

# The Effect of Elevated Temperature on Single Reflection Germanium FTIR-ATR Spectroscopy

JOSEPH P. LUCANIA  
HARRICK SCIENTIFIC PRODUCTS, INC., BOX 277, PLEASANTVILLE NY 10570

ALI KOCAK  
JOHN JAY COLLEGE OF CRIMINAL JUSTICE, 445 WEST 59TH STREET, NEW YORK, NY 10019

POSTER PAPER NO. 1870-3P; NEW DEVELOPMENTS IN ANALYTICAL INSTRUMENTATION AND SOFTWARE;  
PRESENTED AT THE 2011 PITCON, GEORGIA WORLD CONGRESS CENTER, ATLANTA, GA, MARCH 13, 2011.



Figure 1. RangeIR™.

## OBJECTIVE

This paper investigates the effects that elevated temperature has on analyses employing the single reflection germanium FTIR-ATR technique.

## ABSTRACT

Germanium is a common optical material for both transmission and internal reflection spectroscopy in the mid-infrared, where it is used for windows and ATR elements, respectively. It is particularly valued in ATR spectroscopy for its wide spectral range, chemical resistivity, and high refractive index. This latter property is of particular use in two areas. First, there is a special configuration, grazing angle ATR spectroscopy, in which it is the material of choice for the analysis of monolayers on silicon and metal substrates. Second, there is a general application in avoiding dispersion effects when obtaining spectra on substances with intense absorbance bands. One drawback of germanium, however, is its increased opacity at elevated temperatures. It is common practice to avoid its use at temperatures over 100 °C. However, few, if any examples of the actual effects on the performance of a real accessory have been presented. In this work, a temperature-controllable 45° single reflection Ge ATR accessory, along with a suitable organic liquid sample, is used to demonstrate the effects on throughput, sensitivity, and noise of increased temperature. It is expected that the loss in throughput which accompanies increased temperature will cause an increase in noise. Since the refractive index of germanium increases with increasing temperature, a concomitant decrease in sensitivity is expected. The increase in noise and decrease in signal will both contribute to a significant decrease in the signal-to-noise ratio. As these quantities will be studied as a function of

temperature, the effects on a system which is not temperature-controlled will become apparent. On the other hand, certain areas of the mid-infrared may be less affected by limited temperature increases and remain useful under those conditions.

## EXPERIMENTAL

### *Spectrometer*

All spectra were taken with a Thermo/Nicolet Nexus™ 670 FTIR spectrometer equipped with a DTGS detector and a standard KBr mid-IR beamsplitter and using Thermo/Nicolet Omnic™ Version 6.1 software. All spectra were run at 4000 to 400  $\text{cm}^{-1}$ , using a velocity of 0.6329  $\text{cms}^{-1}$ , Happ-Genzel apodization, Mertz phase correction, and no zero filling. The aperture was set to 100 (fully open). The gain was set to 1 for throughput spectra and for spectra taken using a ZnSe ATR element and to 4 for all others. The resolution was set to 4  $\text{cm}^{-1}$ . Spectra were derived from 64 co-added scans. For all throughput spectra, one background spectrum of the open sample compartment, at room temperature, was taken. For all other spectra, the background spectrum was taken prior to each sample spectrum using the ATR accessory without any sample on the ATR element and at the same temperature used for the sample spectrum. The purge inputs of the spectrometer and the installed accessory were connected to filtered air (water and carbon dioxide removed) produced by a Parker Balston Model 75-62 FT-IR Purge Gas Generator at 30 SCFH.

Spectra taken for noise and sensitivity tests were converted to absorbance units using the Omnic™ “Absorb” function. Spectra taken for sensitivity tests were also baseline corrected using the Omnic™ “Aut Bsln” function and then peak maxima and associated wavelengths were found using the Omnic™ “Analyze Find Peaks” function.

