Multisampler Instructions

Option SH003

Diffuse Reflectance, Photoacoustic Absorbance, and Transmittance Sampling

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Warning:
Please read the entire instructions before attempting to use Option SH003. Failure to do so may lead to damage of Option SH003 and the photoacoustic detector. Be sure to read Sections 3.1, 3.2, and 3.3.

1 Introduction

Option SH003 allows MTEC Models 100, 200, and 300 photoacoustic detectors to measure diffuse reflectance (DR), photoacoustic absorbance (PA), and transmittance (TR) spectra of solid materials by simply changing the SH003 sampling heads. The ease of sample head exchange greatly facilitates the analysis of materials by the method best matched to their optical properties. If materials are known to have strong light scattering, absorbing, or transmitting properties, spectra can be measured to best advantage by selecting the DR, PA, or TR sampling heads, respectively.

A major category of samples, however, have unknown or a mixture of the above properties. In these instances option SH003 is particularly valuable because it allows a rapid survey of the spectra that can be obtained from diffuse reflectance, photoacoustic absorbance and transmittance measurements. In some cases these spectra will prove to be complimentary. For example, IR bands of low concentration species may be more prominent in DR spectra whereas stronger absorbance bands may have better spectral contrast in photoacoustic absorbance spectra.

Figure 1.1 shows photoacoustic absorbance and diffuse reflectance (Kubelka-Munk units) spectra of a plastic coated paper sample. The diffuse reflectance spectrum shows the sharp clay band clearly at 3700 cm^{-1} whereas the band near 1725 cm^{-1} is best observed in the photoacoustic spectrum.

The polyvinyl formal polymer spectra of Figure 1.2 provide a comparison of results using the three types of measurements on both powder and thin film samples. Of particular note is the near absence of the polymer's strongest absorbance band at 1000 cm^{-1} in the diffuse reflectance powder spectrum.

In Figure 1.3, on the other hand, the spectra of a polystyrene polymer film are very consistent in terms of displaying the absorbance bands of this sample although there are variations in band intensities. The spectra of Figures 1.1 - 1.3 illustrate the scope of variations in spectra that can occur depending on the sample characteristics and on the measurement type.

Figure 1.4 illustrates schematically how options SH003 (DR, PA, and TR sampling) and SH004 (microsampling) operate in MTEC photoacoustic detectors. The DR sampling head operation is shown in cross-sectional view. The infrared beam enters through the detector window, passes through the axial hole and window of the sampling head before impinging on the sample. The specularly and diffusely reflected fractions of the infrared beam pass back through the sampling head window. The central cone of reflected light (mainly specularly reflected light) exits through the axial hole. Light reflected at larger angles (mainly diffusely reflected light) is intercepted and absorbed by a black ring which is concentric to the hole and internal to the sampling head. The hole and absorber ring geometry results in detection of diffusely reflected light with rejection (through the hole) of most of the unwanted specularly reflected light. The absorber ring converts diffusely reflected light into heat resulting in a photoacoustic signal which is detected by the photoacoustic detector microphone. The DR head window prevents the microphone from simultaneously detecting a photoacoustic signal from the sample.

The PA sampling head is also shown in cross-sectional view in Figure 1 with an axial hole which allows the infrared beam to impinge on the sample. The photoacoustic signal is generated directly by the sample when heat is produced by infrared absorption in the sample and transported into the adjacent gas. The sampling head's purpose is to reduce gas volume in the sample chamber where thermal expansion occurs thus boosting the signal level. The PA and DR heads can be exchanged without repositioning the sample. This provision allows PA and DR spectra to be obtained under identical sample conditions and consequently any differences observed in spectra are to be assigned to the PA and DR methods of measurement rather than to variations in sample presentation.

