



PCA PHOTOCALORIMETER ACCESSORY



Photocalorimeter Accessory for Discovery DSC Getting Started Guide

Revision E Issued September 2018

Notice

The material contained in this manual, and in the online help for the software used to support this instrument, is believed adequate for the intended use of the instrument. If the instrument or procedures are used for purposes other than those specified herein, confirmation of their suitability must be obtained from TA Instruments. Otherwise, TA Instruments does not guarantee any results and assumes no obligation or liability. TA Instruments also reserves the right to revise this document and to make changes without notice.

TA Instruments may have patents, patent applications, trademarks, copyrights, or other intellectual property covering subject matter in this document. Except as expressly provided in written license agreement from TA Instruments, the furnishing of this document does not give you any license to these patents, trademarks, copyrights, or other intellectual property.

TA Instruments Operating Software, as well as Module, Data Analysis, and Utility Software and their associated manuals and online help, are proprietary and copyrighted by TA Instruments. Purchasers are granted a license to use these software programs on the module and controller with which they were purchased. These programs may not be duplicated by the purchaser without the prior written consent of TA Instruments. Each licensed program shall remain the exclusive property of TA Instruments, and no rights or licenses are granted to the purchaser other than as specified above.

©2018 by
TA Instruments — Waters LLC
159 Lukens Drive
New Castle, DE 19720

Introduction

Important: TA Instruments Manual Supplement

Please click the [TA Manual Supplement](#) link to access the following important information supplemental to this Getting Started Guide:

- TA Instruments Trademarks
- TA Instruments Patents
- Other Trademarks
- TA Instruments End-User License Agreement
- TA Instruments Offices

Notes, Cautions, and Warnings

This manual uses NOTES, CAUTIONS, and WARNINGS to emphasize important and critical instructions. In the body of the manual these may be found in the shaded box on the outside of the page.

NOTE: A NOTE highlights important information about equipment or procedures.

CAUTION: A CAUTION emphasizes a procedure that may damage equipment or cause loss of data if not followed correctly.

UNE MISE EN GARDE met l'accent sur une procédure susceptible d'endommager l'équipement ou de causer la perte des données si elle n'est pas correctement suivie.

A WARNING indicates a procedure that may be hazardous to the operator or to the environment if not followed correctly.

Un AVERTISSEMENT indique une procédure qui peut être dangereuse pour l'opérateur ou l'environnement si elle n'est pas correctement suivie.

Safety

CAUTION: The operator of this instrument is advised that if the equipment is used in a manner not specified in this manual, the protection provided by the equipment may be impaired.

MISE EN GARDE : L'utilisateur de cet instrument est prévenu qu'en cas d'utilisation contraire aux indications du manuel, la protection offerte par l'équipement peut être altérée.

There are several major areas of concern pertaining to personal safety when using the Photocalorimeter Accessory (PCA). For all detailed information regarding safety, please refer to the filter photometer manual (Omniscure™ User's Guide).

Electrical Safety

You must unplug the instrument before doing any maintenance or repair work; voltages as high as 120/240 volts AC are present in this system.

WARNING: High voltages are present in this instrument. Maintenance and repair of internal parts must be performed only by TA Instruments or other qualified service personnel.

AVERTISSEMENT: Présence de tensions élevées dans cet instrument. La maintenance et la réparation des pièces internes doivent être effectuées uniquement par TA Instruments ou tout autre personnel d'entretien qualifié.

Radiation Danger

WARNING: NEVER look into the beam from the light guide, or a reflection of the beam. The high degree of ultraviolet radiation can permanently damage the retina of your eye and result in blindness.

AVERTISSEMENT: NE regardez JAMAIS dans le faisceau du conduit de lumière ou dans une réflexion du faisceau. Le degré élevé de rayonnement ultraviolet peut endommager irréversiblement la rétine de votre œil et entraîner la cécité.

WARNING: You should NEVER expose your skin to UV beams. Exposure of skin surface will result in severe burns. ALWAYS wear Nitrile gloves when working with ultraviolet beams.

AVERTISSEMENT: Vous ne devez jamais exposer votre peau aux faisceaux UV. L'exposition de la surface de la peau peut entraîner de graves blessures. Portez toujours des gants de Nitrile lorsque vous travaillez avec des faisceaux ultraviolet.

Additional Safety Warnings

WARNING: For all detailed information regarding safety please read the Omniscure™ User's Guide.

AVERTISSEMENT: Pour obtenir tous les renseignements concernant la sécurité, lisez le guide de l'utilisateur d'Omniscure™.

Warranty Information

WARNING: Please take care when using your PCA to protect it from misuse or mishandling. TA Instruments offers no warranty after the initial installation of the Photocalorimeter Accessory Dual Light Guide or the 200 W Mercury Lamp.

AVERTISSEMENT: Pour protéger votre PCA d'une mauvaise utilisation ou manipulation, faites attention lorsque vous l'utilisez. TA Instruments n'offre aucune garantie après la première installation du double conduit de lumière de l'accessoire photocalorimètre ou de la lampe à mercure 200 W.

The PCA is equipped with dual quartz light guides as the standard light guides. The quartz light guides can be used at temperatures up to 250°C.

Table of Contents

Introduction	2
Important: TA Instruments Manual Supplement	2
Notes, Cautions, and Warnings	3
Safety	4
Electrical Safety	4
Radiation Danger	4
Additional Safety Warnings	4
Warranty Information	5
Table of Contents	6
Introducing the PCA	7
Overview.....	7
Product Description	7
Experimental Considerations.....	8
Wavelength Range.....	8
Light Intensity.....	8
Baseline Noise	8
Exposure Time.....	9
Temperature.....	9
Using a 3rd Party PCA	9
Setting Up the PCA	10
Installing the PCA.....	11
Operating the PCA	14
Preparing the System	14
Operating the PCA.....	15
Additional Experimental Considerations.....	20
Typical Experimental Results.....	24
Maintaining the PCA	25
Replacement Parts	26

Chapter 1:

Introducing the PCA

Overview

The Photocalorimeter Accessory (PCA) is used with the TA Instruments Discovery Differential Scanning Calorimeter. This accessory allows samples placed inside the DSC cell to be irradiated with ultraviolet or visible light. When the samples (usually photopolymers) react to the light, heat is released (i.e., an exothermic reaction occurs). This heat is measured and used to study the relative reactivity and/or kinetics of reaction. The reactions studied are typically rapid and results are obtained in less than 15 minutes.

Product Description

The TA Instruments PCA accessory is based on a filter photometer (Omniscure®), which contains a high pressure mercury lamp that delivers light over the spectral range 250 to 650 nanometers (nm). A broad-band filter (320 to 500 nm) is provided standard with the filter photometer. Light is transmitted from the filter photometer to the DSC cell via a one-meter long, 3-mm diameter, dual extended range (250 to 700 nm), quartz light guide. The light guide attaches to the instrument using a special adapter. The figure below shows those system components.

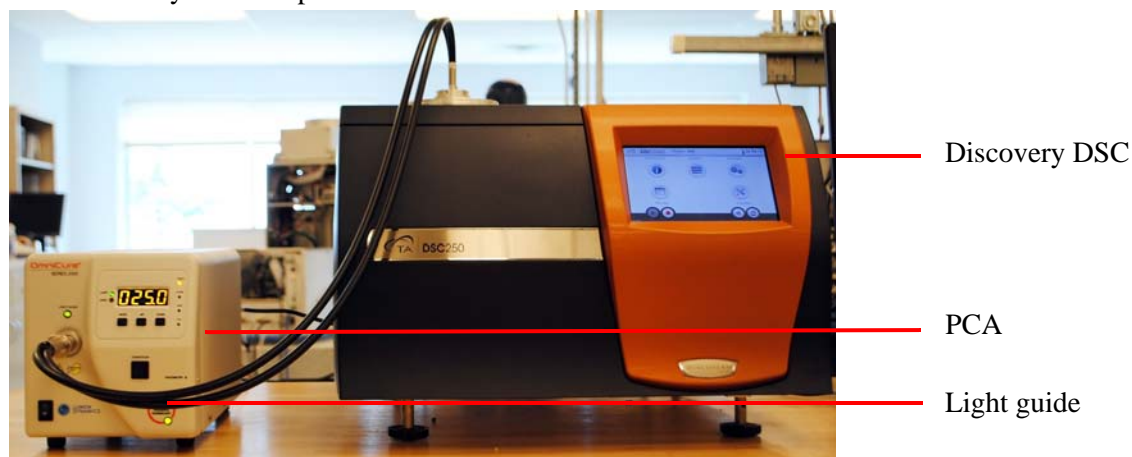


Figure 1 System components (Discovery DSC 250 shown).