### *Accessory*

The Harrick RangeIR™ (RAN-M-NI8) 45° single reflection ATR accessory (Figure 1) was installed in

the sample compartment of the FTIR spectrometer for obtaining spectra. This accessory allows direct temperature control of the ATR element. The two standard 50 W heaters were replaced with two 30 W heaters (Item No. HS12-1; Hotwatt Inc.; Danvers, MA), wired in parallel, to achieve better control at lower temperatures. The tip of the K-type thermocouple contacts the ATR element. The standard anti-reflection coated ATR element (FAS-ATR-M), composed of ZnSe, was replaced with the mechanically identical germanium component (FAS-ATR-J). The germanium ATR element is not anti-reflection coated. The ATR thermocouple and heaters were connected to the Harrick Automatic Temperature Controller (ATC-024-3). All alignments of the accessory were performed at room temperature. For throughput, noise, and sensitivity tests, temperatures were varied from ambient to 180°C, in 20°C intervals. (The maximum temperature specified for the accessory is 200°C.) A temperature controller “autotune” was performed at 60°C, using an autotune set point percentage of 100. A subset of the tests performed using the Ge ATR element were repeated using the ZnSe element for comparison purposes.

### *Sample*

Extra light olive oil (Bertolli brand; distributed by American Rice, Inc.; Houston, TX) was chosen as the test sample for this work. This liquid is non-toxic, has a high smoke point (242 °C),<sup>1</sup> provides a rich mid-infrared spectrum, has low volatility, does not have a noxious or strong odor, is readily cleaned with common organic solvents, and is readily available. The sample was heated to approximately the same temperature as the ATR element before being placed on the ATR element to avoid thermal shock to the element and to reduce the time necessary for the system to come to thermal equilibrium. This was accomplished by placing approximately 20 ml of the sample in a flat-bottomed metal dish (bottom of 1 oz. shallow tin; Item No. CSB712010-EC; Ball Aerosol & Specialty Container; Baltimore, MD) and then heating the sample and dish

on a hot plate. The hot plate consists of a 110 mm diameter x 16 mm thick aluminum disk attached to a 116 mm diameter x 33 mm Teflon™ insulating disk. The aluminum disk has four 100 W cartridge heaters (Harrick Item No. HTRS-24) wired in parallel and a 150 mm long K type thermocouple (Harrick Item No. 008-144). The temperature was then controlled using a Harrick Automatic Temperature Controller (Harrick Item ATC-024-1). The actual temperature of the olive oil in the metal dish was monitored to assure that its temperature was at the desired level.

Methyl ethyl ketone (Item No. 4331002; Hubbard-Hall Inc., Waterbury, CT; [www.hubbardhall.com](http://www.hubbardhall.com)) and cotton-tipped applicators (Item No. 758CH016; Technistat; Worcester, PA; [www.technitool.com](http://www.technitool.com)) were used for cleaning the ATR element. As this solvent has a boiling point of 79.6°C,<sup>2</sup> the heated ATR element was allowed to cool to below 60°C before cleaning.

## RESULTS AND DISCUSSION

### Throughput

Figure 2 presents a summary of the results of raising the temperature from room temperature (24°C) to 180°C, in 20°C increments. At shorter wavelengths, a roughly linear reduction in throughput is observed. At longer wavelengths, the reduction is nonlinear and more aggressive. The curves shown in Figure 2 suggest that the behavior of the system is similar in the 4000 to 2000  $\text{cm}^{-1}$  range. At longer wavelengths, the reduction in throughput with temperature is more severe. At wavenumbers less than 900  $\text{cm}^{-1}$ , the throughput at room temperature starts to decline and is essentially 0% at 550  $\text{cm}^{-1}$ . In this region of 900 to 550  $\text{cm}^{-1}$ , the effect of increased temperature is even more profound, as the throughput at room temperature already starts at a

