Taking the Spectroscopy of Fluids Beyond the Limits

Advances in Sampling at High Temperatures and Pressures

VALENTINE J. ROSSITER

Good summer, gentle readers! What a surprise — it is hot and humid near the nation's capital! Life is slower now that school is out and I can enjoy a cool lemonade in a hammock (although a glass would hold the liquid better).

In any case, as the heat increases, so does the pressure from my editor to produce a column — so I thought this month's offering would be appropriate. Guest author Valentine Rossiter has described a rather interesting cell for liquids that operates to extremes of temperature and pressure. Rossiter is president of Aabspec Instrumentation, 3375 Park Avenue, Wantagh, NY 11793-3712. He can be reached directly from the United States and Canada at (800) 783-9380, fax: (800) 781-4934.

Loss of mechanical strength in optical window materials is a limiting problem under extreme conditions, but Rossiter describes solutions using the cell with samples such as jet fuel and lauric acid. He presents data from FT-IR investigations, but the cell has potential for use in all types of optical spectroscopy. I could see the range of sampling open up a little more and thought I would share this gem with you. Enjoy!

Emil W. Ciurczak
Contributing editor

An earlier series of developments concerned with high-temperature spectroscopic cells for solids had proved to be very successful (1,2). Designs had evolved to provide a very wide temperature range — from −170 to 700 °C, now extended to 950 °C (3) — combined with a very wide pressure range (high vacuum to 2000 psig). The design also provided a variety of optical techniques including transmission, specular reflectance, large angle reflectance infrared (LARI), sample irradiation with UV, Raman, and emission spectroscopy (2). These optical modes also were available over a very wide temperature and pressure range. The resulting cell designs have since found applications in such areas as polymer research, coatings, catalysts, superconductors, and many other research topics.

In the area of liquids research, designs were developed that solved many of the problems in the spectroscopy of liquids (4). These problems included the difficulty caused by the presence of interference fringes in cells with very short path lengths, how to engineer such cells to be pressure tight, how to provide variable path length in cells of high structural integrity, variable temperature, variable pressure, and so forth. But it was still impossible to provide anything approaching the same high temperature plus high pressure experimental facilities for fluids as had been developed for solids with full wavelength range spectroscopy (1,2).

The difficulty is caused by the fundamental difference in the design problem between solid sampling and fluid sampling. In the case of solids, it is possible to heat the solid in a region remote from the optical windows containing the sample environment in the experimental chamber. This still allows control of the atmosphere surrounding the sample. But in the case of a fluid, the retaining window must remain in contact with the sample material when it is at high temperature and high pressure so the window material and the sample material are then at the same temperature. Like all materials, the window material loses mechanical strength as the temperature is increased and its ability to withstand pressure is lost. This is a particularly severe problem with window materials that demonstrate good wide-range transmission in the mid-infrared spectral region. This region (~600 cm^{-1} to 4000 cm^{-1}) is the one widely used in infrared studies of samples with window materials such as ZnS and ZnSe. Such optical materials have limited strength even at room temperature. Loss of strength with increasing temperature is a general problem to materials (2), but with many optical materials, it becomes severely limiting. Even at relatively low elevated temperatures, the loss of strength is severe and unreliable.

Although the earlier development (4) of the liquid cell designs had achieved important technical advances, a critical review of the design was undertaken recently to see if it was possible to simplify the earlier format. This indicated that the fundamental optical design and the consequent complex engineering was necessary. Comparative alternative design studies concluded that simpler (and perhaps less complex) designs of liquid cells would not deliver the needed technical benefits. One change was made to integrate a simple optical unit into the design, rather than having to use an external optical system for beam diversion (4). The arrangement is shown schematically in Figure 1. It was during this redesign exercise that the solution to the fundamental window problem became obvious (5).

DESIGN

As discussed, the retaining, or primary, window of fluid cells is in contact with the fluid and must be at the same temperature and pressure as the fluid. However, consider the situation if the primary window could be supported by external gas