Experimental Considerations

There are several fundamental instrument characteristics that affect the quality of PCA results. Those characteristics are: wavelength range, light intensity at the DSC cell sample and reference positions, baseline noise, exposure time, and temperature. The following paragraphs describe aspects for each which should be considered when planning an experiment using the PCA.

NOTE: The patented Tzero™ design of the Discovery DSC cell provides important advantages when performing PCA experiments, including the ability to directly measure and balance the light intensities at the sample and reference platforms inside the cell. These advantages are obtained only when running in T4 or T4P heat flow mode. Therefore, it is required that PCA experiments be run in T4 or T4P heat flow mode.

Wavelength Range

The PCA is a filter photometer instrument. A broadband filter supplied with the instrument covers 320 to 500 nm and is suitable for most UV and Visible PCA studies. Other optional filters include: 250 to 450 nm, 320 to 390 nm, 365 nm, and 400 to 500 nm. (Visible longpass filters with cutoffs at 390 nm and 490 nm are also available as options. These latter filters mount at the DSC end of the light guide.)

Light Intensity

The PCA is based on a high intensity, high pressure mercury lamp capable of producing a total light intensity of about 25 W/cm². This intensity is far in excess of that required for most photocalorimetry experiments. (Most experiments are performed with intensities between 20 to 100 mW/cm² at the sample.) Therefore, the intensity reaching the DSC cell is adjusted using a combination of aperture control at the PCA unit and neutral density and/or cutoff filters at the end of the light guide.

The light intensities at the end of each “arm” of the dual light guide must not only be regulated to the proper level, but also must be balanced to produce minimum baseline offset. The TA Instruments Discovery DSC is based on a unique, patented design that allows the heat flows at the sample and reference platforms in the DSC cell to be independently measured. In the absence of a sample or reference material and pans (i.e., an empty cell), the heat flows observed are directly related to the light intensities at the platforms. Therefore, the actual intensity experienced by the sample can be determined. In addition, the intensities at the sample and reference platforms can be balanced by a simple adjustment on the cell light guide adapter.

Baseline Noise

Ideally, the light intensity delivered to the DSC cell through the light guide should be constant. However, the high pressure mercury lamp used in the PCA has some inherent fluctuations in its output. The DSC cell is sensitive enough to detect those small fluctuations in light intensity as noise in the heat flow baseline. There is no system adjustment that can be made to eliminate this noise. Fortunately, the noise is typically less than $\pm 100 \mu\text{W}/\text{cm}^2$, which has no effect on the heat flows associated with the photoinitiated events being studied since these heat flows are several orders of magnitude larger.

Exposure Time

Photoinitiated curing reactions are fast thermal events. Complete cure is achieved in several seconds to several minutes. This can make differentiating the curing behavior of similar materials difficult even if low light intensities are used. The ability to vary exposure time provides an additional experimental variable that can help improve differentiation of behavior and/or provide conditions that better mimic those found in real-world processes (e.g., photocuring of a film coating as the film rapidly passes under a light source). The PCA connects to the DSC instrument via a cable that opens and closes a shutter at the light source.

When setting up a PCA method, the minimum possible exposure times are as follows:

- With a combination of “PCA Shutter” and “Isothermal” segments: 0.01 minutes
- With the “PCA Exposure” segment: 0.2 seconds (± 250 ms or 1% of the exposure time, whichever is greater)

Temperature

Most PCA experiments are run isothermally. The PCA is compatible with the TA Instruments Finned Air Cooling System (FACS) and Refrigerated Cooling System (RCS) coolers. PCA experiments can be performed in the temperature range -50 to 250°C with the dual quartz light guides supplied. Furthermore, once the PCA experiment is complete, a standard DSC experiment can be run on the fully/partially cured sample to a maximum temperature of 550°C by making only a few minor changes to the system.

Using a Third-Party PCA

To use a third-party PCA with the Discovery DSC, you must use the PCA Accessory Kit (P/N 935002.903). Note that the instrument touch screen and TRIOS do not work with PCAs other than the Omnicure S2000, and manual operation of the shutter is required. The installation and operation of a third-party PCA is slightly different. Follow the steps specific to third-party PCA in the procedures of this manual.

Chapter 2:

Setting Up the PCA

This section briefly describes the setup of the Photocalorimeter Accessory (PCA) and its connection to the Discovery DSC. For more details on setting up the Discovery DSC, consult the Discovery DSC Getting Started Guide and online help. For more details on operating the PCA, consult the filter photometer manual.

There are many components provided with the PCA and its accompanying accessory kit which will be used in the setup. Those components are identified in the figure below.

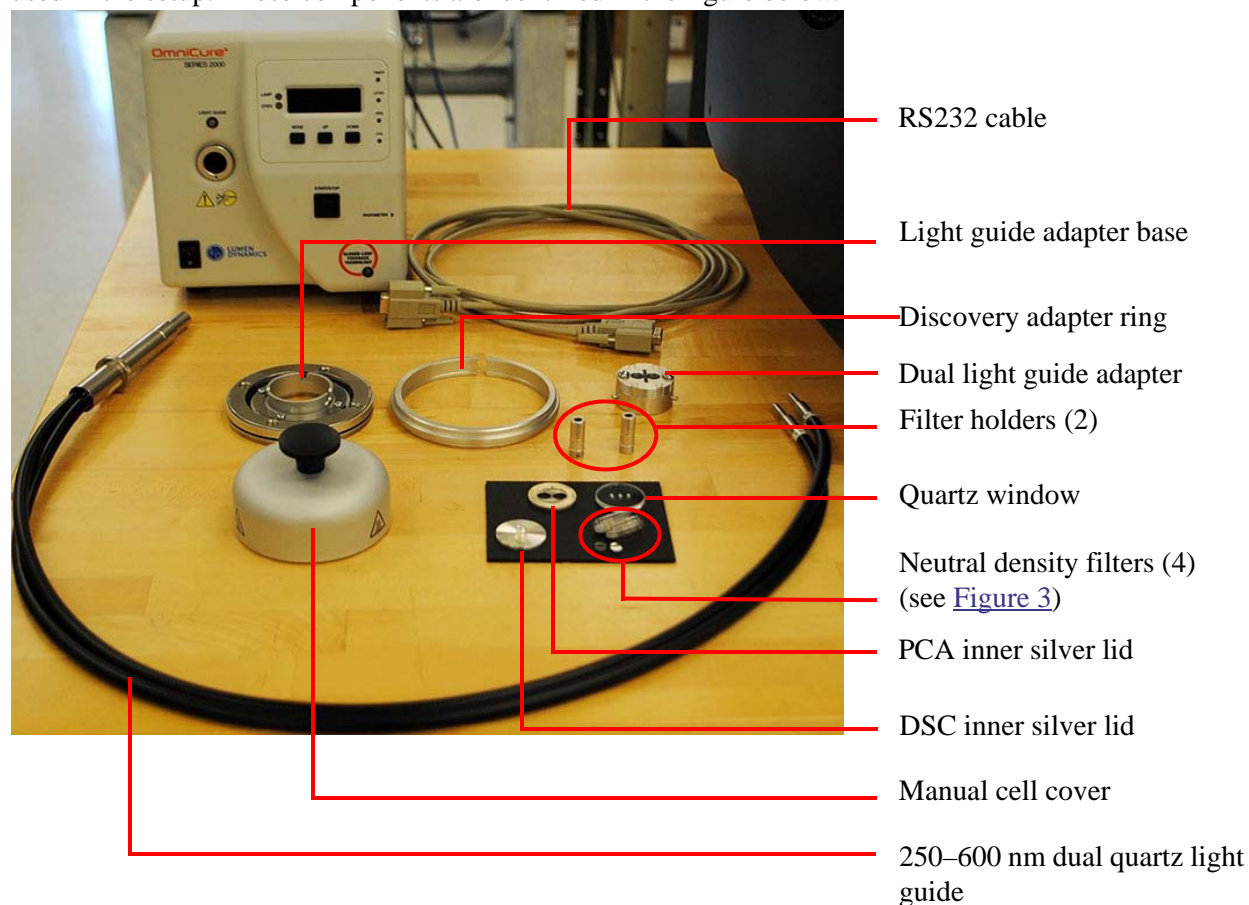


Figure 2 Photocalorimeter Accessory Components.



