This reprint describes the original #2000 Multi-Mode FTIR System. Now we have gone even further in the development of this advanced experimental facility. The new #2000-A extends the upper temperature limit to beyond 900°C while the new '-EXP' sample probes give faster heating rates and the new LTP-2A Programmer provides both heating and controlled cooling cycles. The enhanced performance #2000-A is available from March 1993.

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High-performance IR cell serves in several modes

Now infrared spectroscopists can analyze samples at high temperature and high pressure.

Val Rossiter
AABSPEC Instrumentation Ltd.

IN AN EARLIER ARTICLE, we described a high-temperature cell for infrared (IR) spectroscopy (1). That cell was capable of maintaining a controlled sample environment during routine operation at sample temperatures as high as 700 C. In addition, the cell permitted IR analysis at pressures as low as 10^{-3} torr or in either a reactive or a nonreactive atmosphere at pressures as high as 30 psig (2×10^5 Pa).

We also developed a versatile sample-mounting system to handle samples of various configurations, such as films and discs. Cells of this design were limited, however, to transmission spectroscopy, as well as to the vacuum/pressure ratings just mentioned.

To improve upon these conditions, we would have to design a new cell to provide high-pressure capability and to be more versatile for handling samples in spectroscopical analyses. Central to the design problem was the conflict between the need for high performance and the requirement for high-pressure analysis conditions. In addition to the increased rate of heat transfer at high temperatures, we had to consider the high-pressure structural design in terms of the inevitable loss of mechanical strength.

To provide an acceptable level of chemical inertness, we constructed the cell from 316-grade stainless steel. This material, of course, is not an easy material with which to work, but it provides the needed integrity and inertness for the structure. In addition, the need for integrity prevented us from using any welds or brazing in the manufacturing process. Therefore, we machined the main body of the cell (*i.e.,* the pressure chamber) from a single piece of stainless steel.

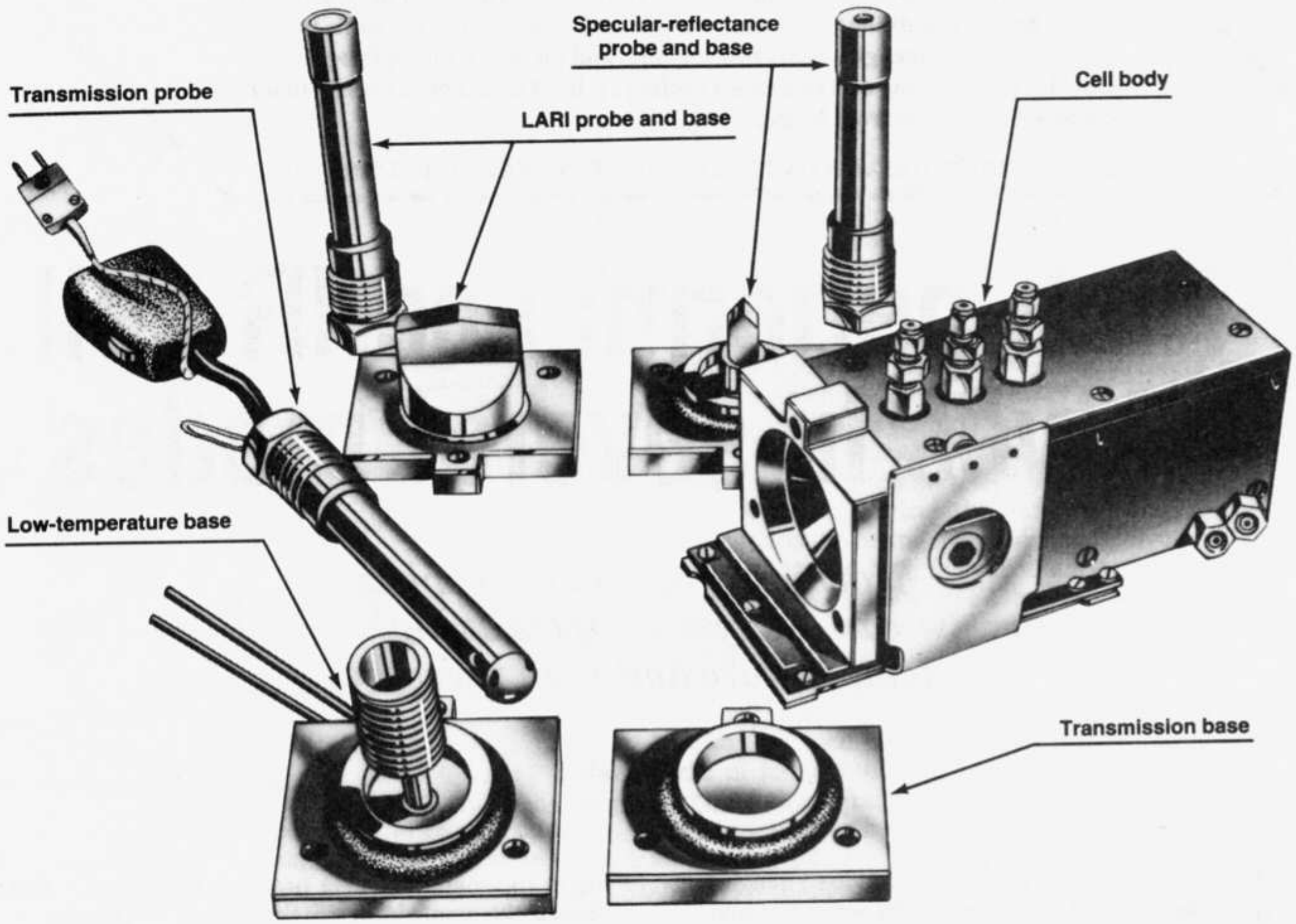
Fundamental to the design was the concept that we wanted to be able to heat only the immediate zone containing the sample. As completely as possible, this heated zone should be isolated from the rest of the structure, which would be water-cooled.