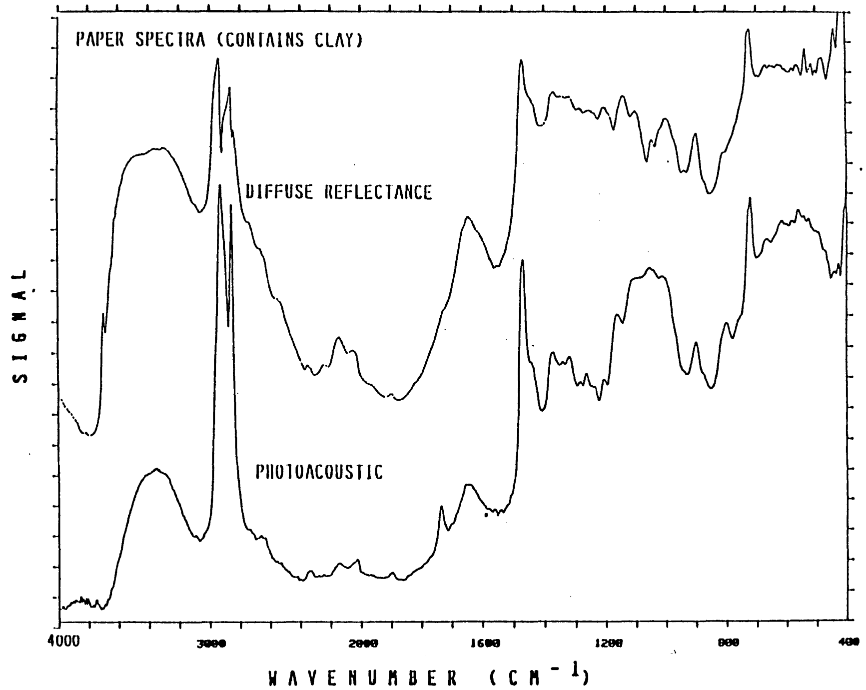

Figure 1.1: Diffuse reflectance and photoacoustic spectra of paper containing clay.

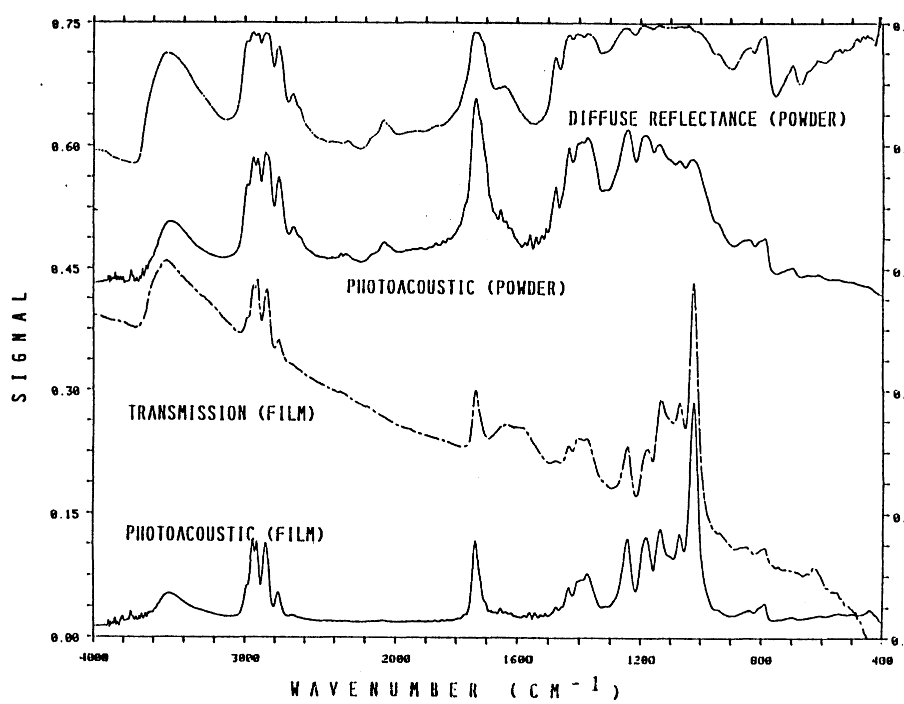

Figure 1.2: Spectra of polyvinyl formal polymer in powder and thin film forms measured by diffue reflectance, photoacoustic aborbance, and transmittance sampling.

The cross-sectional view of the TR sampling head shows the sample position, window, and black absorber surface where the light fraction transmitted through the sample and window is converted into heat and subsequently detected by the detector microphone as a photoacoustic signal. The TR sampling head window and extra o-ring prevent simultaneous detection by the microphone of the photoacoustic signal which is produced directly by the sample.