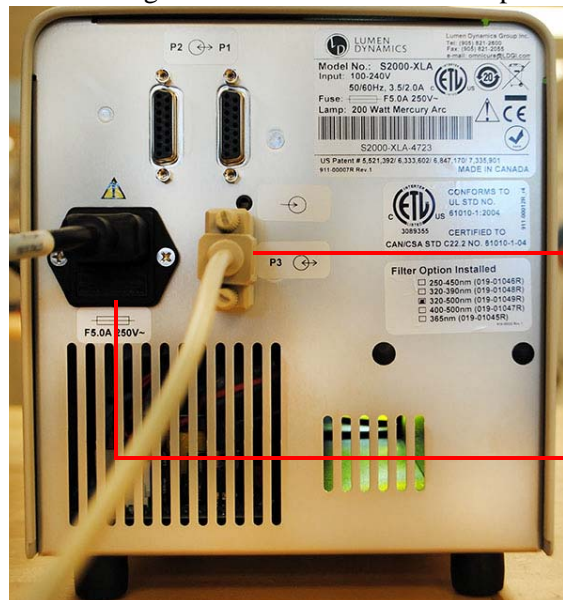
Figure 3 Neutral density filters: 1% (2, bottom) and 10% (2, top).

Installing the PCA

- 1 Install the mercury lamp in the PCA unit. (See the filter photometer manual for details.). If using a third-party PCA, skip this step.
- 2 Install the appropriate cooling accessory and heat exchanger on the DSC. The PCA can be used over the temperature range -50 to 250°C and is compatible with the FACS and RCS40/RCS90.
- 3 Replace the dress cover surrounding the cooler heat exchanger after installing the cooler. The PCA light guide adapter base anchors on this dress cover.
- 4 Place the PCA unit on the lab bench next to the DSC. The RCS coolant line connects to the DSC heat exchanger from the right, so be sure to position the PCA in a way that allows the light guide to be connected between the PCA unit and the cell without putting strain on the light guide.
- 5 Connect the PCA to the DSC using an RS232 cable:

NOTE: Third-party PCAs do not use an RS232 cable; the PCA will not be able to communicate to the instrument touchscreen or TRIOS software. If you are using a third-party PCA, skip to [step 6](#)

- a Plug the RS232 cable into the P3 port on the rear of the PCA unit.

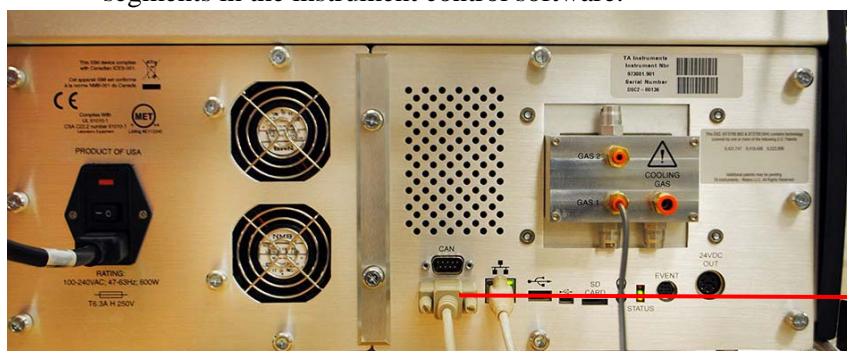


RS232 cable in P3 port

PCA power cord

Figure 4 Back of PCA unit.

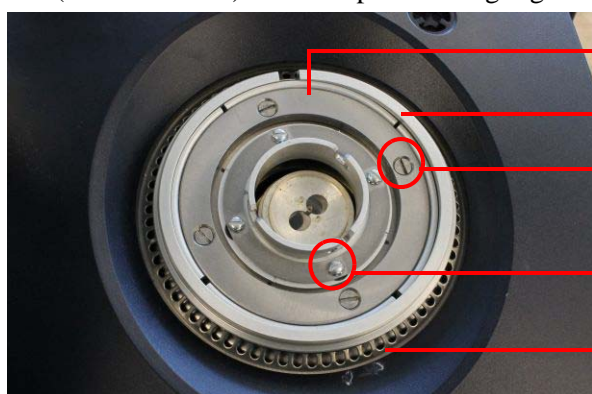
- b Connect the other end of the RS232 cable to the RS232 port on the back of the instrument. This allows the PCA light source shutter to open and close using the “PCA Shutter” and “PCA Exposure” segments in the instrument control software.



RS232 cable in RS232 port

Figure 5 Back of DSC.

- 6 Place the Discovery adapter ring into the metal grill of the DSC dress cover so that it rests on the cooler (FACS or RCS) and then place the light guide adapter base inside the Discovery adapter ring.



Adapter base
Adapter ring
Outer adjustment screws
Inner adjustment screws
DSC dress cover

Figure 6

- 7 Before tightening, adjust the position of the adapter so that the two holes in the light guide adapter are centered over the DSC cell sample and reference platforms with the light guide adapter rotated into the locked position in the collar.
- 8 Evenly tighten the four outer adjustment screws so that they are just snug. Do not over tighten.
The four inner adjustment screws can be used later to make minor adjustments to the position of the light guide adapter, if needed.
- 9 Mount the filter holders on the ends of the light guide arms.



Figure 7 Filter holders.

NOTE: The visible cutoff filters are an option for the PCA. See [Chapter 3](#) for part number information.

- 10** Insert the light guide arms in the two holes of the cell light guide adapter. Adjust the position of the PCA unit (if necessary) so that the light guides bridge from the PCA unit to the cell without twisting, kinking, or mechanical strain. See the figure below.

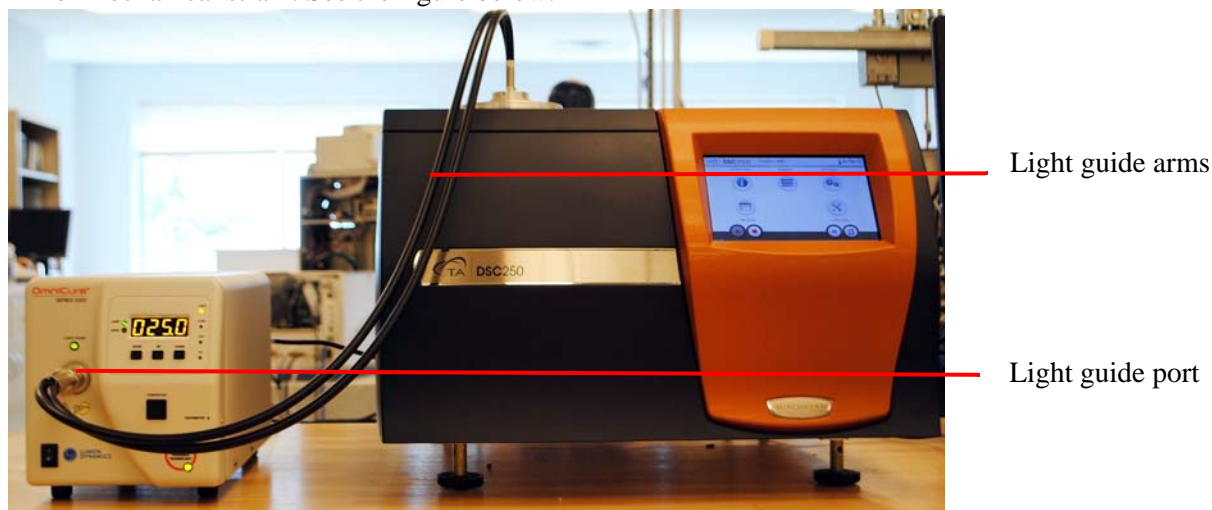


Figure 8 Light guides bridge from PCA to cell.

NOTE: The below steps are not applicable to third-party PCAs. If you are using a third-party PCA, skip to [Chapter 3](#) for operation instructions.

- 11** Insert the light guide into the light guide port on the left side of the PCA unit until it seats with a positive click.

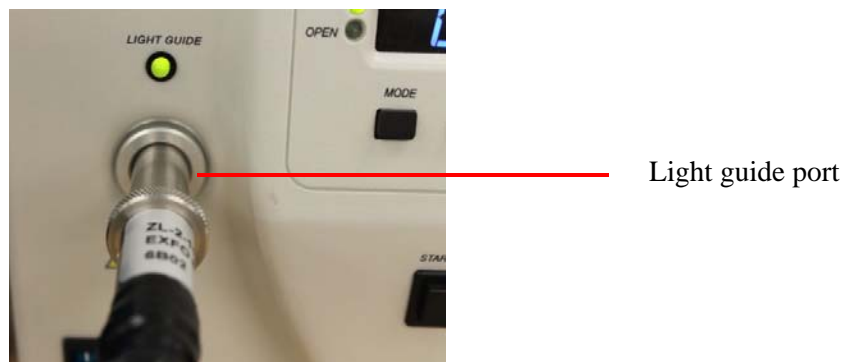


Figure 9 Light guide port on PCA unit.