With this approach, we would be able to use elastomer O-ring seals in relatively cool areas. We also could be sure that the optical windows would not be subjected to thermal stresses.

Thus, we could use demountable windows to allow the user to choose a window material matched to the application and to accommodate different spectral regions simply by exchanging windows. To make this approach possible, we developed, as a part of the central body of the cell, a screw-down window-insertion assembly suitable for high-pressure applications.

Reflectance modes

As expected, it was relatively easy to meet the requirements for transmission spectroscopy. Still, we wanted to be able to perform analyses in reflectance modes, such as specular reflectance at near-normal incidence and large-angle reflectance infrared (LARI) analysis at near-grazing incidence. In particular, preliminary experiments with the LARI technique had demonstrated its usefulness for the analysis of samples



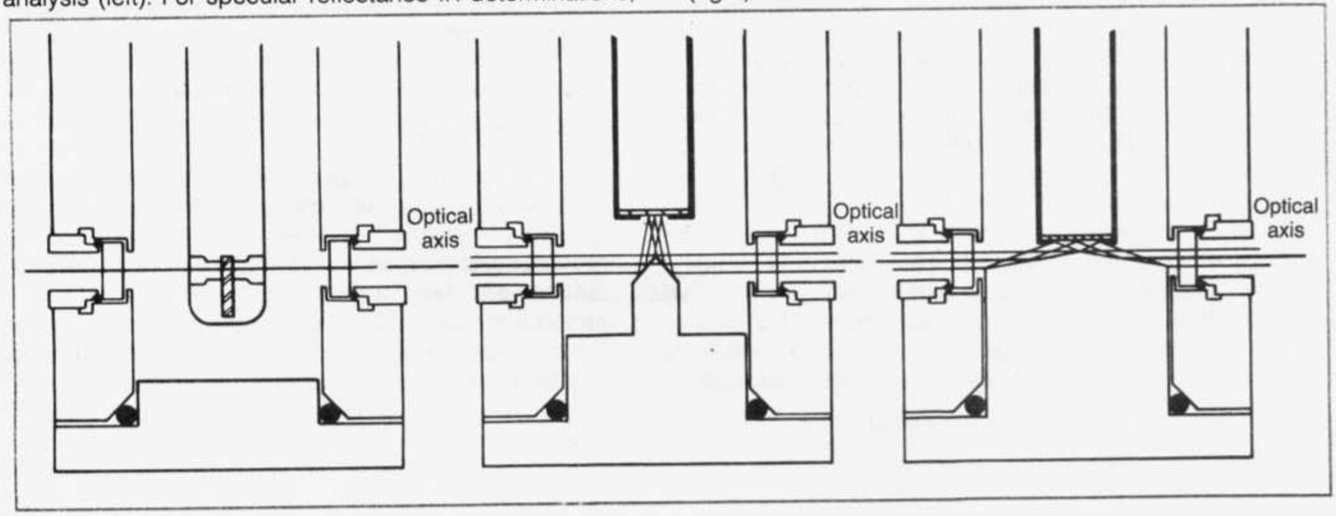
THE INFRARED CELL uses separate sample-probe and back-plate combinations for high-temperature, high-pressure spectroscopic analysis in various modes.