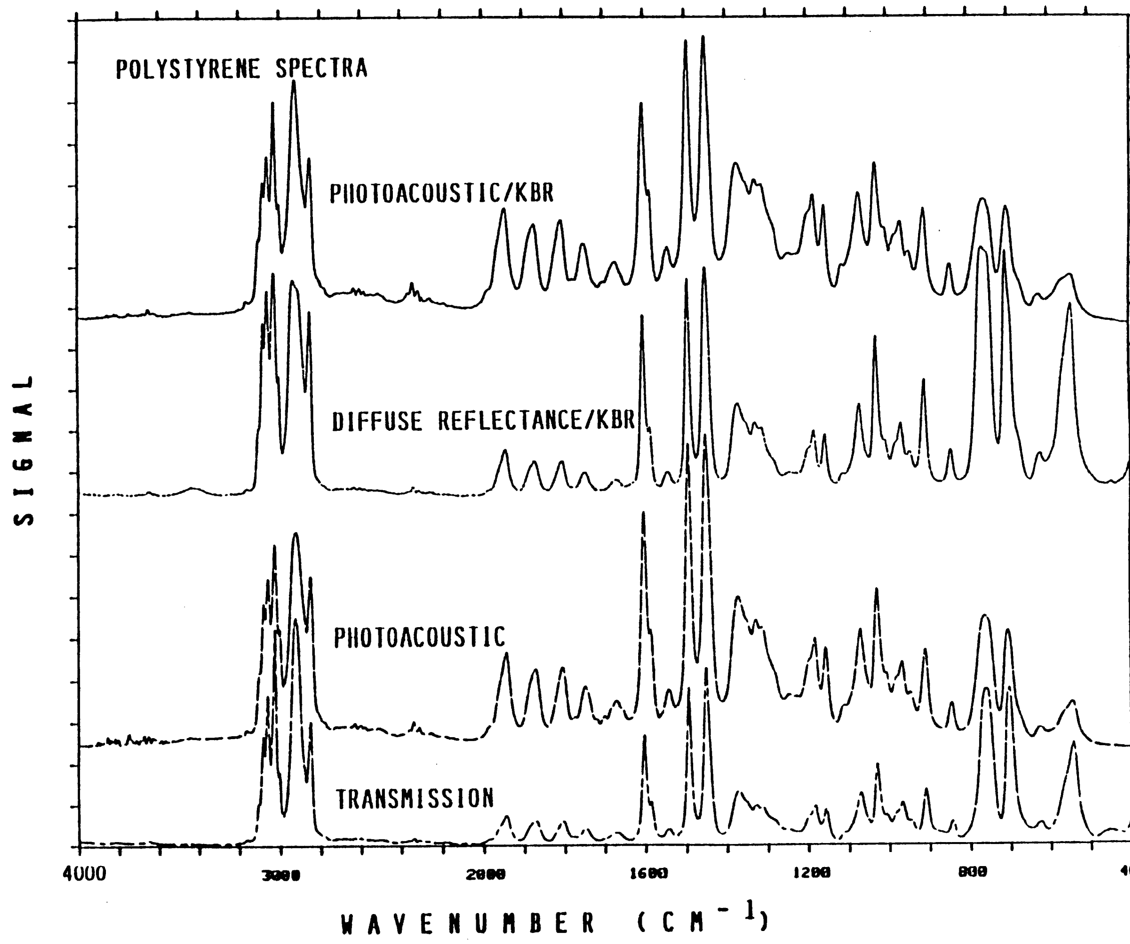

Figure 1.3: Spectra show results for a film of polystyrene (matte finish) measured *with* (upper two spectra) and *without* (lower two spectra) a diffusely scattering backing of KBr powder measured by the sampling method indicated in the figure.