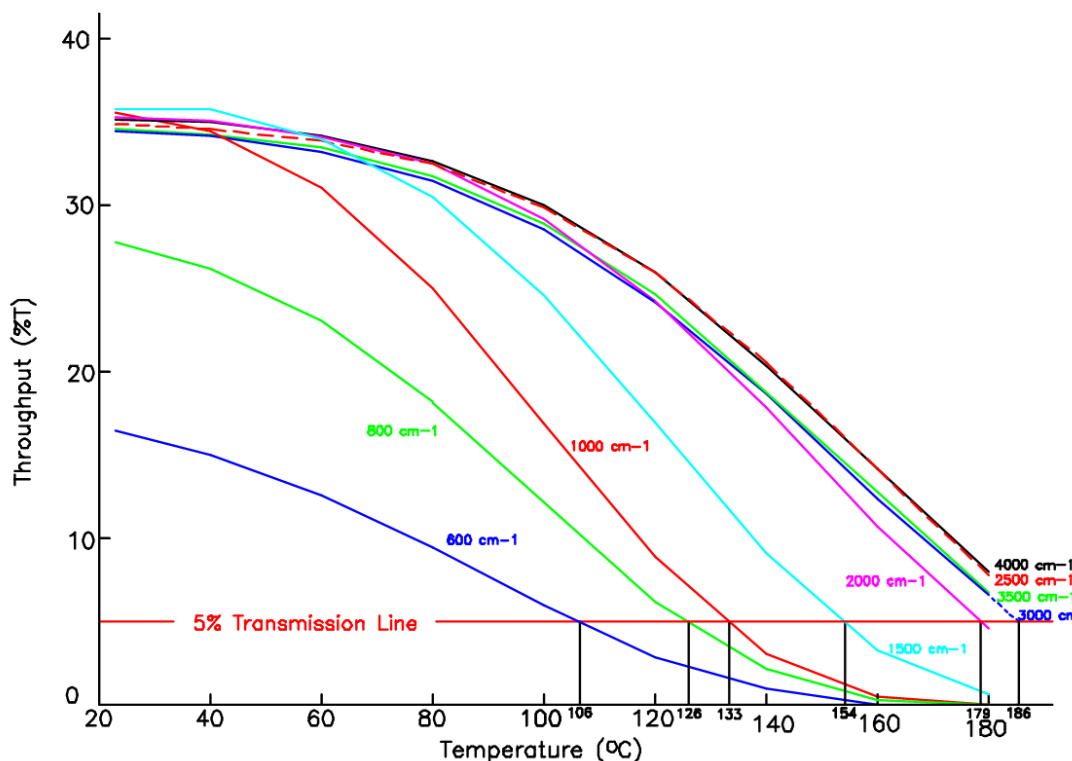


Figure 2. Throughput vs. Temperature at Nine Wavelengths

## HARRICK SCIENTIFIC PRODUCTS, INC.

141 Tompkins Avenue, 2nd Floor, PO Box 277  
Pleasantville, New York 10570

[www.harricksci.com](http://www.harricksci.com) | [info@harricksci.com](mailto:info@harricksci.com)

International: 1-914-747-7202 | USA: 800-248-3847

Fax: 914-747-7209

diminished level. Even at lower temperatures (80°C or less) and shorter wavelengths, definite small losses in throughput are observed as the temperature is increased. In all cases, when the accessory returns to room temperature, the initial throughput curve is restored. That is, any loss in throughput due to increased temperature is reversed when the temperature is lowered. Increased oxidation at elevated temperatures was not observed, but remains a possibility with long-term, elevated-temperature use. A limited comparison run with ZnSe as the ATR material shows essentially no loss in throughput when the temperature is raised from 24 to 120°C.

If one arbitrarily establishes the useful spectral window as that wavelength range in which the throughput is at least 5%, then the full wavelength range of 4000 to 600  $\text{cm}^{-1}$  is available to 106°C. A limited wavelength range of 4000 to 2000  $\text{cm}^{-1}$  is available to 179°C. Maximum long wavelengths for these and intermediate temperatures are summarized in Table 1.

The loss in throughput is attributed mainly to an increase in the opacity of the Ge material itself.<sup>3</sup> There also appears to be a contributor to this loss from an increase in the refractive index, to be discussed later in this report. Increases in the refractive index increase the reflection losses at the input and output faces of the ATR element.

### Baseline

The throughput results summarized above indicate that for Ge it is essential that the background and sample spectra be generated at the same temperature. As an example, Figure 2 shows a 100% T line in which the background was taken at 60°C and the sample was taken at 100°C. Note the relatively flat area at shorter wavelengths and the sloping dip at longer wavelengths. It would prove difficult to accurately baseline correct superimposed sample peaks in the latter region. Mirror image results to Figure 3 would be generated in the case where the background spectrum was taken at a higher tem-

TEMPERATURE (°C)	WAVELENGTH (CM <sup>-1</sup> )
106	600
126	800
133	1000
154	1500
179	2000
(186)*	(3000)*