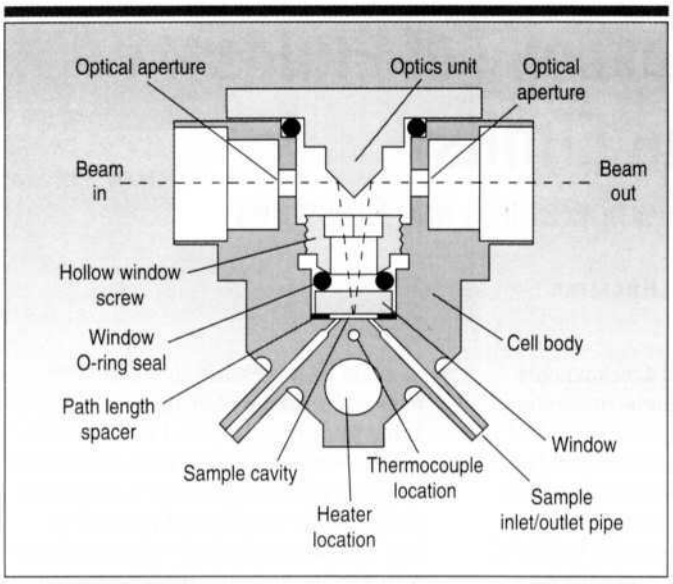

Figure 1. Simplified schematic cross-section of a variable-path-length, variable-temperature transflectance liquid flow cell with integral optics unit (RA4000, Aabspec Instrumentation).

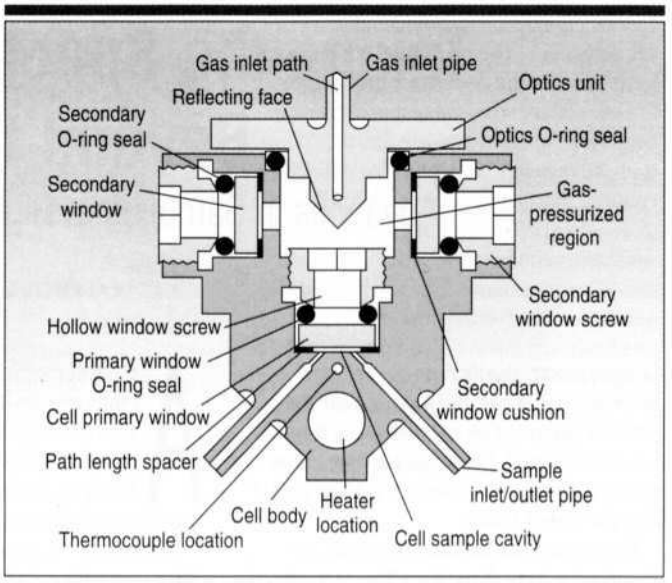

Figure 2. Simplified schematic cross-section of variable-path-length, variable-temperature, high-pressure transflectance fluids cell (RA4000-EXP) incorporating new window technology.

pressure. This external pressure can be used to reduce the pressure differential across the primary window to zero. Under these circumstances, loss of mechanical strength in the primary window becomes irrelevant. Of course, optical access is still required, but this can be through windows that are not at high temperature and so have the mechanical strength to retain the gas pressure. The design is illustrated in Figure 2. This shows how a liquid cell of the earlier type (Figure 1) can be modified to incorporate the deflecting optics unit and the new window technology. The liquid enters through either of the inlet ports into a cavity contained by the primary window. Pressurized gas can be admitted through the port formed in the optics unit. The pressurized gas is contained by an external chamber that incorporates secondary windows. Cooling the location of the secondary windows allows them to operate at their optimal mechanical strength. The gas pressure can be adjusted to match the pressure of the liquid in the cell. In principle, the primary window now needs no significant mechanical strength to retain the liquid that is at high pressure and high temperature. Naturally, the gas-pressurized region should be of low volume, and other appropriate safety features are required for the pressurized gas in the system in addition to the safety requirements for the pressurized sample fluid.

Spin-off benefits. This development in window technology has a number of spin-off benefits. From the spectroscopist's point of view, maintenance and reproducibility of exact cell path length is critical. As a conventional system is pressurized, the window pushes back against the high-pressure seal, increasing the path length in an uncontrolled and nonreproducible way. The exact path length change will depend on factors such as the resilience of the window seals (generally O-rings), which may change with aging. Deformation of the seals or the window as functions of temperature and pressure are among the factors that can cause nonreproducible path length. As system pressure is increased using the new window technology, the external gas pressure can follow the change and the window does not move. Path length is accurately defined and reproducible.

Another benefit is that the method of sealing the primary window can be changed. Because there is no pressure differential, a conventional high-pressure seal is not required. So alternative materials can be used and the system can now operate at temperatures higher and lower than would be possible with conventional sealing methods.

Again, a wider choice of window materials is now available. We can consider using materials that would not be strong enough to be considered for high-pressure systems. We can select on the basis of chemical inertness, for example, irrespective of strength. Again, because of the removal of the strength constraint, windows of much reduced thickness can be used.

The technology can be incorporated into all types of optical cells. It is applicable to all types of optical elements, including windows, optical fibers, and multiple-internal reflectance elements. The spin-off benefits are of such significance that their combined benefits can rival the importance of the discovery of the basic cell technology itself in some applications.