- 12** Plug in the PCA power cord to the back of the PCA unit (see [Figure 4](#) above).

Chapter 3:

Operating the PCA

This section briefly describes the operation of the Photocalorimeter Accessory (PCA). For more details, consult the filter photometer manual.

Preparing the System

The PCA is designed for use with the Discovery DSC. To perform properly, the DSC heat flow being monitored must be T4 or T4P. (This selection is made on the **TRIOS Options/DSC25x/General** page) Therefore, before using the PCA, the DSC must be calibrated. See the TRIOS Online Help for details.

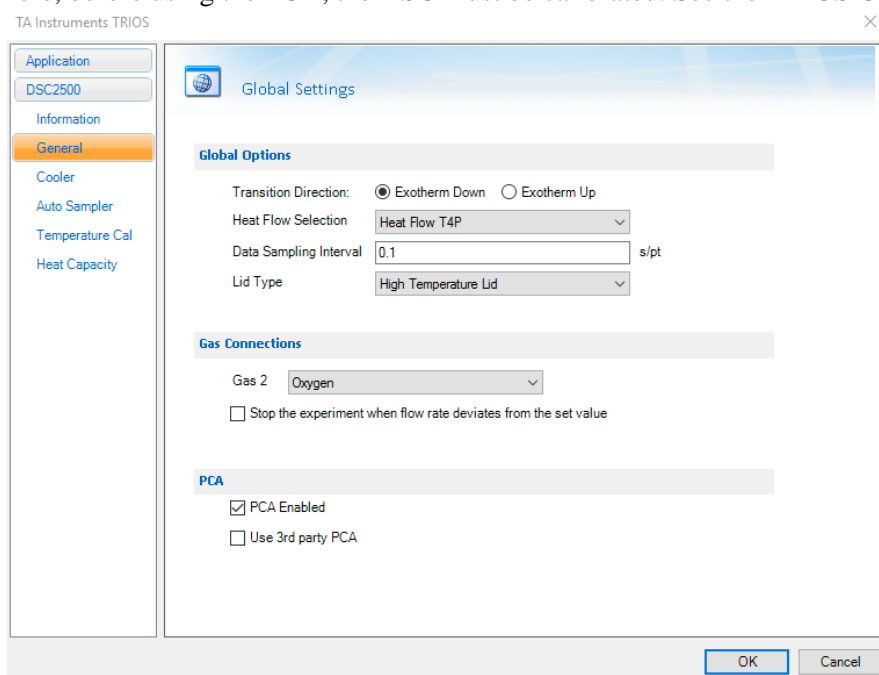


Figure 10 General page in TRIOS Options.

Perform the Tzero calibration procedures with the lid and DSC cell cover in place. During PCA operation a different lid arrangement is used as described later in this chapter. However, if conventional DSC experiments are run on partially or fully cured materials subsequent to PCA evaluation, the manual lid and cover should be used.

NOTE: The following paragraph may not apply to third-party PCAs.

The PCA has the ability to function in two intensity modes: Relative and Absolute. In Relative mode, the display on the front of the PCA shows the percentage of iris opening in steps of 1 percent, from 1 to 100 percent intensity. This is the default mode of the instrument. In Absolute mode, the display on the front of the PCA shows intensity in W/cm^2 . Since the final balancing and reading of the intensity that the sample is exposed to is done by using the DSC, the PCA unit can be operated in either mode effectively. Consult the

R2000 External Radiometers User Manual for information on how to calibrate the S2000 in Absolute mode.

Operating the PCA

After the PCA has been calibrated, you can connect it to the DSC and adjust the system as follows:

- 1 Turn on the unit and allow it to warm up. This process takes about four minutes.

This timing is specific to the Omnicure S2000 PCA and may be different for third-party PCAs. If you are using a third-party PCA, skip to step 3.

- 2 If you are operating in the **Relative** mode, proceed to the next step.

If you are operating in **Absolute** mode, using the optional external radiometer, calibrate the intensity of the unit following the directions found in R2000 External Radiometers User Manual before continuing.

- 3 Mount the filter holders on the ends of the two light guide arms. Tighten the setscrews that keep them in place.



Figure 11 Filter holders and light guide arms.

NOTE: The openings in the light guide adapter are sized to accommodate the light guide arms with the filter holders in place. Therefore, the filter holders must be in place even if no filters are required.

- 4 Insert the desired filters (if any) by unscrewing the holder end cap. Make sure that the filter(s) lie flat in the holder before screwing the cap back on.



Figure 12 Insert filters in the holder.

CAUTION: These filters have semi-hard coatings on one or both surfaces. Since those coatings are softer than glass, they can easily be scratched. EXPOSED COATED FILTERS SHOULD BE HANDLED AT THE EDGES ONLY.

If cleaning is necessary, it should be done carefully. First, remove any foreign materials with dry air, if possible. A very light wiping motion with a soft, lint-free cloth should remove any remaining particles. A final cleaning with a few drops of pure anhydrous alcohol or acetone on a fresh lab towel will

result in a clean and undamaged filter.

MISE EN GARDE: Ces filtres disposent de revêtements semi-durs sur l'une ou les deux surfaces. Étant donné que ces revêtements sont plus doux que le verre, ils peuvent facilement s'égratigner. **LES FILTRES REVÊTUS ET EXPOSÉS DOIVENT ÊTRE MANIPULÉS UNIQUEMENT SUR LES BORDS.**

S'il est nécessaire de les nettoyer, cela doit être fait avec attention. Retirez d'abord tous les corps étrangers à l'air sec, si possible. Un léger mouvement d'essuyage à l'aide d'un linge doux et non pelucheux devrait enlever toutes les particules restantes. Un dernier nettoyage avec quelques gouttes d'alcool ou d'acétone anhydre pur versées sur une serviette de laboratoire neuve permet d'avoir un filtre propre et intact.

- 5 Insert the light guide arms into the reference (R) and sample (S) holes in the light guide adapter until they bottom out ([Figure 13](#) left). Tighten the setscrews to hold them in position. The adapter and light guide arms can now be removed from the cell as a single assembly, if desired, by twisting the adapter until the locking pins disengage from the slots in the mounting ring ([Figure 13](#) right). Note that this single assembly can now be replaced in the exact position needed, each time it is removed for sample loading, due to the fixed position of the slots. Check that the filters are still lying flat in the holders when you remove and replace the assembly.)

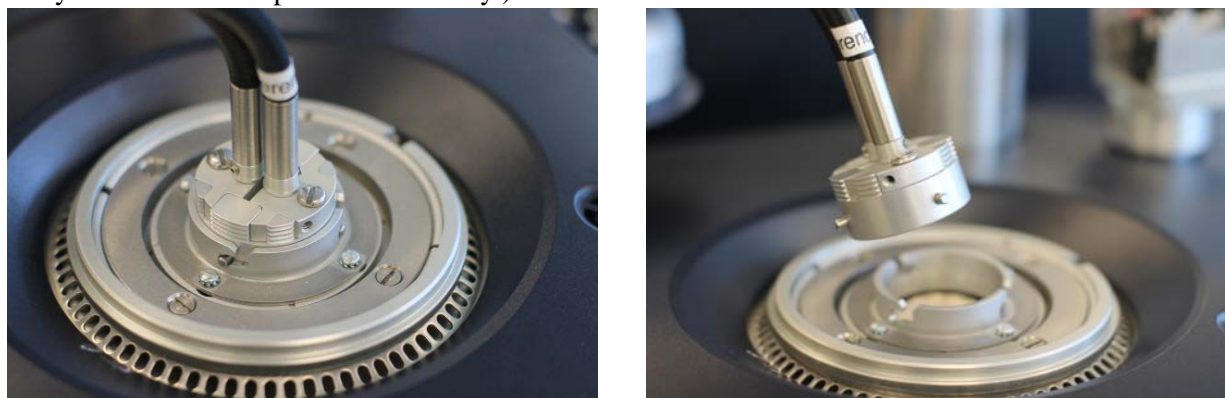


Figure 13 Insert light guide arms (left); adapter and light guide arms removed as a single assembly (right).

- 6 Cover the cell using the modified inner silver lids so that the two holes are positioned directly over the sample and reference platforms in the cell. Make sure that the flat side of the inner lid is facing up.

