Photo-Elastic Modulator Infrared Reflection Absorption Spectroscopy Accessory for 600-IR Series Spectrometers

Hardware Manual

Installation Category II
Pollution Degree 2
Safety Class 1 (EN61010-1)

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Safety Practices and Hazards

The Photo-Elastic Modulator Infrared Reflection Absorption Spectroscopy Accessory (PEM-IRRAS) has been carefully designed to be used as an accessory to Varian FT-IR spectrometers. When used properly it provides an accurate, fast, flexible and safe analytical system.

If the equipment is not used in a manner specified by the manufacturer, the protection provided by the equipment may be impaired.

Information on safety practices appear throughout the documentation (both printed and online) provided with your microscope. Before using the PEM-IRRAS, you must thoroughly read these safety practices.

Observe all relevant safety practices at all times.

Cryogenic Cooling

Detectors used with your PEM-IRRAS are cryogenically cooled. The liquid nitrogen used in this process is extremely cold and can cause damage to the human body. Use appropriate protective equipment when working with liquid nitrogen.

Electrical Hazards

The Varian PEM-IRRAS contains electrical circuits, devices, and components operating at dangerous voltages. Contact with these circuits, devices and components can cause death, serious injury, or painful electrical shock.

Good grounding/earthing is essential to avoid a potentially serious electric shock hazard. Ensure that there is an integral ground connection between the metal surfaces of the PEM-IRRAS and the 3 pin earth-grounded receptacle

Note The safety classification is given as Class 1 (EN 61010-1).

Application of the wrong supply voltage can create a fire hazard and a potentially serious shock hazard, and could seriously damage the PEM-IRRAS.

Replace blown fuses with fuses of the size and rating as stipulated in the text adjacent to the fuse holder or in the manuals where listed.

Do NOT use power cords with faulty or frayed insulation.

Laser Safety

The Varian PEM-IRRAS is used with Varian FT-IR spectrometers which incorporate a He-Ne laser operating in the visible region at 632.8 nm. The spectrometer is a Class 2 laser product, powerful enough to warrant caution in its use. Varian FT-IR spectrometers comply with FDA and CE standards for light-emitting products.

An attenuated portion of the laser beam passes into and through the spectrometer sample compartment and can be directed from there into the accessory. Although not powerful enough to harm your skin should your hand intercept it, the laser light could cause retinal (eye) damage during prolonged direct viewing. This is not possible given the normal optical layout of the spectrometer. However, if a highly reflective surface such as a mirror is allowed to intercept the beam, the beam could be redirected out of the sample compartment resulting in on-axis or direct viewing. Care must be taken to avoid this.

Refer to the spectrometer hardware manual for more information about the laser.

Other Precautions

Use of the PEM-IRRAS may involve materials, solvents and solutions which are flammable, corrosive, toxic or otherwise hazardous. Careless, improper, or unskilled use of such materials, solvents and solutions can create explosion hazards, fire hazards, toxicity and other hazards which can result in death, serious personal injury, and damage to equipment and property.

ALWAYS ensure that laboratory safety practices governing the use, handling and disposal of such materials are strictly observed. These safety practices should include the wearing of appropriate safety clothing and safety glasses.

Warnings and Cautions

Other specific warnings and cautions appear in this manual and in the online help where appropriate, and detail the specific hazard, describe how to avoid it, and specify the possible consequences of not heeding the warning or caution.

Read all warnings and cautions carefully and observe them at all times.

Warning – Name of Warning
A 'Warning' message appears in the manual when failure to observe instructions or precautions could result in death or injury. Symbols depicting the nature of the specific hazard are also placed alongside warnings as well as detail of hazard and information on how to avoid the hazard.

Caution A 'Caution' message is used when failure to observe instructions could result in damage to equipment (Varian supplied and/or associated equipment).

Note A 'Note' is used to give advice or information.

Warning Symbols

The following is a list of symbols that appear with warnings in this manual or on the accessory. The hazard they describe is also shown.

A triangular symbol indicates a warning. The meanings of the symbols that may appear alongside warnings in the documentation are as follows:

Corrosive liquids

Cryogenics

Electrical shock

Eye hazard

Fire hazard

Heavy weight (danger to feet)

Heavy weight (danger to hands)

Hot surfaces

Laser hazard

Moving part

Noxious gases

Sharp object

The following symbol may be used on warning labels attached to the instrument. When you see this symbol you must refer to the relevant operation or service manual for the correct procedure referred to by that warning label.

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Information Symbols

The following symbols may appear on the accessory to provide you with additional information:

I	Mains power on
0	Mains power off

Fuse

Single phase alternating current

When attached to the rear of the product, indicates that the product complies with the requirements of one or more EU Directives

Federal Communications Commission Advisory

The following is a U.S. Federal Communications Commission advisory:

This equipment generates, uses and can radiate radio frequency energy, and if not installed and operated in accordance with the instruction manual may cause interference to radio communications. It has been tested and found to comply with the limits for a Class A computing device pursuant to Subpart J of Part 15 of Federal Communications Commission (FCC) Rules, which are designed to provide reasonable protection against such interference when operated in a commercial environment. Operation of this equipment in a residential area may cause interference, in which case the user will be required to take whatever measures may be necessary to correct the interference at his or her expense.

CE Compliance

The Photo-Elastic Modulator Infrared Reflection Absorption Spectroscopy Accessory (PEM-IRRAS) has been designed to comply with the requirements of the Electromagnetic Compatibility (EMC) Directive and the Low Voltage (electrical safety) Directive (commonly referred to as the LVD) of the European Union.