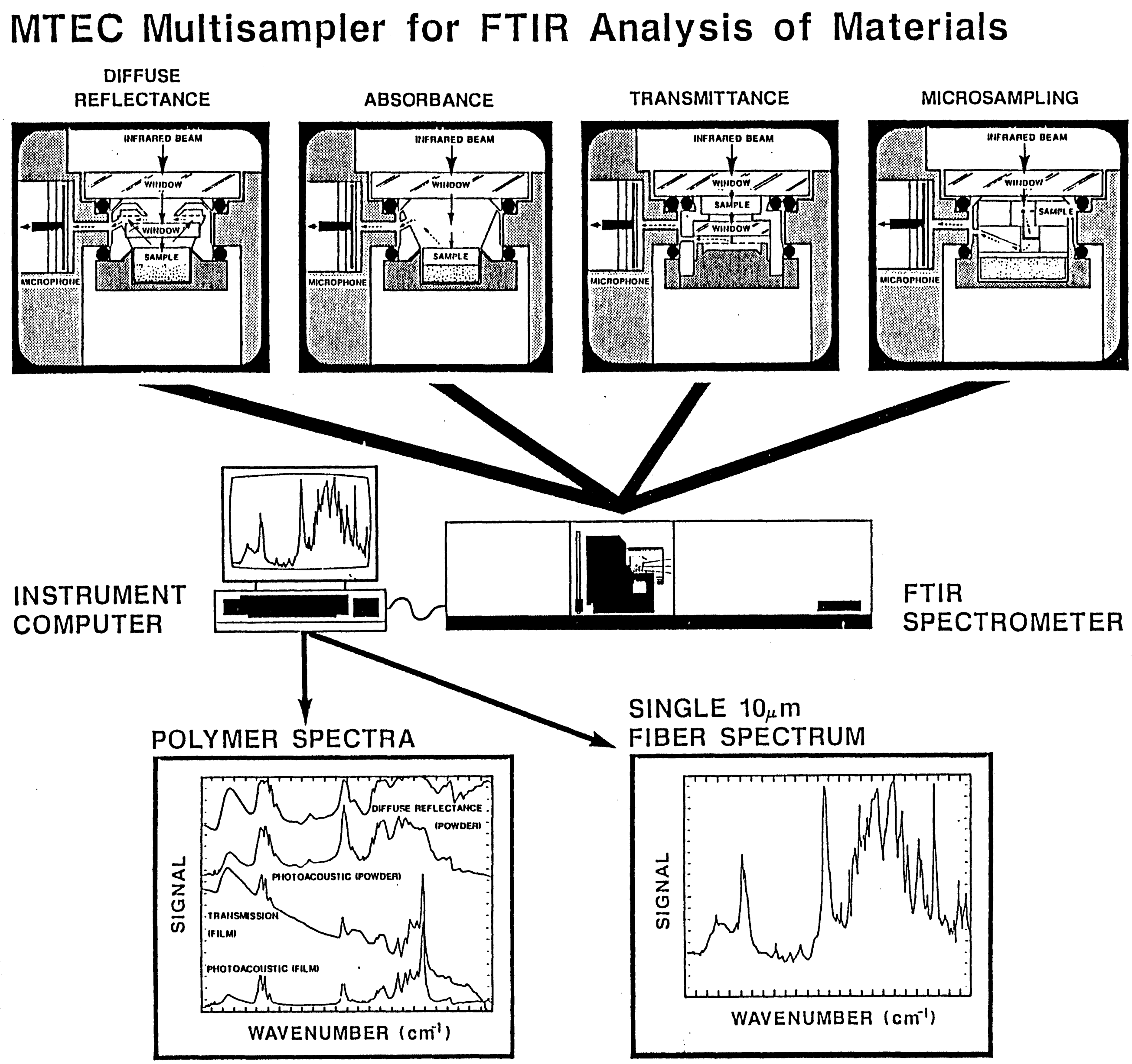

Figure 1.4: Schematic showing how the MTEC multisampling heads operate in MTEC photoacoustic detectors. The SH004 head for micro-particle analysis is in the upper right. The other heads are for option SH003.

2 Operation of the Sampling Heads

The components discussed in this section are identified in the photograph of Figure 2.1. Do not leave sampling heads or desiccant in the detector when not in use. Store heads in their vials in a dry atmosphere.