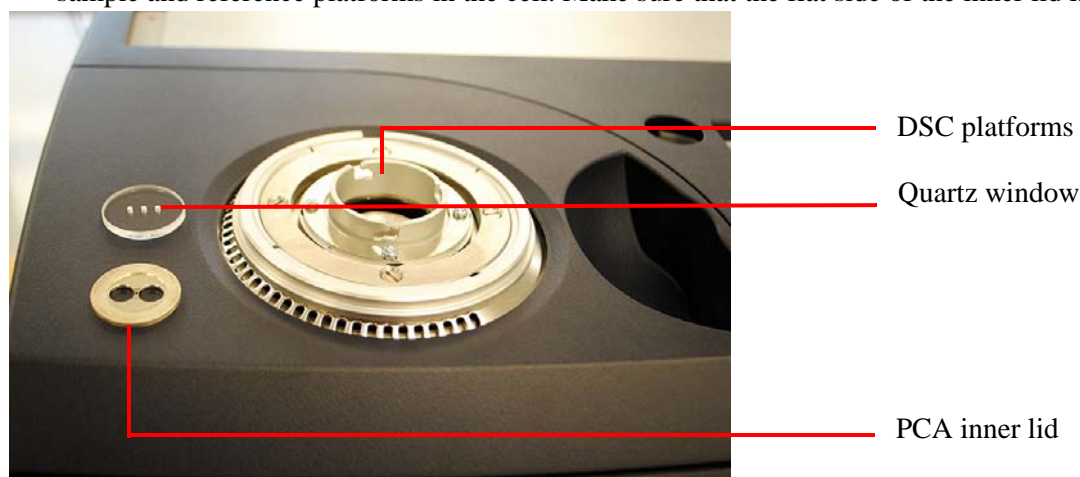


Figure 14

- 7 Use tweezers to place the quartz window over the silver lid. Turn the quartz window making sure that the holes are not positioned over the sample or reference platforms so they do not interfere with the light coming into the cell during the PCA experiment.

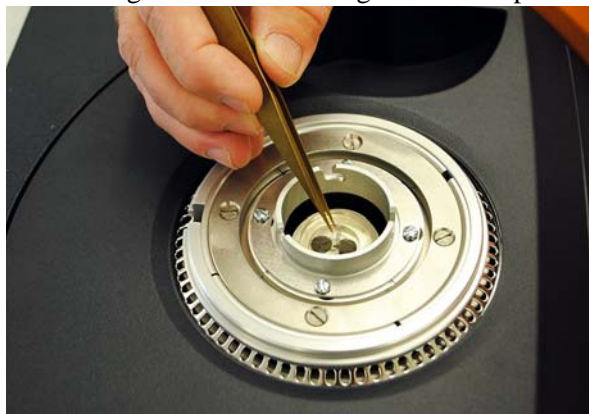
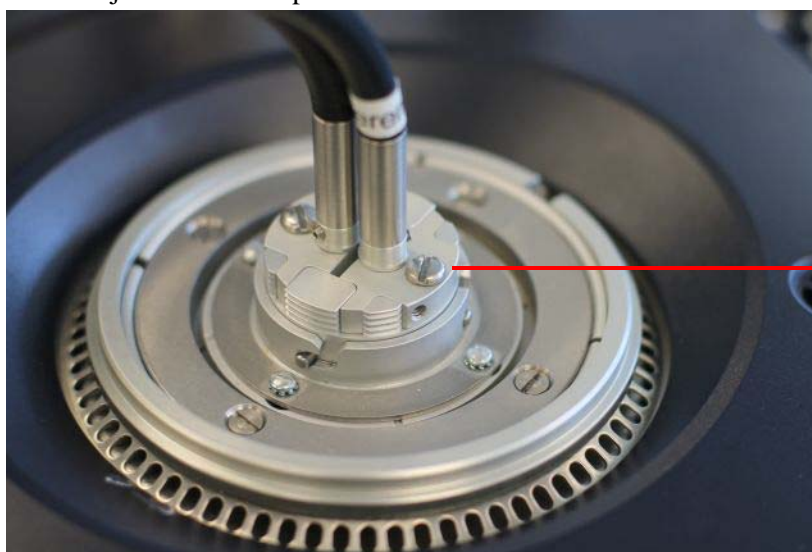


Figure 15 Place the quartz window over the outer lid.

- 8 Locate the vertical positioning screws on the light guide adapter. They are used to adjust the vertical distance between the end of the light guide arms and the sample or reference platform, thereby balancing the light intensity at the cell platforms. Initially turn the positioning screws clockwise until they are tight to adjust the arm-to-platform distance to its minimum.




Sample/reference
vertical positioning
adjustment screw

Figure 16 Sample/reference vertical positioning adjustment screw.

- 9 Press the MODE/UP/DOWN adjust buttons on the PCA unit until the mode is set to Level. From the TRIOS DSC instrument control program, go to **TRIOS Options > General** and make sure **PCA Enabled** is checked (see [Figure 10](#)). If using a third-party PCA, also select **Use 3rd Party PCA**. Click **OK**.

Once the PCA is enabled, you will need to open the shutter to monitor the real-time intensity signals.

The shutter can be opened/closed using the **Shutter**  button located in the **General** tab in TRIOS Controls view or using the Shutter **Open/Close** button located on the touch screen **Utilities > Diagnostics > PCA** page (see [Figure 18](#)).

If you are using a third-party PCA, the shutter must be opened and closed manually; additionally, to enable/disable the real-time intensity signals, use the **Shutter** button in the **General** tab in TRIOS Controls view or use the **Event 2** button located on the touchscreen **Utilities > Diagnostics > PCA** page

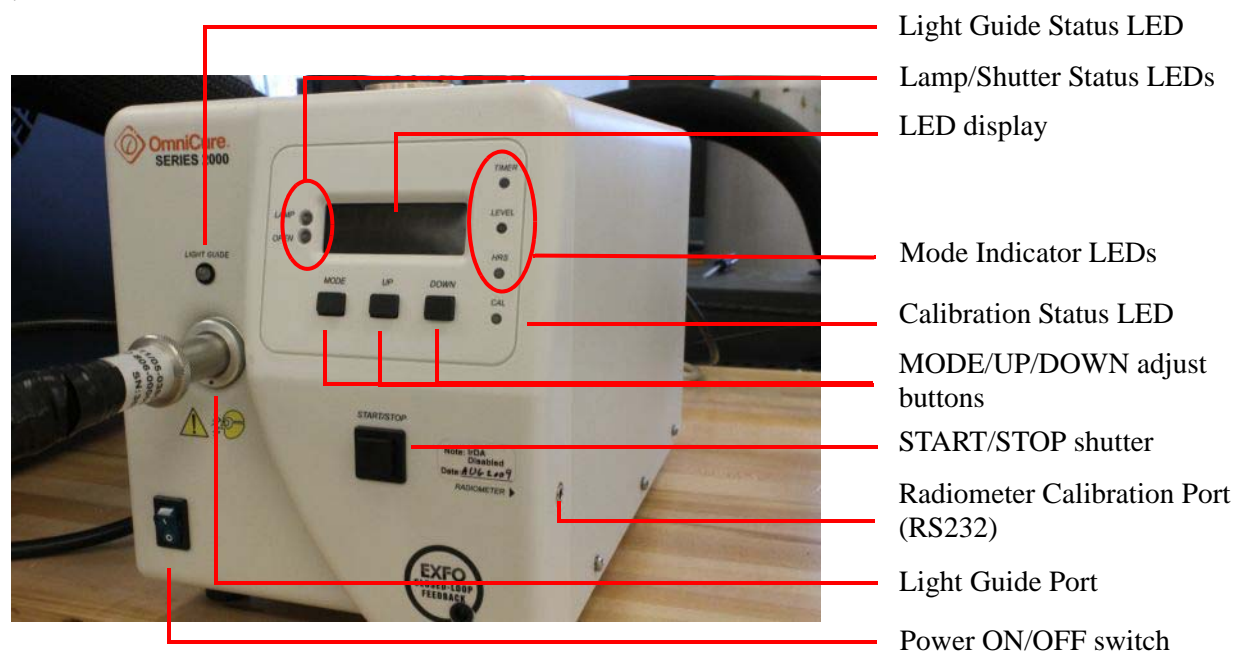


Figure 17 OmniCure S2000 PCA.