Varian has confirmed that each product complies with the relevant Directives by testing a prototype against the prescribed EN (European Norm), IEC or CISPR standards.

Proof that a product complies with these directives is indicated by the CE Marking appearing on the rear of the product, and the documentation that accompanies the product containing a copy of the Declaration of Conformity. The Declaration of Conformity is the legal declaration by Varian that the product complies with the directives listed above, and shows the EN standards to which the product was tested to demonstrate compliance. It is also signed by Varian's Authorized Representative in the EU, and by the representative of the manufacturing plant.

1. Introduction

1.1 Specifications

The PEM-IRRAS is designed for indoor use. It is suitable for the following categories:

- Installation category II
- Pollution degree 2
- Safety Class 1 (EN 61010-1)

1.2 Environmental

The conditions below are required for proper operation of your PEM-IRRAS:

- Temperature: 20 °C to 26 °C (68 °F to 80 °F)
- Temperature gradient: 1 °C/hr (1.8 °F/hr) maximum
- Relative humidity: 20% to 50% non-condensing
- Altitude: 3000 m (10,000 ft) maximum
- Free from corrosive and flammable fumes
- Free from strong electromagnetic fields[1]
- Free from vibrations

[1] Performance degradation may result from the exposure of the spectrometer to strong radio frequency energy. If degradation is experienced, the user should reorient or relocate the spectrometer or the radio frequency source.

1.2.1 Power

- PEM controller: 60 VA
- 100 to 240 VAC, 60 Watts, 50 or 60 Hz. An auto-ranging power supply is used. No reconfiguration is required for voltage changes.
- Dedicated, 10-ampere circuit with grounded receptacle.

1.2.2 Purge Gas

- A source of clean, dry air (dried to dew point of -70 °C) or liquid nitrogen boil-off to be used as a purge gas. Where compressed nitrogen is used, it must be dry, oil–free and uncontaminated, with purity of 99.996% or better.
- Purge: at a flow rate of 13 L/min (30 ft^3/hr) maximum is required to assure a non-condensing environment.
- Gas supply must be equipped with fittings to accept 6 mm outside diameter (OD) tubing.
- Tubing should be clean and free of any dust and debris. Do not use tubing treated with talcum powder.

1.2.3 Liquid Nitrogen

Warning – Cryogenics
Liquid nitrogen is very cold and can cause damage to the human body. Use appropriate protective equipment when handling liquid nitrogen.

The detector in the PEM-IRRAS will require a supply of liquid nitrogen to cool it. It takes about 500 mL (16 oz) of liquid nitrogen for the initial fill to bring the Dewar to an equilibrium temperature. It will take about 20 minutes to reach equilibrium. Then add an additional 200 mL (7 oz) of liquid nitrogen to top off the Dewar.

1.2.4 Weights and Dimensions

	Width cm / (inch)	**Depth cm / (inch)**	**Height cm / (inch)**	**Weight kg / (pound)**
PEM-IRRAS	67.5 / (27)	61 / (24)	27.5 / (11)	45 / (100)

1.2.5 Space

- Flat and level surface rigid enough to support the weight of the spectrometer and the PEM-IRRAS and any additional accessories if applicable without warping or sagging.
  Loaded flatness tolerance: 0.4 mm per 300 mm of length.
  (1/64 in. per foot of length).
- Minimum of 30 cm (12 inches) of free space behind the rear of the spectrometer and PEM-IRRAS.
- Overhead space of 75 cm (30 inches).

1.3 Installation Requirements

Before receiving your Varian FT-IR spectrometer and PEM-IRRAS accessory you will have been given a copy of the FT-IR spectrometer pre-installation manual (part number 8510246400), which describes the environmental and operating requirements of the spectrometer system. You must prepare your laboratory according to these instructions before the system can be installed. You should keep the pre-installation manual for future reference. If you have misplaced your copy, you can obtain a replacement from your local Varian office.

1.4 Training

The software provided with your Varian FT-IR spectrometer includes extensive online help applicable for the spectrometer and the PEM-IRRAS. If you require additional instruction or training contact your local Varian office.

1.5 Documentation

This hardware manual provides basic instructions for operating and maintaining your PEM-IRRAS.

In addition to this manual you may receive other hardware and software manuals depending on the type of configuration purchased.

Further information and instructions about software, analysis methodology, operating procedures and various accessories is provided in the online Help and electronic manuals saved onto your PC hard drive during software installation for your Varian FT-IR spectrometer.

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2. Hardware

2.1 Overview

The Photo-Elastic Modulator Infrared Reflection Absorption Spectroscopy Accessory (PEM-IRRAS) is designed to be used as an accessory to Varian FT-IR spectrometers. The PEM-IRRAS is used for grazing-angle reflection spectroscopy.