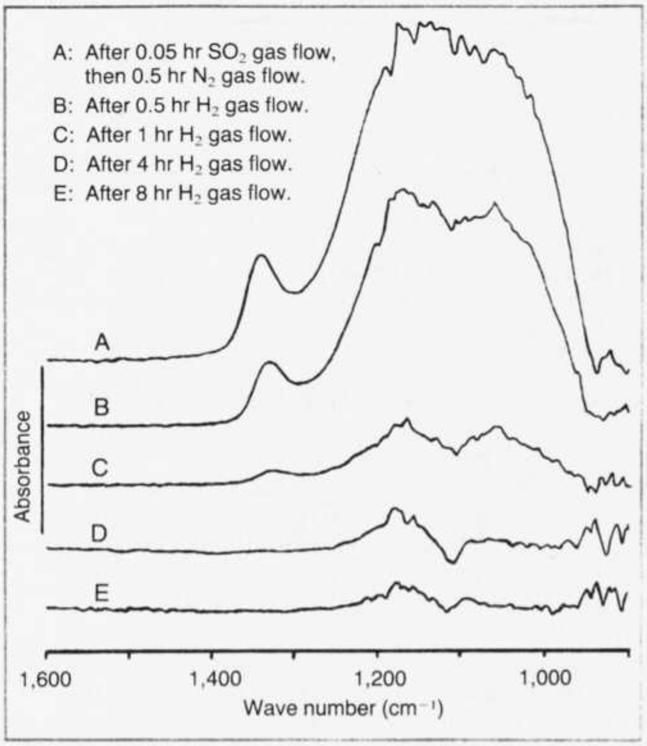
that otherwise had been difficult to determine.

By developing the cell design in such a way that the optics needed for the reflectance modes could be close to the sample and within the sample chamber, we were able to describe a simple format. This, in turn, became a central consideration to the overall design.

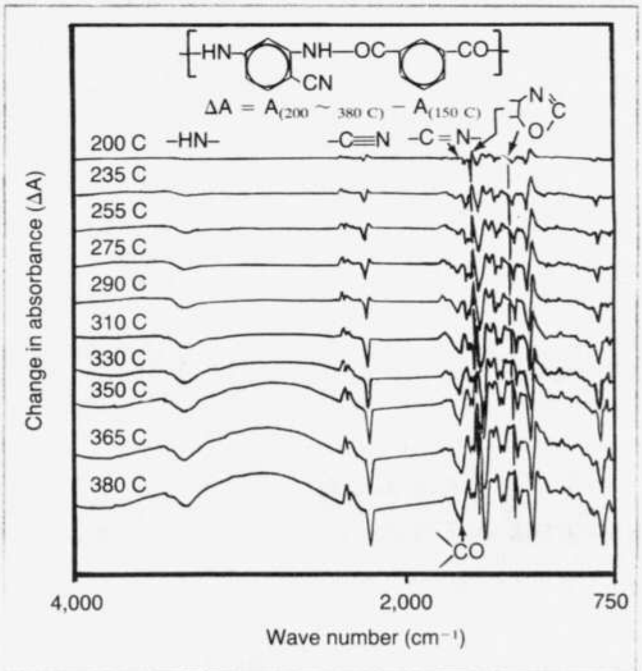
In effect, the cell structure consisted of three parts: the cell body (common to all formats), a sample probe, and a related end plate. The probe section contains the heating system, which is, consequently, outside the cell body. By changing the sample probe/end plate pair, the user can change the form of spectros-