Table 1. Maximum Wavelength at Various Temperatures  
\*extrapolated

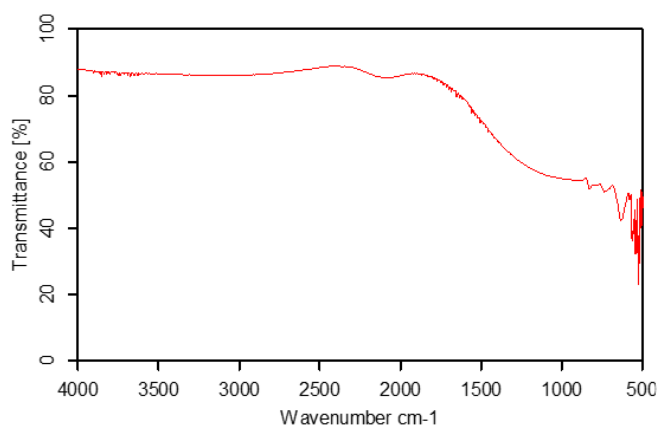


Figure 3. 100% Transmission Line with Sample Spectrum Taken at 100 °C and Background Spectrum Taken at 60°C.

perature than the sample spectrum. In this case, all %T values would be greater than 100. Figure 3 also illustrates another result of temperature differences between background and sample spectra. Uncompensated spectral structures of Ge at longer wavelengths can be erroneously interpreted as sample peaks.

Since the accessory is typically aligned at room temperature, and some small misalignment might be expected at alternate temperatures, it is good practice, in any case, to take the background and sample spectra at the same temperature for any ATR configuration.

*Noise*

One hundred percent transmission spectra were taken at room temperature and at 40 to 180 °C, at 20 °C intervals. In each case, the sample and background spectra were obtained at the same temperature. Five areas were chosen in the transmission spectra that are relatively free of artifacts from water or carbon dioxide: 3300 to 3200  $\text{cm}^{-1}$  (region 1), 2950 to 2850  $\text{cm}^{-1}$  (region 2), 2200 to 2100  $\text{cm}^{-1}$  (region 3), 1200 to 1100  $\text{cm}^{-1}$  (region 4), and 900 to 800  $\text{cm}^{-1}$  (region 5). For each area at each temperature, the peak-to-peak noise levels (in absorbance units) were determined. These are summarized in Table 2.

More data would have to be accumulated to offer exact quantitative conclusions. However, it appears from the data that was acquired that noise levels exceed 1 mA starting at 120°C for region 5 and at 140°C for region 4. The increases in noise levels are caused by the decreased throughputs at elevated temperatures.

The noise data was taken using 64 scans for the sample and background spectra and lower noise levels would be expected if a larger number of scans were used. So, for example, the noise level in region 5 at 140°C could be reduced from 3.26 mA to 1.63 mA, a factor of one-half, by increasing the number of scans by four times from 64 to 256. The number of scans required to get comparable performance in region 5 at 160°C and in regions 4 and 5 at 180°C, however, would be impractical. An alternate scheme that would significantly reduce apparent noise and analysis time would be to reduce the resolution from 4 to 8  $\text{cm}^{-1}$ . Not all applications can tolerate this approach, however.

*Sensitivity*

Spectra of the olive oil sample were taken at room temperature and at 40 to 180°C, at 20°C intervals. In each case, the sample and background spectra were obtained at the same temperature. The five peaks chosen for data analysis are shown, with their

TEMPERATURE (°C)	PEAK-TO-PEAK NOISE (MA)				
	3300-3200 CM <sup>-1</sup>	2950-2850 CM <sup>-1</sup>	2200-2100 CM <sup>-1</sup>	1200-1100 CM <sup>-1</sup>	900 - 800 CM <sup>-1</sup>
24	0.19	0.10	0.09	0.12	0.32
40	0.14	0.12	0.12	0.16	0.78
60	0.12	0.11	0.14	0.24	0.65
80	0.13	0.09	0.12	0.27	0.56
100	0.15	0.12	0.18	0.55	0.98
120	0.17	0.16	0.33	0.72	1.86
140	0.31	0.25	0.22	1.60	3.26
160	0.36	0.32	0.72	7.88	26.2
180	0.81	0.54	0.81	98.8	244