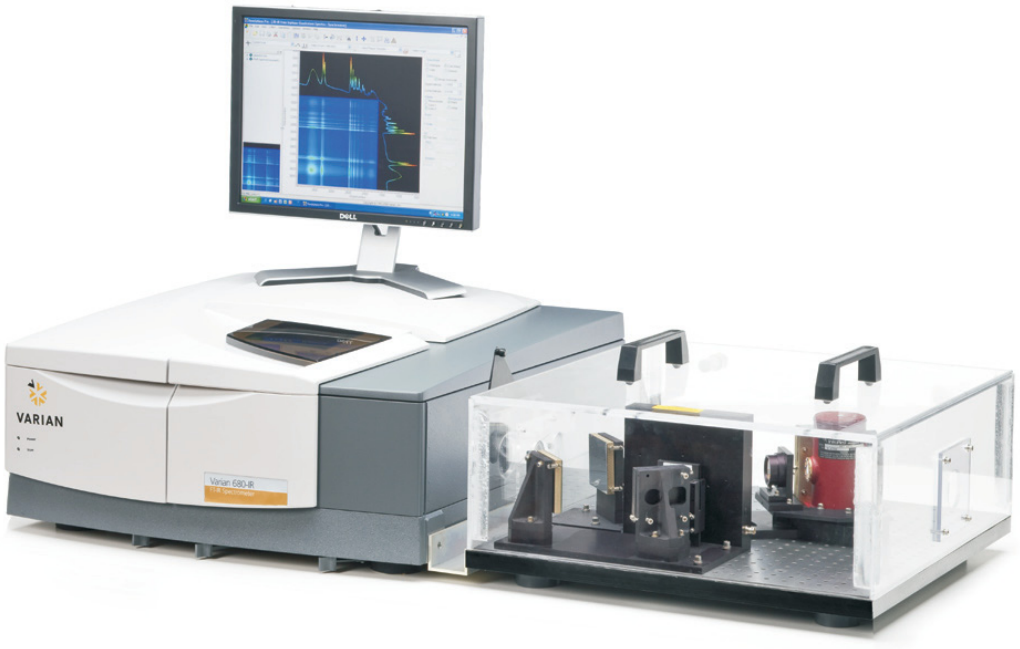


Figure 1. Varian 680-IR spectrometer and PEM-IRRAS accessory

The PEM-IRRAS includes:

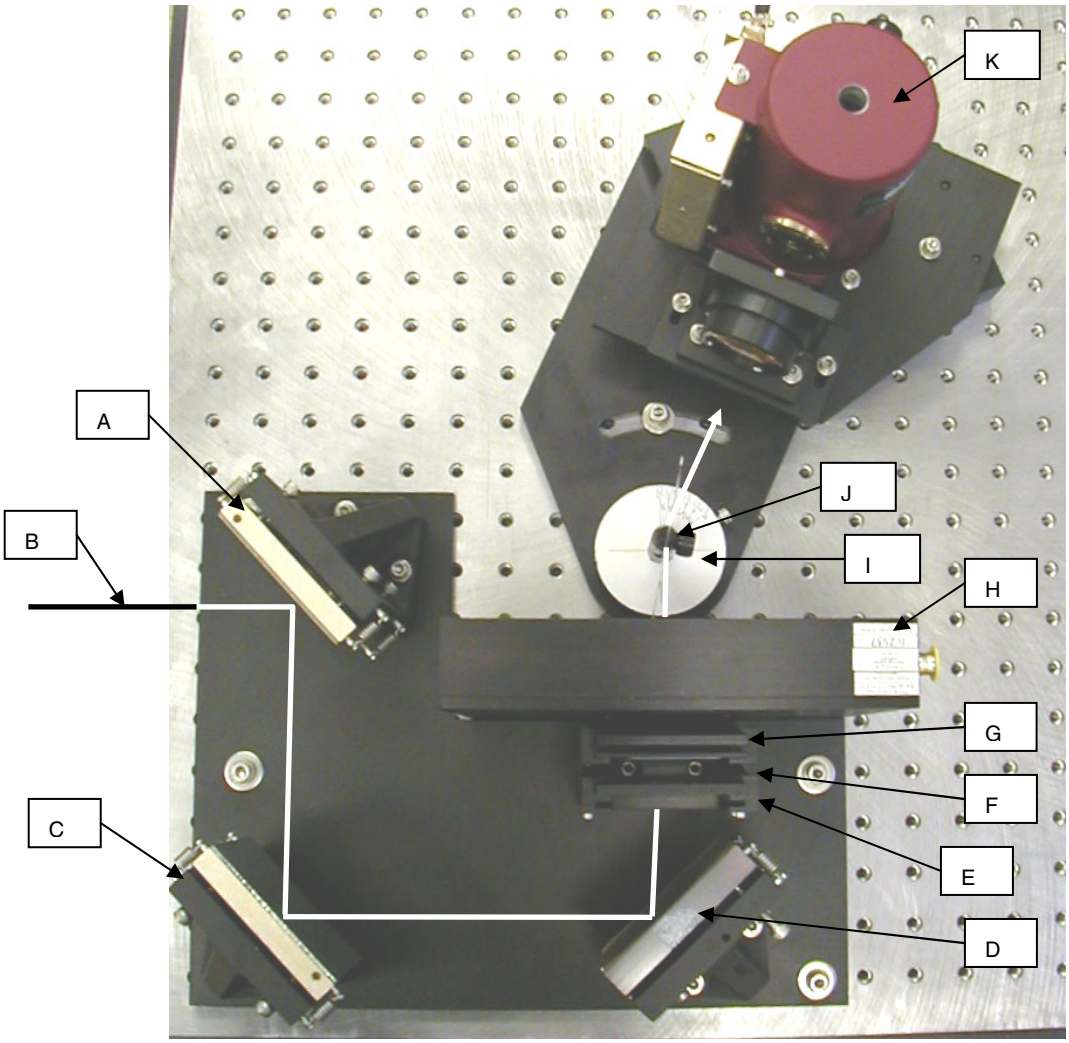
- External Experiment Module (EEM) (including Plexiglas™ cover).
- Base plate with optics mounts.
- Base plate with one liquid nitrogen-cooled detector.
- PEM.
- PEM controller (complete with user's manual).
- This hardware manual (8510258800).