EXPERIMENTAL

Testing jet fuel. The first unit of this type (RA4000-EXP, Aabspec Instruments, Wantagh, NY) was provided to Henk Meuzelaar of the University of Utah's Center for Microanalysis and Reaction Chemistry. The system was supplied with a dual specification. In the standard operating range, the cell provides temperatures to 250 °C at pressures as high as 4000 psig. In the experimental range, temperatures to 450 °C at pressures to 4000 psig are available. Within the standard range, conventional sealing techniques are used for the primary window, while in the experimental range we are exploring new materials and methods with various user groups. The cell's path length is stepwise variable from 0.05 to 2 mm within a single-piece, 316 stainless steel body. No welds, brazes, or joins are used in the body. Connections are by modified Swagelok connectors (Crawford Fitting Company, Solon, OH). Temperature control is provided by a dual-range digital temperature controller

(DTC-2, Aabspec) or programmer (LTP-2A, Aabspec). The cell's dual cooling systems provide the necessary cooling for the secondary window system and have been developed to provide the necessary thermal distribution within the cell. This ensures that the sample-containment region of the cell is at a high temperature while the secondary window region operates at near ambient. The engineering required for optimal thermal distribution in this design of fluids cell is considerable. A temperature read-out location is provided in the cell body, close to the sample cavity. This location accommodates a stainless steel–sheathed thermocouple that monitors real-time sample temperature. Read-out thermocouples can also be introduced directly into the sample through the cell inlet/outlet ports. Figure 3 shows such a cell with the dual-range digital temperature programmer option, which provides a range of thermal programs including controlled cooling rates and subambient temperature operation.

Meuzelaar's research group is interested in a variety of very high temperature and pressure applications. This includes work on supercritical fluid extraction and on the high temperature/high pressure oxidation of jet fuels. The high-temperature cell allows the research group to obtain full mid-range infrared spectra using ZnS windows to greater than 400 °C and 4000 psig. Such a temperature, pressure, and optical combination exceeds anything previously possible. Figure 4 shows preliminary spectra obtained for JP7 jet fuel showing progressive degradation as a function of time under high temperature/high pressure conditions.

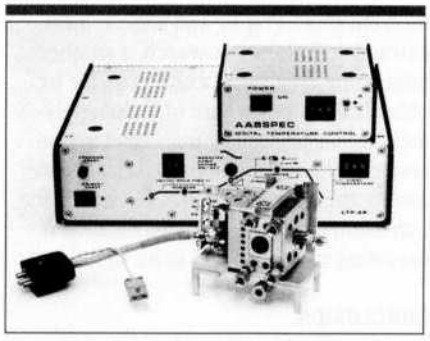

Figure 3. The RA4000-EXP cell shown with the LTP-2A temperature programmer.

Testing fatty acid decomposition. Brian D. Kybett at the Energy Research Unit of the University of Regina (Alberta, Canada) has been using the new technology to examine the thermal decomposition of fatty acids at high pressure. Experiments are being conducted in a carbon tetrachloride medium using the high-temperature cell. The spectrum shown in Figure 5 is that of lauric acid (1% in carbon tetrachloride) at 260 °C and an initial pressure of 900 psig. This full-range spectrum was obtained at 4-wavenumber resolution with 64 scans on a Fourier transform–infrared (FT-IR) spectrometer (FTS40, Bio-Rad, Digilab Division, Cambridge, MA) using the manufacturer's 3200 software. The pressure is allowed to increase during the experiment to 1200 psig and the thermal decomposition can be observed as a function of time. The deconvoluted spectra for the C=O region are shown in Figure 6. The spectra

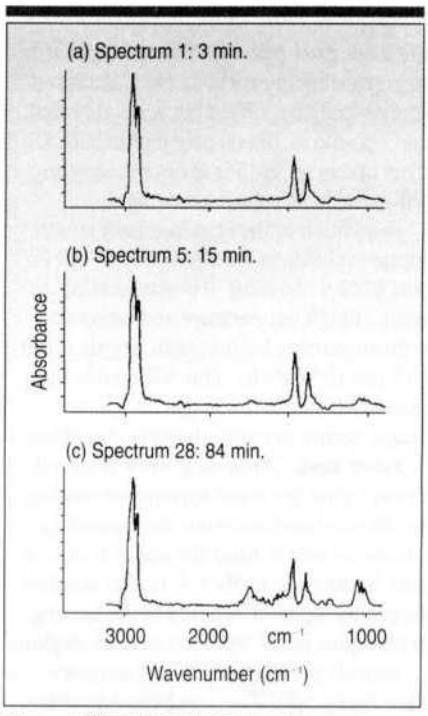

Figure 4. Time-based spectra showing oxidization processes in JP7 jet fuel.

can be interpreted as showing the thermal decomposition of the acid to form ketone and possibly some anhydride; this is subject to further work. The intensities of the ketone C=O stretch at 1810 wavenumbers increase while those of the acid dimers (1720 wavenumbers) and monomers (1760 wavenumbers) decrease.