IN THE TRANSMISSION MODE, the cell looks like a standard unit modified for high-temperature, high-pressure IR analysis (left). For specular reflectance IR determinations, the angle of incidence is nearly normal (center). For large-angle reflectance IR, the incidence angle is near-grazing (right).





A SERIES OF DIFFERENCE spectra of the gettering catalyst plus the additive sulfated and regenerated at 600 C shows control of SO_x emissions (2).



SPECULAR REFLECTANCE difference spectra of cyano-containing aramid at various temperatures show how the polymer degrades on exposure to heat.

copy from transmission to specular reflectance or LARI.

In addition, special end plates are useful for other functions, such as providing liquid-nitrogen cooling for the transmission probe or for emission spectroscopy.

When the sample cell is completely assembled, it is about 6 in. (150 mm) long and about 3 in. wide—small enough to fit into the sample compartments of any of the standard infrared spectrophotometers. The cell is mounted on a bracket that fits a standard 2-in. spectrometer slide and incorporates a positional adjustment device.

The cell body, which is housed within a water-cooled outer case, is a complex shape formed from a single piece of stainless steel. To allow the introduction of probes or gas connections, the body contains three access ports, one of which is located directly above the optical axis and, thus, can be used to bring reactive gases or other materials to the sample.

Modes of operation

During an operation of this type, the other two ports might be used, for example, to introduce a gas or liquid to flush the cell or to exhaust the system. A 0.0625-in. tube fed through a port into the cell chamber can facilitate the conducting of experiments in this kind of arrangement.

The optical windows are mounted on either side of the cell body. The sample probe is inserted through a high-pressure O-ring seal at one end of the body, and the end-plate assembly seals the opposite end of the cell by means of an additional O-ring.

For infrared analysis in the transmission mode, the operator mounts the sample in a cavity within the transmission-sample probe in such a way that it is perpendicular to the optical axis of the spectrometer beam. For most applications, the standard end plate serves merely to close the end of the cell. For special uses, the standard end plate can be replaced by a low-temperature end plate that surrounds the sample zone with a jacket containing liquid nitrogen or other low-temperature fluid.

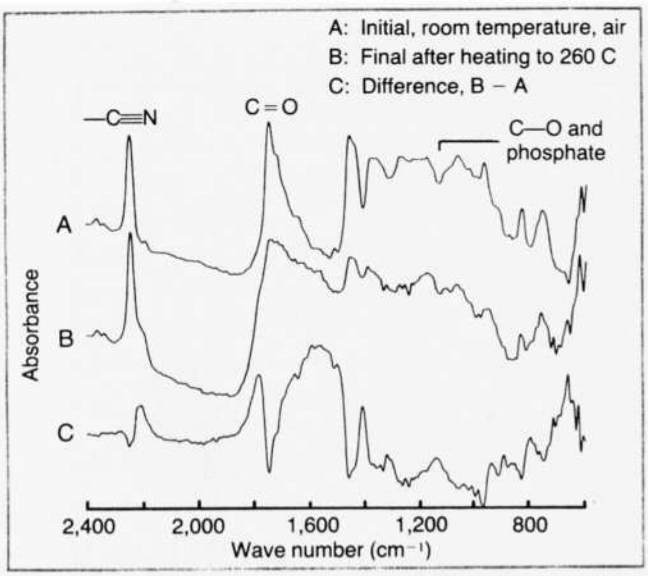
At Unocal Science & Technology Div., Pat Ritz and his co-workers have applied the transmission probe to high-temperature studies of catalytic reactions (2). These *in situ* spectroscopic studies of SO_x emissions from fluid catalytic cracking units (FCCUs) are a part of a program designed to assure the refinery's compliance with increasingly stringent environmental regulations.