Note The PEM and the PEM controller are manufactured by Hinds™ Instruments, Inc. Details concerning operation and specifications of these devices are not provided in this manual. Should you require information about these devices please contact Hinds Instruments, Inc. directly.

The PEM-IRRAS is attached to the right-hand side of a Varian 600-IR series spectrometer. It is installed and aligned by your Varian Customer Service Representative (CSR).

2.2 Beam Path

The infrared beam exits the spectrometer and is directed by two flat mirrors to the parabolic mirror for focusing.



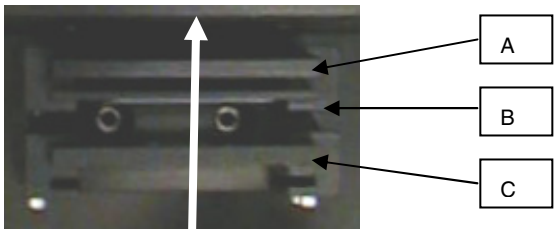
A = Flat mirror
B = Beam from spectrometer
C = Flat mirror
D = Parabolic mirror
E = Quartz window
F = UDR filter
G = Polarizer
H = Photo-elastic modulator
I = Angle Indicator
J = Sample
K = Detector

Figure 2. Varian PEM-IRRAS accessory beam path with cover removed for clarity

2.3 Filters

The focused beam may pass through three optical elements before passing through the Photo-elastic Modulator (PEM). These elements are:

- **Quartz window** (optional), acting as a high pass optical filter transmitting above 2,000 cm^{-1}. When used with the UDR4 filter (see below), allows data collection at UDR=8 for the bandpass between 3,950 and 2,000 cm^{-1}. To display data in the required range click **Transforms > Fourier Transform > Advanced** and use the 'Included Frequency' parameter.
- **UDR filter** location for UDR4 or UDR8 filter. The UDR filters are optical lowpass filters which transmit below 3,950 cm^{-1} (UDR4 filter) or 1,975 cm^{-1} (UDR8 filter), and are used with the UDR=4 or UDR=8 parameter setting, respectively, of Resolutions™ Pro software.
- **Infrared Polarizer** with the plane of polarization set parallel to the surface of the sample.



Direction of beam

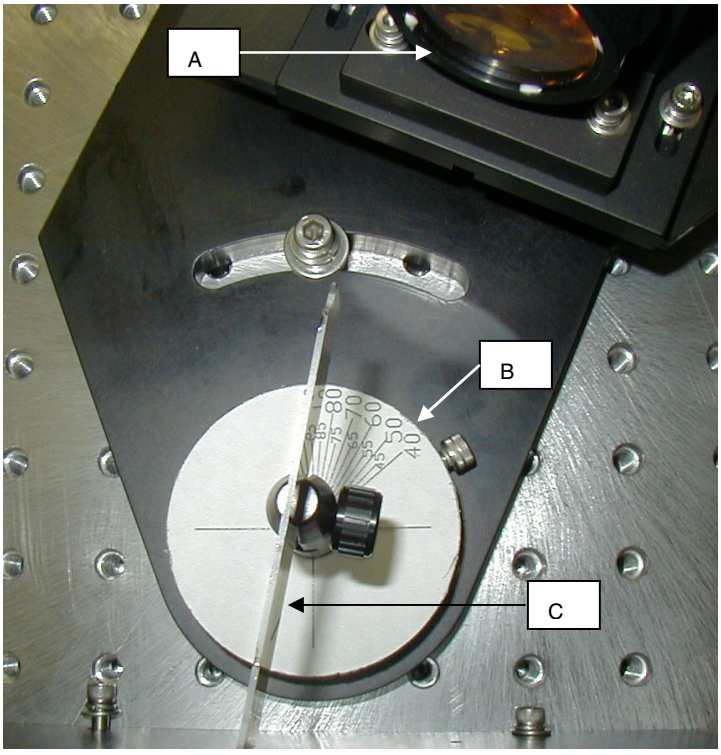
A = Polarizer B = UDR filter C = Quartz window

Figure 3. Infrared polarizer plane of polarization

The filters and polarizers must be placed in the order as shown in the figure above.

2.4 Orientation of Sample and Detector

Mount the sample (maximum sample size 75 mm) in the optical clamp so that the clamp grips the edge of the sample. The detector should be offset from 90° by twice the sample angle. The beam exits the PEM along the 90° line. Typically, the sample should be set along the 80° line (10° offset) and the detector set at 70° (20° offset). The detector position may be optimized by maximizing the magnitude of the interferogram centerburst in rapid scan setup mode while making small adjustments of the detector angle. The ZnSe lens assembly has been optimized on installation. Do not adjust the lens relative to the detector.



A = Detector B = Angle indicator C = Sample

Figure 4. Sample and detector orientation

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3. Basic Operation

3.1 Introduction

A schematic diagram of an IRRAS experiment is shown in the figure below. Broad band infrared radiation from a ceramic source is phase modulated by a step scan interferometer, typically at phase modulation frequencies of 400 or 800 Hz at an amplitude of 1.0 or 2.0 λ HeNe, and stepping at 0.5-2.5 Hz. The modulated radiation is filtered with a lowpass optical filter transmitting radiation below 3,950 cm^{-1} or 1,975 cm^{-1}. The IR light is filtered to undersample the interferogram by 4 or 8, thereby reducing the measurement time. After filtering, the IR radiation is polarized by a gold grid polarizer. Then this polarization is modulated by a Hinds ZnSe PEM operating at 37 kHz and amplitude of 0.5 λ (strain axis 45° to the polarizer), before reflecting off the sample at grazing angle of incidence; 80° to 85° from normal. The sample is a self-assembled monolayer film on a metallic substrate, typically gold. The IR light is subsequently focused onto a narrow band MCT detector with on-axis refractive optics. The spectrometer step and phase modulation are controlled by the master clock on the spectrometer. The PEM operates asynchronously with the spectrometer.