DISCUSSION

The applications reported here are based on what is effectively transmission spec-

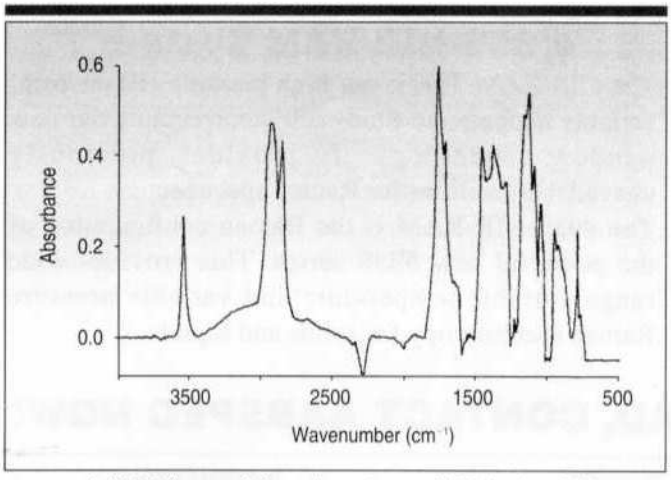

Figure 5. Initial full-range infrared spectrum of 1% lauric acid in carbon tetrachloride at 260 °C and 900 psig. Total scans: 64; resolution: 4 wavenumbers.

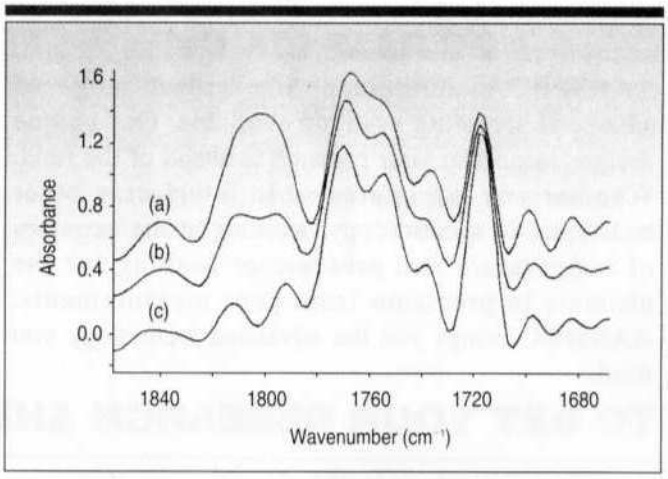

Figure 6. Deconvoluted spectra of lauric acid decomposition (1% solution in carbon tetrachloride) in the C=O region. Total scans: 64; resolution: 4 wavenumbers. Spectrum taken (a) initially; (b) after 10 min.; (c) after 35 min.

troscopy, but other forms of spectroscopy are also made possible. For example, it is now possible to provide a back-scattered Raman cell (BS-RAM-10K, Aabspec) that can operate to 10,000 psig and to 250 °C. This opens up further areas of study and will provide interesting new data.

In addition to the standard path length range available in the RA4000-EXP cell format (0.05 to 2.0 mm), it is also possible to work at high temperature and pressure with an extremely short path length, down to 5 μm (RA-SP-4K). This will enable the system to handle fluids that, in spectroscopic terms, are very strongly absorbing.

Future work. Continuing work is aimed at exploring the most appropriate sealing techniques and materials for various applications and to raise the upper temperature limits even further. It is also possible to use the spin-off benefits of the sealing techniques in the low temperature region to provide pressure-tight, low temperature fluids cells. This has been a problem area for spectroscopists for some time.

Topics of immediate interest include FT-IR interfacing for both supercritical fluid chromatography and supercritical extraction. Polymer research is another interesting area, as it is now possible to obtain full-range spectra of molten polymers under previously inaccessible process conditions. Fuels and lubricants are among the many other areas in which the extension of the available experimental operating range is likely to be significant.

CONCLUSION

A new method has been developed to solve the problem of loss of strength in the retaining window of fluid cells. The method is general to all types of optical arrangements and all forms of optic elements, including fibers. The method provides significant spin-off benefits for optical spectroscopy and greatly extends the temperature and pressure range available. Applications in the areas of jet fuel decomposition and fatty acid decomposition have been shown.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Henk D. Meuzelaar and his research group at the University of Utah for providing their data on jet fuel samples and to Brian D. Kybett and his research group at the University of Regina for providing their data on fatty acids. The engineering assistance of Alan Wilkie and Brian O'Neill of Aabspec International (Dublin, Ireland) in implementing the cell designs discussed in this article is very much appreciated.

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