Table 2. Effect of Increased Temperature on Noise.

assignments,<sup>4</sup> in Table 3. To determine peak heights and exact positions, peaks 1 and 2 were isolated in the 3200 to 2600  $\text{cm}^{-1}$  region, peak 3 was isolated in the 1900 to 1600  $\text{cm}^{-1}$  region, and peaks 4 and 5 were isolated in the 1600 to 900  $\text{cm}^{-1}$  region. Each region was converted to absorbance units, baseline corrected, and processed for peak identification, as previously described in the Experimental section. Exact wavelength positions in wavenumbers to the second decimal place as well as intensities in absorbance units to the fourth decimal place were recorded.

Peak heights were then normalized with respect to the peaks obtained at room temperature. The results are presented in Table 3. Significant decreases in sensitivity are observed. For the peaks at 2924, 2854, and 1745  $\text{cm}^{-1}$ , peak heights are reduced at 180°C to 0.55 to 0.65 of their values at room temperature. Peaks at 1465 and 1162  $\text{cm}^{-1}$  show similar declines at lower temperatures.

The change in the refractive index of germanium with temperature,  $dn/dt$ , is positive.<sup>5</sup> Examination of the formula for the depth of penetration,  $d_p$ ,<sup>6</sup> shows that as the refractive index of the ATR element increases,  $d_p$  (and hence, sensitivity) decreases. It is difficult to obtain readily usable  $dn/dt$  values for Ge as many references<sup>7,8</sup> give values only at short wavelengths or lower temperatures. From one reference<sup>9</sup>, an approximation for  $dn/dt$  of  $5 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  can be made. Three superior references<sup>10-12</sup> provide a value of  $3.96 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ . At 2924  $\text{cm}^{-1}$  the room temperature refractive index for Ge is 4.03.<sup>3</sup> The refractive index of Ge at 180°C would then be 4.09. Using the room temperature (and visible light) refractive index of olive oil of 1.47,<sup>13</sup> the values of  $d_p$  can be calculated for the peak at 2924  $\text{cm}^{-1}$  at room temperature and at 180°C. They show a reduction in sensitivity to only 0.98 of the room temperature value in going to 180°C. The observed change, however, is 0.65. From this, it appears that although there is some effect, it is small compared to actual results.

It is believed that this loss in sensitivity is mainly a property of the sample itself.<sup>14-16</sup> (Similar decreases

PEAK NUMBER	ROOM TEMPERATURE WAVELENGTH ( $\text{CM}^{-1}$ )	ASSIGNMENT
1	2924	C-H STRETCH
2	2854	C-H STRETCH
3	1745	C=O
4	1465	CH <sub>3</sub> BEND
5	1162	C-O STRETCH

Table 3. Olive Oil Peaks Used for Sensitivity Tests.

in sensitivity are observed when ZnSe is substituted for Ge as the ATR material.) If the refractive index of the sample itself decreases with increased temperature, the formula for  $d_p$  shows that a decrease in sensitivity would also take place. Perhaps this is part of the answer. In any case, the increase in noise is further aggravated by the decrease in signal, as discussed in the following section.

#### Signal-to-Noise

The absorbance peak height levels obtained during sensitivity testing were divided by corresponding absorbance noise levels obtained in noise testing to obtain signal-to-noise (S/N) ratios for the peaks at 2924, 2854, and 1162  $\text{cm}^{-1}$ . These values are shown in Figure 5. If an S/N value of 50 is chosen as an arbitrary low limit for valid results, then the 2924  $\text{cm}^{-1}$  peak can be used quantitatively to 180°C, the 2854  $\text{cm}^{-1}$  peak to 140°C, and the 1162  $\text{cm}^{-1}$  peak to only 80°C. From a practical standpoint, it becomes difficult to distinguish peaks and determine peak heights and positions when S/N falls below 20. Some scatter in the lower temperature data for the 2924 and 2854  $\text{cm}^{-1}$  peaks, shown in Figure 5, is attributed to errors in determining exact low noise levels.

Comparisons with similar results obtained for ZnSe show significantly greater peak heights and

lower noise levels, so that S/N values exceed 1000 up to 120 °C. The higher sensitivity is attributed to the refractive index of 2.4 which is considerably smaller than that of Ge, 4.0. Lower noise levels for ZnSe are attributed to higher throughput, gained via an anti-reflection coating.