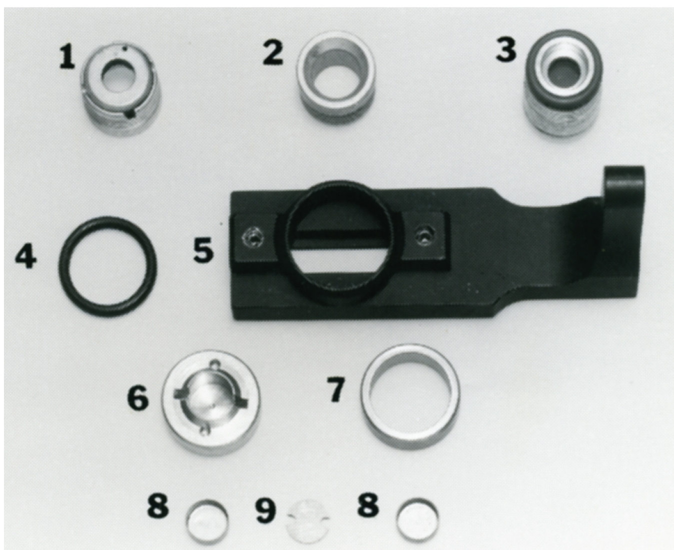

Figure 2.1: Multisampler Components: (1) DR Head, (2) PA Head, (3) TR Head, (4) 12 mm Inner Diameter O-ring, (5) Sample Holder Handle, (6) DR and PA Pedestal, (7) TR Ring, (8) Sample Cup, (9) Spacer Disk.

2.1 DR and PA Head Operation

The DR and PA heads both mount on a brass pedestal which fits into the sample holder handle. Stainless steel desiccant and sample cups stack into an axial hole in the pedestal and are separated by a brass spacer disk which permits gas circulation to the lower desiccant cup. The stainless steel cups may be filled using either the cup fixture and funnel (supplied with PAC100, PAC200, or PAC300 systems), a spatula alone, or by gripping the cup with tweezers and scooping up powdered samples. Regardless of the method employed, the sample should be approximately flush with but should not extend above the rim of the cup in order to prevent the sample from contacting the DR head window. A spatula held in contact with and passed across the rim is an effective means of insuring that the sample does not extend above the rim. After this procedure, it is advisable to tap the cup on a hard surface in order to seat the powder particles because both DR and PA measurements can have some sensitivity to particle-to-particle contact. Hence, it may be important that the tapping procedure be done in a reproducible fashion if quantitative analyses are being done. The contact sensitivity of a given sample type can be explored by measuring spectra before and after tapping and doing a spectral subtraction to reveal small changes in spectra.

Before loading samples into the pedestal, place the pedestal into the sample holder handle. It is necessary to be sure that the pedestal well is free of any debris so that both cups and spacer seat fully into the pedestal. This insures that the sample cup rim will not extend too far above the pedestal and break the DR head window. It is also necessary to use the desiccant cup as a spacer even if desiccant is not in use in order for the sample to be properly positioned relative to the DR head detector. The DR or PA sampling head is put in place on the pedestal after the sample and desiccant are loaded into the pedestal. The sampling head should be engaged in the pedestal (the end of the sampling head opposite the 45 degree level engages), and then the o-ring should be slipped over the sampling head. The o-ring will be seated when the sample holder with the sampling head and o-ring in place are inserted in the photoacoustic detector and sealed by rotation of the rear lever. Follow the purging instructions provided for the particular detector in use.

Photoacoustic spectra should be normalized by dividing the sample spectrum by a carbon black spectrum. Diffuse reflectance spectra are normalized by dividing by a spectrum obtained with KBr powder in the sample cup.

The signal-to-noise ratio of spectra can be optimized by using FTIR operating parameters which are best matched to photoacoustic detection and solid sample spectroscopy. The photoacoustic signal magnitude increases with FTIR infrared beam intensity and decreases with mirror velocity. Hence, operation of the FTIR is desirable with its aperture open and at the lowest *stable* mirror velocity. The lowest resolution setting adequate for the infrared structure being observed should be set on the FTIR instrument in order to conserve spectrum acquisition time. A setting of 8 cm^{-1} is often adequate for infrared spectroscopy of solids.

Moisture band interference, particularly in the 1600 - 1700 cm^{-1} region, is a common problem in FTIR spectroscopy and the causes may be moisture in either the FTIR optical path or photoacoustic detector sample chamber due to either the sample or to the reference sample or to a combination of these. The dominant source of moisture can be determined by examining single beam spectra of the sample and reference. Positive pointing moisture bands are due to photoacoustic signal generation which occurs when the infrared beam of the FTIR is absorbed by moisture in the sample chamber. Negative pointing moisture bands are observed when the beam is absorbed by moisture while transversing the optical path within the FTIR or within the sample volumes of the DR or TR heads. Moisture concentration can be reduced in the FTIR by increasing the purge gas flow and/or by better sealing the purge enclosure.