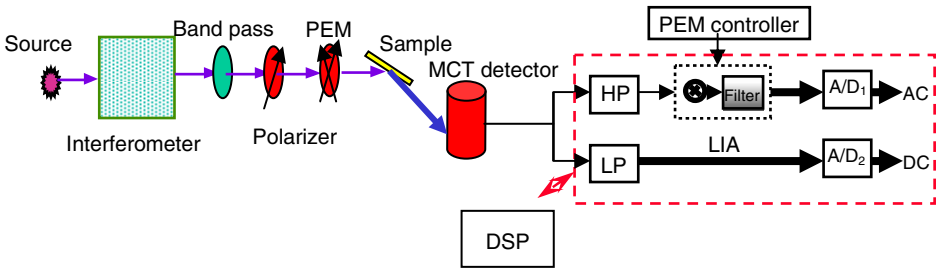

Figure 5. Schematic diagram of an IRRAS experiment

After the detector and preamplifier, the demodulation method as first described by Marcott (C. Marcott, Applied Spectroscopy, 38, 442 (1984)) is displayed in Figure 5. This method employs a set of electronic filters and a lock-in amplifier (LIA) along two parallel signal paths. The top path, shown in Figure 5, after a high pass filter, demodulates for polarization modulation (LIA). The output of the LIA provides the dichroic difference spectrum between ‘s’ and ‘p’ polarized light, often called the AC spectrum. Since the electric field of ‘s’ polarized light has a node at the surface of a metallic substrate, the dichroic difference, Rp-Rs, is the only polarization-sensitive component in the optical path. Thus, the upper signal path is sensitive only to the thin film on the substrate, allowing the surface signal to be digitized with high dynamic range, enhancing the sensitivity for analysis of such samples. In the lower path above, the detector is low-pass filtered to eliminate the high frequency PEM component, providing the single beam spectrum of the substrate. The final step of data processing is to ratio the AC to the DC spectrum to obtain the surface spectrum with high sensitivity and free from atmospheric contamination and other artifacts. The latter statement is true if the AC and DC channels are sampled simultaneously with parallel A/D converters. As shown by the dashed box, the digital signal processing (DSP) software will replace the function of the LIA, the electronic filters and second A/D converter.

3.2 Data Collection

Data is collected using DSP(3) software. See the DSP(3) section in the online Help.

3.3 Prepare the PEM-IRRAS

3.3.1 Power

The PEM controller should be plugged into an AC outlet. For power requirements refer to the PEM-100™ User Manual.

Power for the detector is supplied from the FT-IR spectrometer.

3.3.2 Detector Cooling

Fill the detector Dewar with liquid nitrogen for each detector to be used as described in Section 1.2.3.

Warning – Cryogenics
Liquid nitrogen is very cold and can cause damage to the human body. Use appropriate protective equipment when handling liquid nitrogen.

3.3.3 Sample Purge

Turn on the purge, if desired. The purge fitting is in the back of the PEM-IRRAS accessory and accepts 6 mm (OD) tubing. Set the purge rate to 13 L/min.

3.3.4 Scanning

To setup and scan:

1. Install the UDR4 filter and the Polarizer ('0 deg' should be at top).
2. Install the IR Reflective Test Slide (989-0604) in the sample holder on the rotary stage. The coated side of the slide should be facing to the right in the beam path. The coated side will be the side facing you with the etched corner in the upper right hand corner. Set the angle of the slide at 90 degrees.
3. Optical set-up:
   (a) PEM in beam path (TURNED OFF)
   (b) Polarizer in holder
   (c) UDR4 filter
   (d) IR Reflective Test Slide at 90 degrees
   (e) Detector at 70-75 degrees
4. In Method Editor in Resolutions Pro™ set the following instrument parameters:
   (a) Common Settings:
      - Resolution = 8 cm^{-1}

(b) Collect:

- Speed = 25 kHz
- UDR = 2
- Filter = 6.4 kHz
- Sensitivity = 1

(c) Spectrometer Configuration:

- IR Source = Rear: Mid-IR
- Beam Path = Right
- Detector = Ext. 1
- Aperture = 2 cm^{-1}
- Attenuator = 50%

5. Click **Signal Monitor** and rotate the test slide to optimize the interferogram signal.
6. Select **Single Beam** while in Signal Monitor and check that the slide is positioned correctly. Figure 6 shows a spectrum of the coated side and Figure 7 shows a spectrum of the glass side.