### Wavelength Shift

For the peaks at 2924, 2854, and 1745  $\text{cm}^{-1}$ , the peak locations shift approximately 2  $\text{cm}^{-1}$  over the usable temperature range, when compared to peak locations at ambient temperature. The peaks at 1465 and 1162  $\text{cm}^{-1}$  shift approximately -3 to -7  $\text{cm}^{-1}$ . This behavior is believed to be related to the sample rather than the germanium material, as similar behavior, with the same sample, is noted when zinc selenide is used as the ATR material. The breakdown in hydrogen bonding with increased temperature has been noted as a cause for the positive shifts.<sup>15</sup> Relative intensity changes in overlapped bands is the probable cause for the negative shifts.<sup>17</sup>

### CONCLUSION

Common knowledge advising against the use of germanium in the mid-infrared region at elevated temperatures is misleading and contradictory. Four references<sup>18-21</sup> give 100°C as the maximum operating temperature and state that germanium becomes opaque at higher temperatures. (Fifth<sup>22</sup> and sixth<sup>23</sup> references place the limit at 125 and 190°C, respectively.) A seventh reference<sup>24</sup> states that “germanium is very temperature sensitive and thus is unstable in most processing environments.” The implications are that under 100 °C, temperature control is not required and that over 100 °C, no operation is possible. Yet the data presented in this report indicate that decreases in throughput can be observed at temperatures as low as 40°C. From this point onward, good temperature control is required to assure that background and sample spectra are acquired at the same temperature. With such control, useful spectra can be obtained, with certain

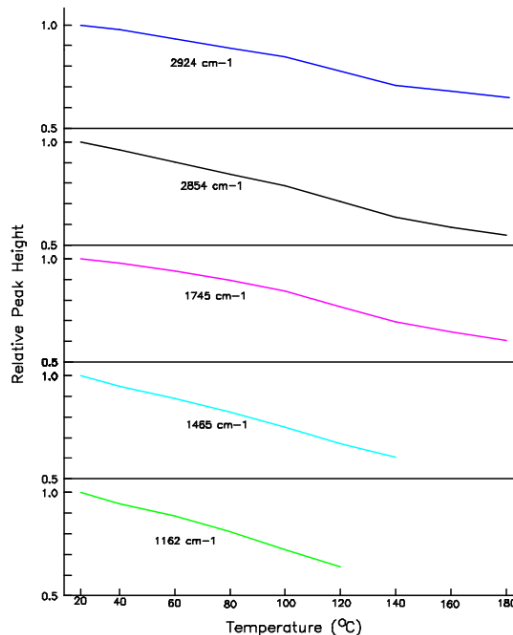


Figure 4. Relative Peak Height vs. Temperature for Five Olive Oil Peaks.

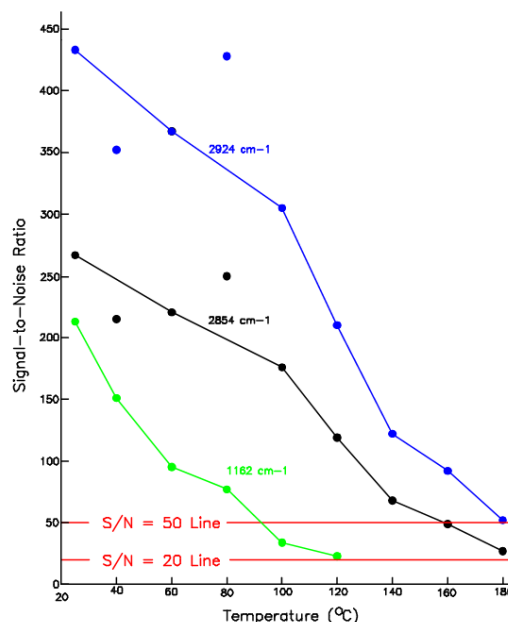


Figure 5. Signal-to-Noise Ratio vs. Temperature for Three Olive Oil Peaks.

limitations, up to at least 180°C. A spectrum of olive oil, taken at 160°C, is shown in Figure 6.