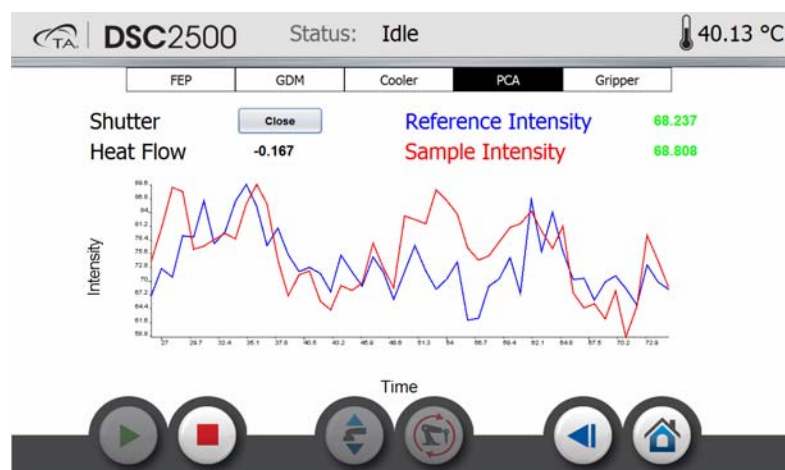



Figure 18 PCA page on the instrument touch screen.

NOTE: Once the PCA is enabled via TRIOS, the Autosampler (if present) will be disabled and will remain disabled to allow for PCA and DSC experiments to run interchangeably with minimal changeover. To reactivate the Autosampler, you must first disable the PCA in TRIOS and then you can enable Autosampler operation via **TRIOS Options > DSC25x > Auto Sampler**.

- 10 Perform the intensity adjustment and balancing process while monitoring the signal display on the touch screen or on the controller. To monitor on the controller, observe the Sample Intensity and Reference Intensity signals in the real-time signals panel within TRIOS. To monitor the touch screen, observe the heat flow and intensity signals on the touch screen **Utilities > Diagnostics > PCA** page (see [Figure 18](#)). If you are using a third-party PCA, skip to step 12.
- 11 Using the UP/DOWN adjust buttons, adjust the intensity reading at the sample and reference positions until the desired intensity is approximately at the level desired. Refer to Chapter 8 of the filter photometer manual for more information.
- 12 Balance the intensities by adjusting the height of the light guide arm, which initially indicates the highest intensity. Turn the positioning screw counterclockwise while watching the chosen display until the two intensities agree within $\pm 2\%$. To aid in balancing the intensities, observe the Heat Flow signal while balancing to try to get it as close to a value of 0 as possible.
- 13 Note the final balanced intensity. This is the actual intensity to which the samples in subsequent experiments will be exposed. Since intensity is one of the key experimental variables that could affect photocalorimetry results, comparative studies should always be performed at similar sample intensities.
- 14 If desired, the shutter can be closed using the **Shutter**  button in TRIOS or by using the Shutter **Open/Close** button located on the touch screen **Utilities > Diagnostics > PCA** page (see [Figure 18](#)). If you are using a third-party PCA, the shutter must be closed manually. Additionally, when using a third-party PCA, you may also want to disable the real-time intensity signals using the **Shutter** button in TRIOS or the **Event 2** button from the touch screen.

NOTE: The sample and reference intensities are “diagnostic” signals used when setting up the PCA. They are not signals that are typically stored in experimental data files. See NOTES below.

NOTE: When the light intensities delivered to the DSC cell are below 10 mW/cm^2 , the sample and reference intensities cannot be measured and balanced using those cell signals. Rather, the intensities must be measured using an external radiometer and a custom mount designed to hold the light guides at the same distance above the radiometer as the distance between the end of the light guides and the cell platforms (0.81 inches) when the lights are mounted on the cell.

NOTE: If you are using a third-party PCA and want to observe and store the intensity signals in experiment data files, you must use the **Event 2** segment. **Event 2 On** enables the outputs of the intensity signals and **Event 2 Off** disables them.

Additional Experimental Considerations

- Obtaining a specific intensity at the sample is a trial and error process. The following guidelines should help in making those adjustments.
 - The PCA unit can be set up to yield an intensity at the end of the light guide between 500 mW/cm² and the maximum intensity available from the lamp (up to 25,000 mW/cm² depending on the age of the lamp).
 - The intensity at the DSC cell platform is roughly one tenth of that measured at the end of the light guide. (This intensity reduction is due to diffusion through the 20 mm air gap between the light guide and the platform.) This can be further reduced by using the 10 percent or 1 percent transmission neutral density filters provided.
 - Intensities at the DSC cell platform in the visible region are roughly one half (using the 390 nm filter) and one quarter (using the 490 nm filter) of those obtained under comparable conditions for the standard 320 to 500 nm broadband filter configuration. (These relative intensities are the result of the number of high intensity wavelengths which occur in the spectral region used. See the plot below for the high pressure mercury lamp.)

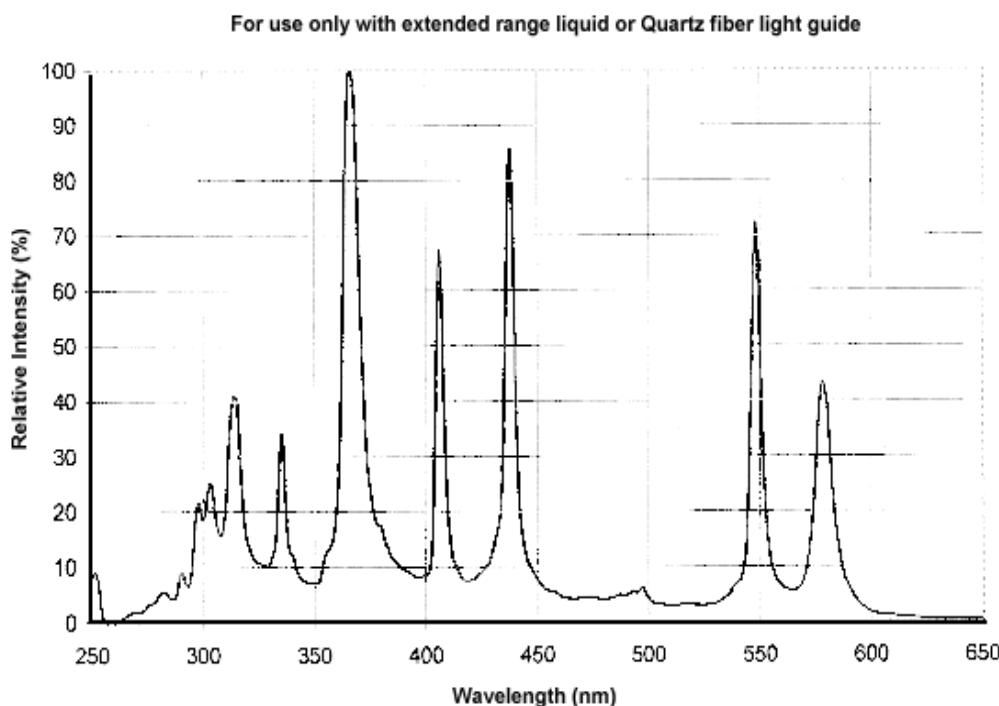


Figure 19 High pressure mercury lamp plot.

- Baseline offset occurs during most experiments when the cell is exposed to light. This offset is associated with the difference in heat capacity between the sample and sample pan and the empty reference pan. This offset is minimal relative to the exothermic events being measured. Furthermore, its contribution during peak integration can readily be eliminated by back extrapolating the baseline after the cure is complete.
- A rise in temperature occurs when the cell is exposed to light. This rise is most noticeable at high intensities ($> 100 \text{ mW/cm}^2$) and is influenced to some extent by the cooling accessory being used. However, due to the speed of most curing reactions and the modest size of the temperature change ($< 1^\circ\text{C}$ at 100 mW/cm^2 intensity), the kinetics of reaction should not be affected.
- Several variables can affect PCA results, including wavelength range, light intensity, temperature, and exposure time:
 - If “PCA Shutter” segments are used in combination with an “Isothermal” segment, then exposure time is controlled by the length of the “Isothermal” segment in between the “PCA Shutter” open and “PCA Shutter” close segments. The shortest exposure time is limited by state transitions between the “PCA Shutter” and “Isothermal” segments and also by the minimum allowable length of the “Isothermal” segment.
 - If the “PCA Exposure” segment is used, the exposure time is controlled by the value specified for the segment. When using the “PCA Exposure” segment, the shortest exposure time that can be set is 0.2 seconds ($\pm 250 \text{ ms}$ or 1% of the exposure time, whichever is greatest).