The FCCUs are large-volume gasoline-producing units. During the past few years, the reduction of SO_x from these refineries has received a large amount of attention. As emission standards have become more exacting, new technologies for the management of SO_x emissions have become necessary.

In the specular-reflectance mode, the IR beam strikes the sample at near-normal incidence. In practice, the angle of incidence usually is close to 10 deg.

A solid-gold mirror surface on the end plate reflects the entering beam so that it strikes the sample. A second beam then redirects the reflected beam so that it continues along the optical axis. This technique is particularly useful for examining thin samples such as coatings on metal surfaces.

At the Polytechnic Institute of New York (Brooklyn), Soonsik Kim and his co-workers have been studying polyamides containing cyano groups (3). With the polymer coated onto a metal substrate, they obtained, at a 10-deg angle of incidence, the FTIR spectra for a cyano-containing aramid polymer as a function of temperature. They were able to correlate FTIR data with



LARI SPECTRA show differences in nitrile resins cured under various conditions. Degree of cure affects adhesion, cohesion, and rust resistance of the coating.

thermal analysis data to show structural changes and degradation processes across the temperature range of 350 to 620 C.

As the technique's name implies, LARI provides an angle of near-grazing incidence. In practice, this angle of incidence often is close to 70 deg.

Large-angle infrared reflectance

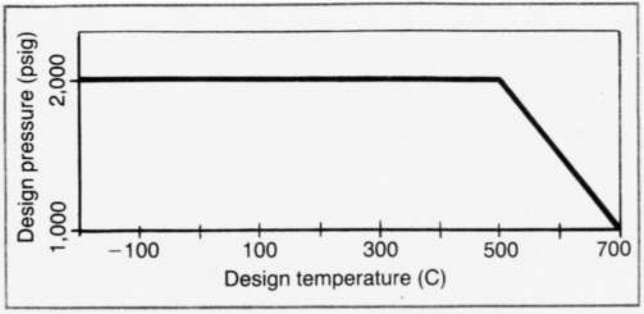
In our cell, we have provided for two versions of the standard LARI technique. In one of these, the sample is kept in the vertical plane during analysis. In the second, the sample is held in a horizontal plane to permit analysis of samples that may melt at the elevated temperatures and of samples that exist as liquids or powders.

In general, the LARI technique requires use of a high-sensitivity detector to insure a good signal-to-noise ratio in the recorded spectrum.

At Standard Oil of Ohio, Rachael Barbour and her associates have studied the effects of temperature on polymeric coatings (4). Using the LARI facility at a 70-deg angle of incidence, they obtained FTIR data after *in situ* curing of nitrile resins on steel substrates, both untreated and zinc phosphated.

To control the sample-heating rate, they used a linear temperature programmer. The researchers then interpreted the data in terms of the role of surface phosphate functional groups on the behavior of the polymer. The adhesion, cohesion, and rust resistance observed could be seen as measures of the anticorrosion protection provided by the film.

The operator can control the cell temperature in either of two ways. One method uses a digital isothermal controller to heat the sample to the required temperature. The other uses a linear temperature programmer, which permits selection of a controlled rate of heating, as well as of initial and final hold times.



LOSS OF MECHANICAL STRENGTH restricts 700-C usage of the cell to a pressure of 1,000 psig, but permits operation at 2,000 psig and 500 C.

The latter method allows the operator to study samples under different temperature/time cycles, a technique that is particularly useful for studying processes such as the curing mechanisms of polymers.

For either method, the maximum design pressure of 2,000 psig is available to a temperature limit of 500 C. The loss of mechanical strength of the construction materials imposes a limit of 1,000 psig at the upper design temperature of 700 C.

The spectroscopic-cell design we have described here can be used for IR analysis throughout a wide range of temperatures and pressures. In addition to transmission and reflectance spectroscopy techniques, operators also can perform other experiments by using alternative end-plate assemblies.

Typical applications for the IR spectroscopy cell include the study of catalysts, polymers, adhesives, and various topics in the general area of materials characterization and the establishment of physical and chemical properties of materials at high temperatures and pressures. **R&D**

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