Moisture concentration in the sample chamber can be reduced in photoacoustic measurements by pre-drying samples (a heat lamp or vacuum oven are useful), by purging with dry helium, or by using a desiccant in the sample chamber or by a combination of these. Usually there is little problem with moisture bands being introduced by the carbon black reference spectrum in photoacoustic measurements.

2.2 TR Head Operation

When the TR head is used, the brass pedestal for the DR and PA heads is removed from the sample holder handle and the brass ring put in place. The end of the

TR head with the set screw is then inserted into the handle and the o-ring is placed over the TR head. The smaller o-ring on the TR head should always be left in place. This o-ring seals the sample off from the microphone so that a photoacoustic signal is not detected from the sample itself.

Samples should be cut with a cork bore or other means and placed in the sample well in the TR head. The maximum sample diameter and height are 7 mm and 1.5 mm, respectively. It is important not to exceed the maximum height in order to prevent the sample from contacting and possibly breaking the detector window. It is also important not to put samples in the TR head that would damage or contaminate its KBr window.

Normally the minimum sample diameter is approximately 5 mm. If smaller diameter samples are used some of the infrared beam will reach the TR head detector without being transmitted through the sample. Qualitative spectra can still be measured in this way but better spectra can be obtained with smaller samples which are placed on masks fashioned from aluminum foil with holes appropriate for the sample size. In this case the background spectra for normalization should be taken with the mask in place and the sample removed. In all measurements spectra should be normalized (ratioed) with a spectrum taken with no sample in the TR head and then converted by the FTIR computer to absorbance spectra.

The TR head can be used to measure KBr or other pellet spectra utilizing a 7 mm diameter pellet press manufactured by Graseby Specac in England, telephone: voice: 1-689-873134, fax: 1-689-878527 (Graseby Specac in U.S., telephone 1-800-447-2558).

Purged operation of the TR head with helium will increase the signal level relative to air operation. Follow the purging instructions given in your detector manual.

Moisture bands are usually not a serious problem with the TR head. If problems occur, pre-drying samples and additional purging of the FTIR and/or photoacoustic detector can be employed.

2.3 Special Directions for Operation of SH003 with Model 100 Photoacoustic Detectors

SH003 can be operated in the earlier PAC100 photoacoustic detectors if several factors are considered. First, when the sample handle is inserted to mate into the brass lifter plate of the Model 100, it is necessary to lift up slightly as the handle is slid in. This allows the o-ring compression adjustment screws to slide over the 90 degree corner of the lifter plate. On Model 200 and Model 300 units, this corner has been beveled to automatically lift the handle.

If the SH003 unit is operated with a Model 100 detector using a helium purge, the directions in the Model 100 operator's manual for purged operation should be followed. Be sure to turn down the helium flow rate to the specified value before inserting the sampling head in the sample chamber.

3 User Service Instructions

3.1 Special Adjustments for SH003 Units Not Originally Shipped with a Photoacoustic Detector

If your SH003 unit was not shipped together with a detector system, two adjustments must be checked prior to use. Failure to do so may damage both SH003 and the photoacoustic detector. These adjustments set the compression on the small o-ring of the TR head and on the larger (12.7 mm inner diameter) o-ring that makes the main sample chamber seal. The TR head o-ring compression is adjusted by the single 4-40 set screw in the bottom of the head. The larger o-ring compression is adjusted by two 5-40 set screws in the sample holder handle.

3.2 TR O-ring Adjustment

Initially, turn each of the 5-40 screws counter-clockwise (as viewed from above) until their heads are flush with, but not projecting above, the top of their holes. Place the TR ring and head in the sample handle. Do not use the larger 12.7 mm inner diameter o-ring with the TR head at this point in the adjustment procedure.

Before inserting the handle in the detector, rotate the rear lever several times in order to get a sense of the amount of resistance-to-motion present in the lever action when no o-ring compression occurs. When the o-ring compression screw on the TR head is properly set, there will be a very slight increase in the lever's resistance-to-motion just before the SEAL position is reached. If the 4-40 screw is set for too much compression, the lever will have too much resistance-to-motion and the detector window may be broken. Screwing the 4-40 set screw into (clockwise) the TR head will reduce o-ring compression (i.e., reduce the lever's resistance-to-motion). Counter-clockwise rotation will increase compression.