CAUTION: Do not use the “PCA Exposure” segment unless you are using an Omnicure S2000 PCA unit containing software version 2.6/3.2 or newer; use of the “PCA Exposure” segment on units with older software may result in inadvertent termination of a running experiment, especially for longer durations of the “PCA Exposure” segment. Consult the Omnicure™ User’s Guide for instructions on determining the software version of your S2000 unit.

MISE EN GARDE: N'utilisez pas le segment "Exposition PCA" sauf si vous utilisez une unité PCA Omnicure S2000 contenant la version logicielle 2.6 / 3.2 ou plus récente; L'utilisation du segment "Exposition PCA" sur des unités avec un logiciel plus ancien peut entraîner la fin accidentelle d'une expérience en cours d'exécution, en particulier pour des durées plus longues du segment "Exposition PCA". Consultez le Guide de l'utilisateur Omnicure™ pour obtenir des instructions sur la détermination de la version logicielle de votre unité S2000.

- The Discovery DSC is designed to run with “active” cooling in place throughout the whole temperature range. Several items need to be considered when selecting the cooling accessory that will be used for PCA experiments.
- While the use of the dual quartz light guides permit PCA experiments from -50 to 250°C , most analyses are conducted isothermally between ambient and 50°C . The quartz light guides, if carefully used, should last indefinitely.
- The Finned Air Cooling System (FACS) is not designed for Tzero calibration within 5°C of ambient temperature. It should be used primarily for PCA experiments between 30 and 250°C .
- The RCS cooling accessories allow PCA measurements to be made from -50 to 250°C (for RCS90) or -40 to 250°C (for RCS40). Since portions of the DSC cell will achieve temperature below ambient during RCS operation, good experimental procedure must be followed to ensure that moisture condensation (from the atmosphere) on the outer surfaces of the system does not occur. The DSC has an auxiliary purge that is automatically activated at the end of the PCA experiment to help minimize any potential for condensation. (This purge automatically shuts off when the next experiment begins.) Loading and unloading samples should always be done when the cell has reached ambient temperature or above.

NOTE: It is recommended that the “Unload Temperature Range” parameter (selected on the Advanced Options window when you set up your experimental procedure) be set to 35 to 40°C. After prolonged PCA experiments at -50°C, the outside of the quartz window on top of the DSC reaches about 17°C. However, at the end of an experiment, in the few minutes it takes for the cell to achieve the recommended 35 to 40°C unload temperature, the outer quartz window temperature has increased back to the 24 to 26°C range.

- There may be situations where it is desirable to run an isothermal PCA experiment followed immediately by a DSC heating ramp experiment either to complete the curing process for materials where curing is photoinitiated but completed by heating or to evaluate the glass transition or other thermal properties once partial or full cure has occurred. The TA Instruments PCA has been designed to facilitate rapid conversion between PCA and standard DSC experiments. The upper temperature limit for use of the DSC with the light guide adapter base in place on the instrument is 550°C. If operation above this limit is required, the light guide adapter base must be removed. Simply follow the steps below:
 - Remove the dual light guide adapter with the light guides still in place. There is no need to remove the light guide adapter base. In fact, as mentioned previously, once the Autosampler (if present) has been disabled, those capabilities have to be deliberately re-enabled when switching back to standard DSC. The reason for this arrangement is so that the types of experiments described in this section can be performed without removing the light guide adapter base and potentially changing the alignment of the light guide with the cell platforms.
 - Replace the PCA silver lid and quartz window with the standard DSC inner and outer silver lids and the manual cell cover.
 - Disable the PCA by deselecting the check box in **TRIOS Options > DSC25x > General** (see [Figure 10](#)).
 - Set up the desired DSC method and start the experiment.
- Another unique feature of the Discovery DSC/PCA system is the ability to run quasi-isothermal Modulated DSC® measurements on the material before and after photocuring. Modulated DSC measurements should not be made while the sample is exposed to light because the temperature change generated by the light as well as the exothermic curing process disrupts modulation. However, it is possible to create an experimental method such as the one shown on the next page where a quasi-isothermal MDSC® segment is run before and after the PCA exposure, which uses the “PCA Shutter” or “PCA Exposure” segments. Most materials undergo a decrease in heat capacity as cure progresses because the internal structure becomes more rigid and less molecular motion can occur.

NOTE: Because the heat capacity signal during PCA light exposure is not valid information, it may be desirable when plotting results to only show the heat capacity before and after exposure as shown in the figure below. This can be accomplished by using the “hide data” function in TRIOS software.

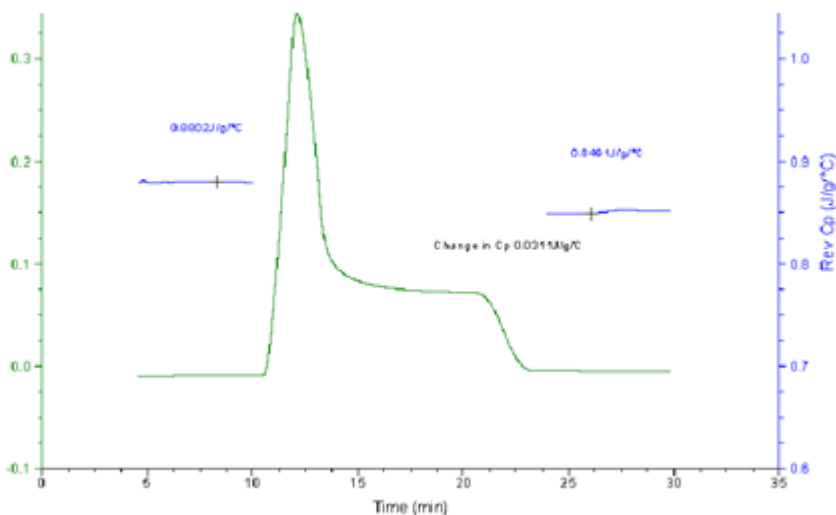


Figure 20 Heat capacity before and after exposure.

The MDSC reversing heat flow signal is directly related to heat capacity. Therefore, measuring the change that occurs in MDSC reversing heat flow as the result of specific PCA exposure conditions, is another option for differentiating similar materials.

Equilibrate at 35°C

Data Storage: ON

Data Collection: 0.1 seconds/data point

Isothermal for 0.5 minute

Modulate $\pm 0.2^{\circ}\text{C}$ every 40 seconds

Isothermal for 1 minute

Modulate $\pm 0^{\circ}\text{C}$ every 40 seconds

Isothermal for 0.5 minute

Shutter Open

Isothermal for 2 minutes

Shutter Closed

Isothermal for 1 minute

Modulate $\pm 0.2^{\circ}\text{C}$ every 40 seconds

Isothermal for 5 minutes

Modulated DSC® and MDSC® are registered trademarks of TA Instruments–Waters LLC, 159 Lukens Drive, New Castle, DE 19720.

Typical Experimental Results

The following figures illustrate typical PCA results. [Figure 21](#) shows a visible-curing adhesive. The time of exposure was sufficient to completely cure this material.

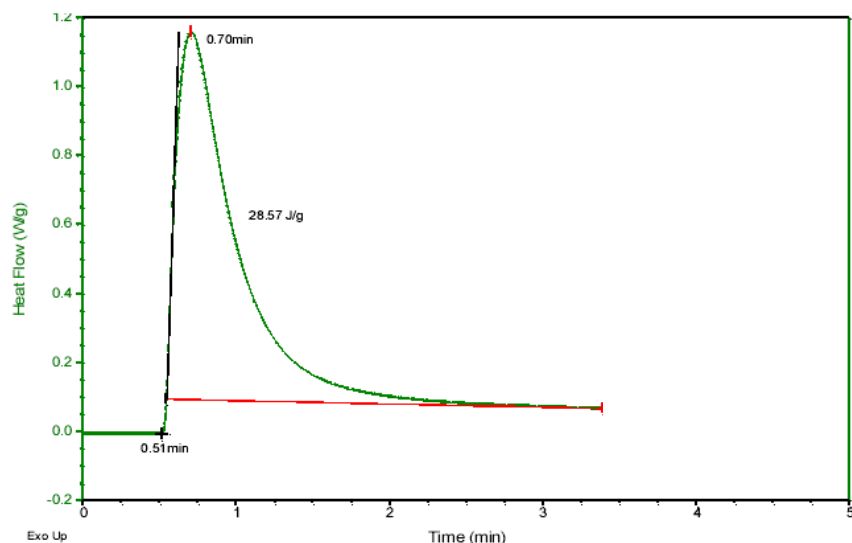


Figure 21 Visible Curing Adhesive.