It is possible that the erroneous 100°C limit is derived from a figure presented in the 1959 Willow Run report.<sup>3</sup> This shows a series of transmission curves for a 1.15 mm Ge window in the 2 to 8.5  $\mu$  range at temperatures of 25 to 300°C. The 25 and 100°C curves are nearly superimposed. The limits of 125 and 190°C are less easily explained as the Willow Run curves show some transmission even at 300°C in the 2 to 6  $\mu$  range.

Increasing the temperature has been shown to reduce throughput, increase noise, decrease sensitivity, decrease signal-to-noise, and decrease wavelength range, although it is probable that the decrease in sensitivity is mainly sample related. Yet the existing equipment is certainly capable of collecting useful spectra at higher temperatures. If one assumes that 5% transmission at 3000  $\text{cm}^{-1}$  is a minimum requirement, an extrapolation in Figure 2 shows that this equipment and methodology will be adequate to 186°C. The pathlength of light through the Ge ATR element is approximately 38 mm. Using a smaller ATR element would improve performance as would the use of an anti-reflection coating on the input and output faces of the element. This coating would sustain temperatures up to 250°C.<sup>25</sup> Increasing the number of scans from 64 to 256 would double the S/N, allowing lower acceptable throughput values. These improvements should extend the range for Ge to the 200 to 250 °C region.

The degradation in performance with increasing temperature begs two questions. First, “Will the performance of Ge be enhanced at sub-ambient temperatures, say 0 or even -196 °C?” Certainly decreases in the refractive index on the order of 0.05 would be expected in going from room temperature to liquid nitrogen temperature.<sup>7</sup> Such decreases would lower reflection losses and increase sensitivity. Data in the critical area where wavelengths exceed 10  $\mu$ , however, could not be found, so that it would remain for further experimentation to answer

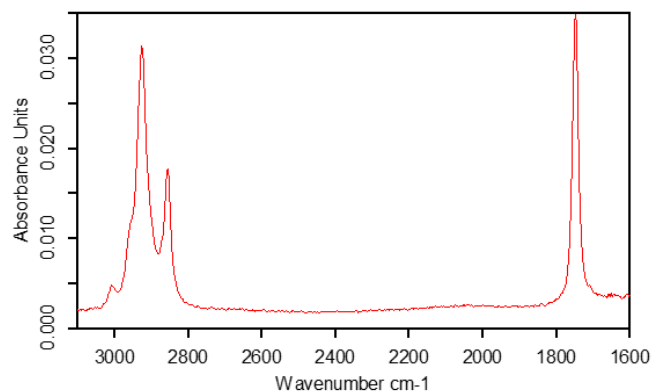


Figure 6. Spectrum of Olive Oil at 160°C.

the question fully. Second, “Do other ATR materials also exhibit reduced performance at elevated temperatures?” Some preliminary work, recently conducted in this laboratory, indicates such degradation occurs for diamond. Further work would be required to quantify the effect and to compare diamond with germanium.

## REFERENCES

- <sup>1</sup>Wikipedia, Smoke point. [http://wikipedia.org/wiki/Smoke\\_point](http://wikipedia.org/wiki/Smoke_point). (accessed Oct 6, 2010).
- <sup>2</sup>Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 47<sup>th</sup> ed.; Chemical Rubber Company: Cleveland, OH, 1966; p C-230.
- <sup>3</sup>Ballard, S. S.; McCarthy, K. A.; Wolfe, W. L. *Optical Materials for Infrared Instrumentation, Report Number 2389-11-S IRIA*; The University of Michigan Willow Run Laboratories: Ann Arbor, MI, 1959; pp 50-51.
- <sup>4</sup>Yunus, W. M. M.; Fen, Y. W.; Yee, L. M. *Am. J. Applied Sci.* 2009, 6 (2), 328-331.
- <sup>5</sup>Ballard, S. S.; McCarthy, K. A.; Wolfe, W. L. *Optical Materials for Infrared Instrumentation Supplement, Report Number 2389-11-S<sub>1</sub>*; Infrared Laboratory, Institute of Science and Technology, The University of Michigan: Ann Arbor, MI, 1961; p 8.
- <sup>6</sup>Harrick, N. J. *Internal Reflection Spectroscopy*; Harrick Scientific Corporation: Ossining, NY,