3.3 Main Sample Chamber O-ring Adjustment (12.7 mm inner diameter o-ring)

Place the DR/PA head pedestal, the PA head, and a 12.7 mm o-ring in the sample handle. Turn the 5-40 set screws (clockwise from above) in the sample handle until they project approximately the same distance as the ones on the standard sample holder. Insert the sample handle and check the o-ring compression as indicated by the lever's resistance-to-motion at the SEAL position. The resistance should be comparable to that experienced when the detector's standard sample cup and handle are used. Clockwise rotation of the 5-40 screws will increase o-ring compression (lever resistance) and counter-clockwise will reduce it. Be sure to keep symmetric the depth to which the 5-40 screws are advanced into the sample handle. Otherwise the o-ring will not be symmetrically compressed. After the 5-40 screws are set, the adjustments are complete for all three of the sampling heads.

3.4 Replacement of O-rings

O-rings will need to be replaced periodically. They can be ordered from MTEC in sets of three large and one small o-ring (Part No. SH003-OR). These o-rings are pregreased.

3.5 Sampling Head Windows

The DR and TR sampling head windows should be protected from moisture, sample contamination, and scratching. Windows can be dusted off using a gentle gas jet. Use caution. Destruction of the DR or TR head will result if the gas jet is directed into the top or side holes of the DR head or into the side holds of the TR head. In some instances, it may be necessary to use a cotton swab to lightly wipe the windows. Some scratching may result but this will not alter the performance significantly in the infrared spectral region.

If window damage/breakage occurs, the complete sampling head must be replaced.

3.6 Removal of Sampling Heads Stuck in the Detector

If a sampling head becomes stuck in the detector due to debris in the sample chamber or some other cause, it may be necessary to remove the detector's window. The head can then be gently pushed down by applying force to its outer perimeter and then withdrawn.

It may also be possible to extract heads by rotating the lever back to the seal position and then unsealing the sample holder in the normal way. Do not force the rear lever when attempting to dislodge sampling heads.

MTEC is equipped to remove jammed sampling heads if necessary.

4 Directions for Returning SH003 Units for Factory Servicing

Please contact MTEC for authorization prior to shipping any items for repair. (MTEC telephone: 515-292-7974; telefax: 515-292-7125.) All transportation charges and insurance are the customer's responsibility. A purchase order number must be provided before repairs will be made.

4.1 Special Instructions for Foreign Returns

If possible, ship the package via a courier, such as Federal Express or Airborne Express, who will act on behalf of MTEC as a customs broker. This simplifies the return, expedites clearance through U.S. Customs, and saves extra freight forwarder costs to MTEC which are billed back to the customer. Prepay the air waybill through to Ames, Iowa. Consign to the shipping address above, and list MTEC's telephone number (515-292-7974).

To avoid complications and delays, label the shipment "free domicile." This simplifies U.S. Customs clearance. A copy of an invoice showing the total value is required for customs. This invoice must state the value, that the product was "Made in the U.S.A., and is a "Returned American Product for Repair Only." Please follow your local shipper's instructions concerning all shipping requirements.

If the return is made through a freight forwarder, be sure the freight is prepaid to Ames, Iowa. Use the "free domicile" declaration to avoid complications and delays.

5 Warranty and Disclaimer

Product Warranty

MTEC Photoacoustics, Inc. warrants the Multisampler Option SH003 to be free from defects in material or workmanship and to operate as described in this manual, under normal use, for a period of one year from the date of original shipment. No other warranty is expressed or implied.

If examination by MTEC Photoacoustics, Inc. discloses a product defect, obligation is limited to repairing, replacing, or giving credit for the purchase price, at our option.

KBr windows and the absorber elements are not warranted. MTEC Photoacoustics is not liable for any consequential damages. Components other than those manufactured by MTEC Photoacoustics, Inc. will carry the original manufacturer's warranty. All transportation charges on items returned are the customers's responsibility. Contact MTEC for authorization prior to returning any items for warranty claims. (See Section 4.)

Product Disclaimer

MTEC Photoacoustics, Inc. will not assume responsibility for any damages to persons or to property due to the operation of or to results obtained with the MTEC photoacoustic detector systems and/or the multisampler option.