[Figure 22](#) and [Figure 23](#) illustrate results from “multiflash” experiments on two similar adhesives, where each was exposed to a series of short (0.6 second) “flashes” of broadband (320 to 500 nm) light. The amount of curing which occurs in each flash is different. The amount of curing which occurs in the initial flash indicates that Adhesive A cures faster.

Based on a series of photocuring experiments at different isothermal temperatures, evaluation of curing kinetics is possible using the TA Instruments DSC Isothermal Kinetics software.

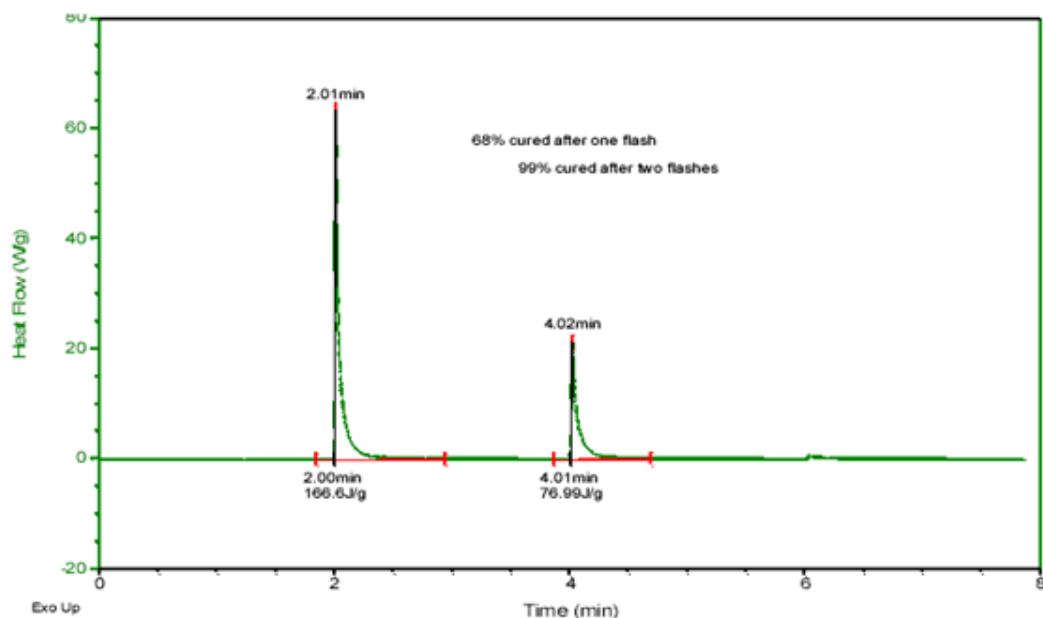


Figure 22 Adhesive A Flash Curing.

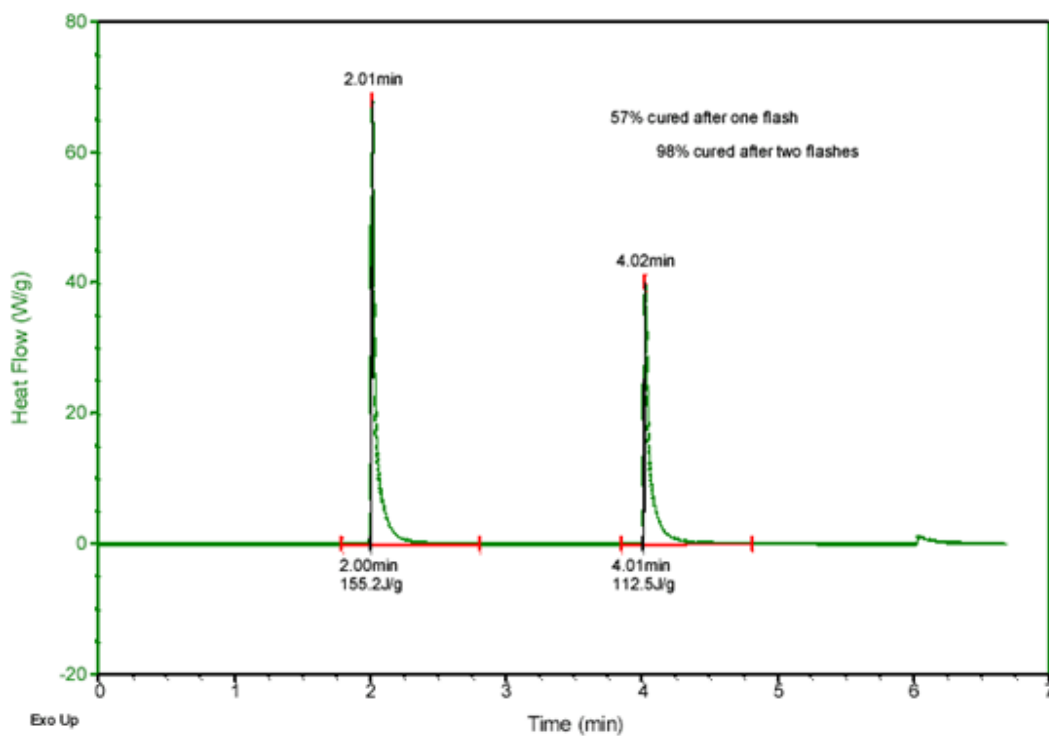


Figure 23 Adhesive B Flash Curing.

Maintaining the PCA

Maintenance of the photocalorimeter accessory consists primarily of minor cleaning and replacement of the air filter at the back of the fan, along with other routine care. See the filter photometer manual for details on these procedures.

Replacement Parts

Replacement parts for the PCA that are available from TA Instruments. See the tables below when ordering parts.

Table 1: PCA Replacement Parts

Part Number	Description
200177.001	Adapter, Radiometer, 3mm, PCA
203947.026	Wrench, Hex, 1/16"
205087.109	Setscrew, #4-40 x .12", Flat Point
265981.001	Wrench, Hex, .050"
269920.026	Wrench, Hex, 7/64"
270712.002	RS-232 Cable, 10' long (Discovery DSC 25, DSC 250, DSC2500, DSC Q2000 and Q200 only)
271400.001	Setscrew, #6-32 x.12", Nylon Tip
271388.001	Fuse, F 5A 250 VAC, 5A, 250V, Fast Blo, 5x20mm
271636.001	Lubricant, Precision, .5 oz Tube, PCA
935003.001	Lid, Inner, Silver, PCA (Q Series only)
935004.001	Lid, Outer, Silver, PCA (Q Series only)
973081.901	Lid, Inner, Silver, PCA, Discovery DSC 25, DSC 250, DSC 2500)
935005.901	Cable, Event, PCA (DSC Q1000 and Q100 only)
935006.008	Filter, Internal, 320 to 500 nm, PCA
935007.901	Window, Quartz, PCA
935008.901	Cap, UV Protective, PCA
935010.901	Adapter Base, PCA
935011.901	Adapter, Dual Light Guide, PCA
935012.001	Light Guide, Dual, 250 to 600 nm NO WARRANTY*
935015.901	Filter, Neutral Density, 1%, 2 ea
935016.901	Filter, Neutral Density, 10%, 2 ea
935021.002	Lamp, 200W Mercury, PCA NO WARRANTY*
973252.001	Silver, Lid, Manual, DSC 25, DSC 250
935022.901	Filter Holder Assy, Dual Light Guide

Part Number	Description
935034.901	Cell Cover, Manual, PCA
935050.001	Adapter Discovery PCA
970282.001	Lid, Upper, Silver, Manual, DSC (Q Series)
970283.001	Lid, Inner, Silver, Manual, DSC (Q Series)
972734.901	RS232 to USB adapter (First Generation Discovery DSC only)

* NO WARRANTY: TA Instruments offers no warranty, after the initial installation, on the Dual Light Guide or the 200 W Mercury Lamp.

Table 2: Additional Replacement Parts

Part Number	Description
271626.001	O-Ring, 3.239" ID x.070" W, PCA (originally included as part of the Adapter Base PN 935010.901)
935006.004	Filter, Internal, 365 nm, PCA
935006.005	Filter, Internal, 250 to 400 nm, PCA
935006.006	Filter, Internal, 400 to 500 nm, PCA
935006.007	Filter, Internal, 320 to 390 nm, PCA
935013.001	Air Filter Kit, Pkg. Of 10, PCA
200700.001	Radiometer, 250-600 nm, PCA
935018.901	Filter, Longpass, 390 nm, 2 ea
935019.901	Filter, Longpass, 490 nm, 2 ea