- 1987; pp 30-32.
- <sup>7</sup>Rank, D. H.; Bennett, H. E. *J. Opt. Soc. Am.* 1954, *44* (1), 13-16.
- <sup>8</sup>Frey, B. J.; Leviton, D. B.; Madison, T. J. *Proc. SPIE* 2006, *6273* 62732J.
- <sup>9</sup>Lukes, F. *Czech. J. Phys.* 1960, *10* (10), 742-748.
- <sup>10</sup>Icenogle, H. W.; Platt, B. C.; Wolfe, W. L. *Appl. Optics* 1976, *15* (10), 2348-2351.
- <sup>11</sup>Crystran, Ltd. Materials, Germanium (Ge). <http://www.crystran.co.uk/germanium-ge.htm> (accessed Oct 21, 2010).
- <sup>12</sup>Hawkins, G. J.; Sherwood, R. E.; Djotni, K. *Proc. SPIE* 2008, *7101*, 710114.
- <sup>13</sup>United Nations Conference on Trade and Development (UNCTAD), Market Information in the Commodities Area, Codex Standard for Olive Oil, Virgin and Refined, and for Refined Olive-Pomace Oil, Codex Stan 33-1981 (Rev.1-1989), p26. [http://www.unctad.org/infocomm/anglais/olive/doc/Cxs\\_033e.pdf](http://www.unctad.org/infocomm/anglais/olive/doc/Cxs_033e.pdf) (accessed Oct 6, 2010).
- <sup>14</sup>Remspec Corporation, Process Monitoring: Crystallization. [http://www.remspec.com/pdfs/Remspec\\_Crystallization.pdf](http://www.remspec.com/pdfs/Remspec_Crystallization.pdf) (accessed Oct 15, 2010).
- <sup>15</sup>Stuart, B. H. *Infrared Spectroscopy: Fundamentals and Applications*; Wiley: West Sussex, England, 2004; pp 50-51, 128-129, 139-140.
- <sup>16</sup>Agulyanskii, A. I.; Zalkind, O. A.; Masloboev, V. A. *J. Appl. Spectrosc.* 1983, *39* (6), 1408-1411.
- <sup>17</sup>Ryu, S. R.; Noda, I.; Jung, Y. M. *Appl. Spectrosc.* 2010, *64* (9), 1017-1021.
- <sup>18</sup>Harrick Scientific Products, Inc., RangeIR™ Liquid Analyzer. <http://www.harricksci.com/ftir/accessories/group/RangeIR%E2%84%A2-Liquid-Analyzer> (accessed Jan 14, 2011).
- <sup>19</sup>Harrick Scientific Products, Inc., MVP-Pro Star™ Diamond ATR Accessory. <http://www.harricksci.com/ftir/accessories/group/MVP-Pro%E2%84%A2-Star-Diamond-ATR-Accessory> (accessed Jan 14, 2011).
- <sup>20</sup>Griffiths, P. R.; de Haseth, J. A. *Fourier Transform Infrared Spectrometry*, 2<sup>nd</sup> ed.; Wiley: Hoboken, NJ, 2007; p 252.
- <sup>21</sup>Vidrine, D. W. Thermal properties of transmissive optical materials. <http://www.vidrine.com/iropmat4.htm> (accessed Oct 6, 2010).
- <sup>22</sup>Harrick Scientific Products, Inc., Germanium Optical Material Information. [http://www.harricksci.com/sites/default/files/pdf/optical\\_materials/optical\\_materials\\_germanium.pdf](http://www.harricksci.com/sites/default/files/pdf/optical_materials/optical_materials_germanium.pdf) (accessed Jan 14, 2010).
- <sup>23</sup>Specac Limited, Optical Materials for Spectroscopy. <http://www.specac.com/optical-materials-for-spectroscopy> (accessed Oct 8, 2010).
- <sup>24</sup>Wilks, P. A. Process Monitoring Applications of Multiple Internal Reflection Spectroscopy. In *Internal Reflection Spectroscopy, Theory and Applications*; Mirabella, F. M., Ed.; Marcel Dekker: New York, 1993; p 106.
- <sup>25</sup>Private email correspondence with Lambda Research Optics, Costa Mesa, CA (Sept 24, 2010).