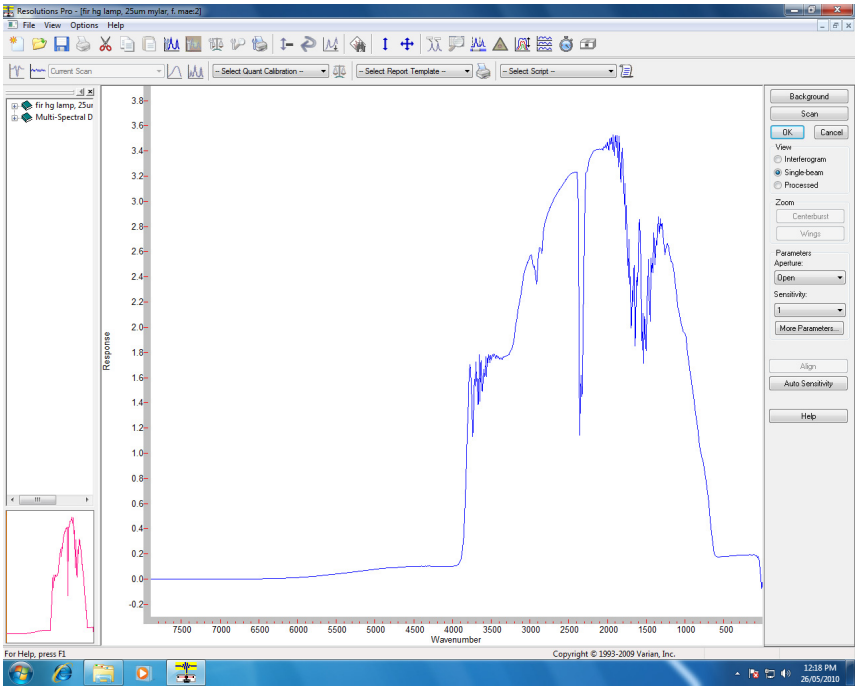

Figure 6. Single beam spectrum of the coated side of the test slide

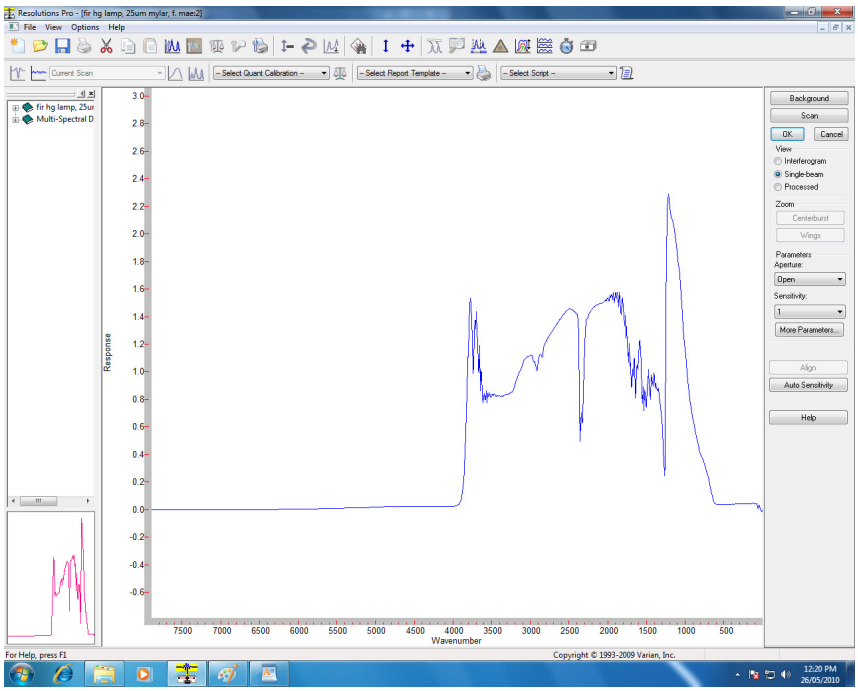

Figure 7. Spectrum of the glass slide

7. Set up the PEM controller as follows: (refer to the PEM-100™ controller manual for details)
   (a) λ = 7500 nm
   (b) Retardation = 0.5 λ
   (c) Frequency = 2F

Note The PEM frequency may take several minutes to stabilize after it has been turned on or settings have been changed (for example, retardation amplitude or wavelength). Allow the PEM to stabilize before starting data collection.)

8. Go to **Collect > Step Scan > Step Scan.** Select the following parameters:
   (a) Electronics:
   - Speed = 800 Hz
   - UDR = 2
   - Filter = NONE

(b) Optics:

- Source = Mid-IR
- Beam Path = Right
- Detector = Ext. 1
- Aperture = 2 cm^{-1}
- Attenuator = 50%

9. Click **Setup**.
10. Click **Align**.
11. Click **Find Centerburst**.
12. Go to **Collect > Step Scan >PM-IRRAS DSP(3)** and set the parameters as:

(a) PM-IRRAS DSP(3)

- Linear Dichroism (Signal at 74KHz)
- Sample Modulation Frequency = 50 Hz
- Modulation Amplitude = 1 λ
- Delay After Step (ms) = 55
- PEM Frequency in Hz = Set to equal the 2F frequency displayed on PEM controller (may need to be calculated)
- Save Raw Data, Starting Step = 75
- Save Raw Data, Total Step Number = 1

(b) Electronics:

- Speed = Grayed Out
- UDR = 4
- Filter = Grayed Out
- Resolution = 8 cm^{-1}
- Sensitivity = 1
- Scans to Co-add = 1

(c) Optics:

- Source = Mid-IR
- Beam Path = Right
- Detector = Ext. 1
- Aperture = 2 cm^{-1}
- Attenuator = 50%

(d) Advanced:

- Interferogram Symmetry = Asymmetric

13. The switches on the DSP3 Filter Box should be set as follows:
    - Filter = IN
    - Frequency = 74 kHz
14. Now do a Setup from PM-IRRAS DSP(3) window. Click on the **DSP Calibrate** button. When the calibration is complete click **OK**.
15. Click **Scan**.
16. When the scan is complete look at Spectrum 1 and 5. Both should be strong interferograms. If either interferogram is weak, or only noise, then the actual PEM frequency must be calculated.
17. To calculate the PEM frequency, select Spectrum 11. Go to **Transforms>Fourier Transforms**. A Compute window will open. On the **General** tab select **Apodization Function = Triangular, Zero Filling Factor = AUTO**. On the **Advanced** tab select **Use Standard Processing**. Click **OK**.
18. In the resulting spectrum there should be a strong peak at approx. 0.41 as shown in Figure 8. Multiply the peak location by 28571. Subtract this product from 85714. This result is the actual frequency of the PEM. Enter this value for the 'PEM Frequency in Hz' parameter and then click **Scan** again. This value may be different than the value on the PEM controller display. Note the difference between the calculated value and the displayed value. This difference will be constant.

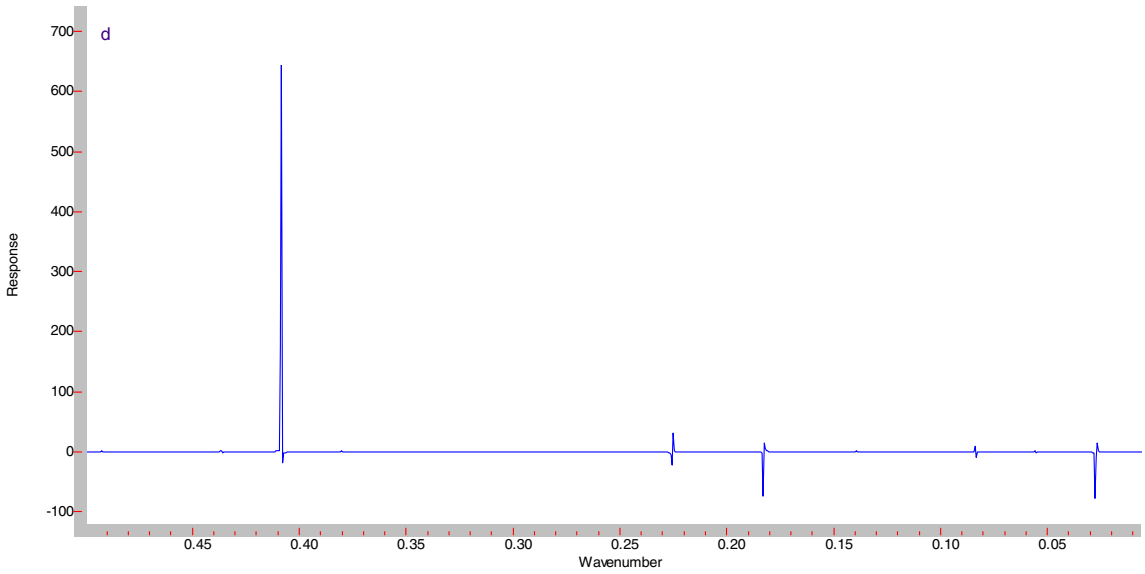

Figure 8. Spectrum 11

19. When the scan is complete select Spectrum 1 and Spectrum 5. Go to **Transforms>Fourier Transforms**. Set **Apodization Function = TRIANGULAR and set Zero Filling factor = 4** and then click **OK** to compute the interferograms. Spectrum 5 should look similar to Figure 9.

