **Adv...** button calls up the **Sampling - Advanced** dialog box (Figure 8).

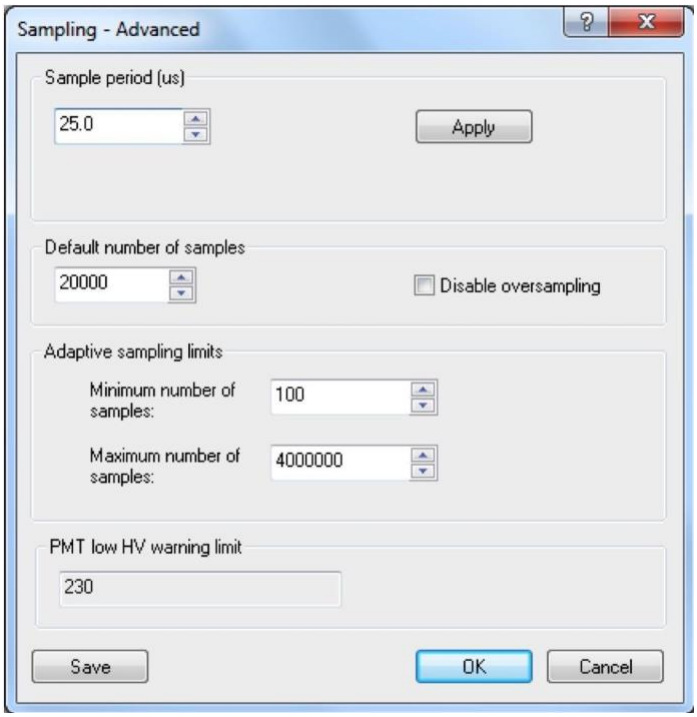

Figure 8. The Sampling-Advanced dialog box

- The **Sample period** (ps) can be set at any value between 10.0 ps and 1000.0 ps in the edit box, followed by clicking on the Apply button.
- The **Default number of samples** can be set anywhere between the minimum and maximum limits (see Sampling limits below). The product of the sample period and the number of samples yields the current time- per-point. The default number of samples is superseded by changing the Time-per-point in the Sampling panel, as described above.
- Selecting **Disable oversampling** will do precisely what it says and is used for diagnostic purposes only. If it is selected, a warning is given (Figure 9). For all non-diagnostic use, oversampling must be used.

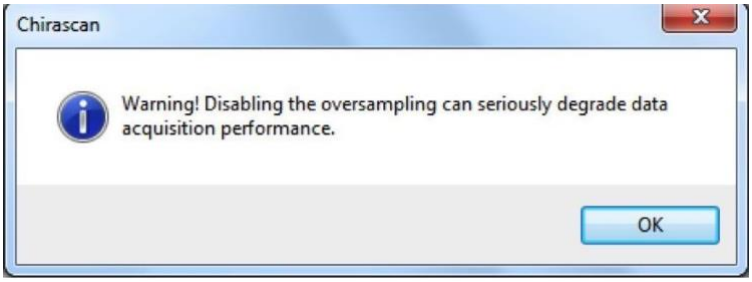

Figure 9. The Disable oversampling warning message.

- Sampling limits can be changed but the default values are best suited to routine operation. The minimum time- per-point will be 25 ps multiplied by 10 samples, i.e., 250 ps; the maximum time-per-point will be 25 ps multiplied by 4000000 samples, i.e., 100 seconds. These limits apply to all experiments, whether set up using constant time-per-point or using adaptive sampling; they are particularly useful in placing limits on the extremes of adaptive sampling.

8.4 The Sequencer Panel

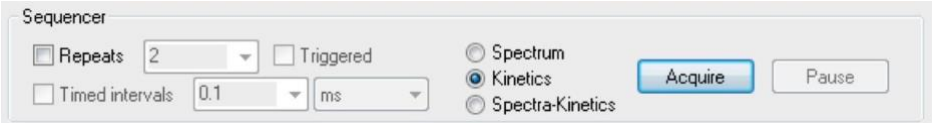

Figure 10. the Sequencer panel

- The **Sequencer panel** (Figure 10) allows you to specify the type of measurement you will make and to control the starting, stopping, pausing, and resuming of data acquisitions.
- Click the **Repeats** check box to run repeats of the same experiment and enter the number of repeats in the adjacent edit box.
- The individual measurement in **Timed intervals** is the time between the beginnings of successive repeats; if it is set to be shorter than the time for each run, then each run will begin after the previous one.
- All data from repeat runs will be written to a single Datastore.
- The radio buttons allow you to select the type of measurement you will carry out. It will usually be **Kinetics** for the SX20.
- Click **Acquire** to begin an acquisition according to the instructions in the SCP; clicking **Stop** (which appears after **Acquire** has been clicked) will abort the acquisition; clicking **Pause** will stop the acquisition without aborting and **Resume** (which appears after **Pause** has been clicked) will restart the acquisition from the point at which it was paused.