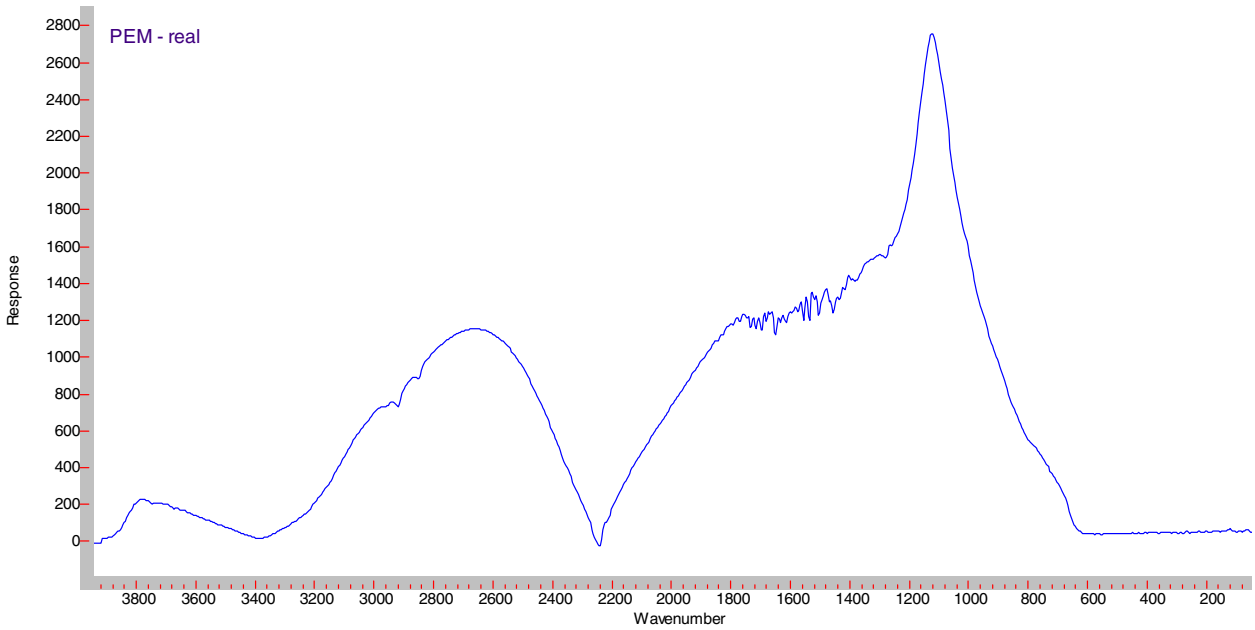

Figure 9. Spectrum 5

20. Now select Spectrum 5 and go to **Transforms>Spectral Calculator>Paired Spectra**. A Spectral Arithmetic: Paired Spectra Operations dialogue opens. Select **{/} Divide by Reference**. Select **Use Current** and then select **1. Phase Modulation – Real** from the list of spectra in the bottom right-hand corner. Click **Replace**.
21. Zoom in on Spectrum 5 between approx 1500-900 cm^{-1}. The spectrum should look similar to Figure 10 with a large broad peak at ~ 1110 cm^{-1} and a weaker peak at ~1265 cm^{-1}.

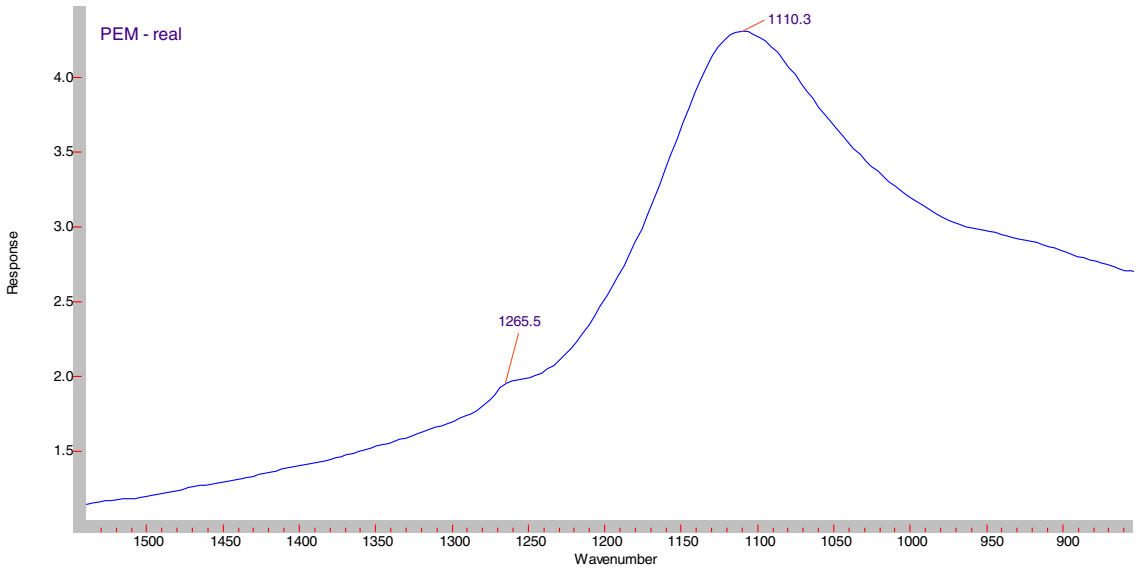

Figure 10. Ratio of spectrum 5 to spectrum 1

4. Maintenance

This chapter includes maintenance procedures for the Photo-Elastic Modulator Infrared Reflection Absorption Spectroscopy Accessory (PEM-IRRAS) that may be carried out by an operator. Any maintenance procedures not specifically mentioned in this chapter or in the online Help should be carried out only by Varian-trained, Varian-qualified or Varian-authorized Customer Service Representative (CSR).

Warning – Shock Hazard
This accessory contains electrical circuits, devices, and components operating at dangerous voltages. Contact with these circuits, devices and components can cause death, serious injury, or painful electrical shock. Always follow the procedures described by Varian, Inc.

4.1 Cleaning

Any spills on the PEM-IRRAS should be wiped up immediately.

The **exterior** surfaces of the PEM-IRRAS should be kept clean. All cleaning should be done with a soft cloth. If necessary, this cloth can be dampened with water or a mild detergent. Do not use organic solvents or abrasive cleaning agents.

4.2 Fuses

The only user-accessible fuse in the PEM-IRRAS is the mains inlet fuse for the PEM controller. Refer to the PEM-100™ User Manual for details. Always turn power off and remove the power cord before replacing fuses. Fuses should be replaced only with the same type and rated fuses as specified on the rear of the controller.

Warning – Shock Hazard, Fire Hazard
This accessory contains electrical circuits, devices, and components operating at dangerous voltages. Contact with these circuits, devices and components can cause death, serious injury, or painful electrical shock. To prevent reduced safety protection or unwanted fusing, ALWAYS ensure that fuses are only replaced with fuses of the correct type and rating.

To check a fuse:

1. Disconnect the instrument from the mains power supply.
2. Remove the fuse holder from the IEC mains power inlet connector with a small flat blade screwdriver.
3. Check that the fuse is the correct type and is not damaged. If necessary, replace the fuse.
4. Fit the fuse holder back into the IEC mains power inlet connector.
5. Reconnect the instrument to the mains power supply.

Note If a fuse blows repeatedly, it may indicate other problems with the accessory. A service call may be required.

4.3 Spare Parts

For information regarding spare parts and their part numbers please refer to the Varian, Inc. Web site found at:

www.varianinc.com.