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Laboratories and Demonstrations

"Do-It-Yourself" Attenuated Total Reflectance Cell Designed and Constructed in a Laboratory Course: A Versatile and Economical Alternative to Commercial Designs

S. LAU[1], J. RIGHT[2], K. STAVENS[2], J. WHITAKER[2], Z. LIU[2], AND **J. LAUTERBACH[2]***
[1]Chemistry Department and [2]School of Chemical Engineering
Purdue University, W. Lafayette, IN 47907
jochen@ecn.purdue.edu

An innovator must be able to identify new opportunities, explore the boundaries of technology, and develop and implement technologies.

An attenuated total internal reflectance (ATR) cell has been designed and constructed by a group of four undergraduate and graduate students during an advanced laboratory course in the School of Chemical Engineering at Purdue University. Details for the assembly, which utilizes commercially available optical components, are given in this paper. The cell employs a 45-degree trapezoidal ZnSe crystal as the ATR element. Both spherical and flat gold-coated mirrors are used to focus and align the IR beam.

The cell design presented here not only provides practical instrumentation design and implementation experience for students, it also has four major advantages important for teaching purposes: a) It can be ported between different FTIR spectrometers with similar sample-compartment sizes; b) it provides an economical means for ATR spectroscopy in laboratory courses as the cost of this cell is less than half the price of similar commercial cells; c) all optical parts of the cell are easily accessible and visible for demonstration and adjustment purposes; and d) it can serve as a starting point for a variety of student experiments.

Introduction

Innovation in a fast-changing technological world requires new skills from young scientists and engineers that go far beyond traditional expertise. An innovator must be able to identify new opportunities, explore the boundaries of technology, and develop and implement technologies. Therefore, it is one of the most important educational tasks of a modern university, in combination with a strong theoretical foundation, to challenge students in laboratory courses to think, explore, hypothesize, plan, solve, and evaluate their experiments. The typical sequence of development of laboratory skills often stops short of introducing students to these critical aspects of experimental work. In many undergraduate chemistry laboratory courses, experiments are closely managed. Students follow instructions and learn by observing the results with equipment that was already set up for them. More and more, students are also taught how new experiments are designed, and hence to have a good appreciation of what care, planning, design, and testing are required to produce equipment that will give reliable and useful results. All these skills require more freedom than is usually allowed to undergraduate students in well-structured laboratory courses.

The opportunity for students to discover and develop experimental skills is expensive in terms of both hardware and the recurring costs associated with the freedom to make mistakes. Therefore, it is important to carefully use the available equipment resources. In addition, equipment design and experiments should be planned so that future generations of students will be able to benefit from the instrumentation. In this paper, we report a student design of an ATR cell from an advanced laboratory course at Purdue University. This cell design can be easily adapted by other laboratory courses. While the first part of the paper describes the technical design, the last part describes some of the learning experiences the students had while designing the ATR cell.

Introduction to ATR Spectroscopy

ATR spectroscopy is a versatile and effective infrared sampling method widely used in industry. This spectroscopy requires little or no sample preparation for rapid analysis;

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it also allows analysis of thick or strongly absorbing samples that cannot be analyzed by traditional FTIR spectroscopy. In the food industry, ATR spectroscopy is commonly used in measuring the fat and protein contents of milk, butter, and meat [1–7]. In the automotive industry, ATR spectroscopy is also used to analyze motor oil, and brake and transmission fluids [8].

The basic element of an ATR cell is a prism made of a high-refractive-index infrared transmitting material (ATR crystal). The IR beam enters the crystal as shown in Figure 1. If the angle of incidence is greater than the critical angle, θ_c (Eq. 1), the beam undergoes multiple internal reflections until the IR beam exits at the other end of the crystal [9–12].

$$\theta_c = \sin^{-1}\frac{n_2}{n_1} \tag{1}$$

n_2 : refractive index of the sample
n_1 : refractive index of the ATR crystal material

Each time the IR beam reflects off the crystal surface in contact with the sample, an evanescent wave extends into the sample and attenuates in regions of the infrared spectrum where the sample absorbs radiation energy. The depth of penetration of the evanescent wave, d_p, is defined as the distance from the crystal–sample interface to the point where the intensity decays to 1/e of its original value and is defined by

$$d_p = \frac{\lambda}{2\pi \cdot n_1\left(\sin^2\theta - \left(n_2/n_1\right)^2\right)^{1/2}} \tag{2}$$

The value of d_p is usually on the order of microns [11, 12]. This makes ATR spectroscopy insensitive to sample thickness, allowing for the analysis of thick or strongly absorbing samples. As can be seen from Equation 2, the depth of penetration depends on the wavelength of the infrared radiation. Longer wavelengths increase the depth of penetration; since a spectrum usually covers a wide range of wavelengths, there needs to be a correction for this in the spectral analysis. The software provided with most IR spectrometers will take into account this varied depth of penetration resulting from the changing wavelength of the IR signal. The efficiency of the sample contact also affects the quality of the ATR spectrum, since the intensity of the

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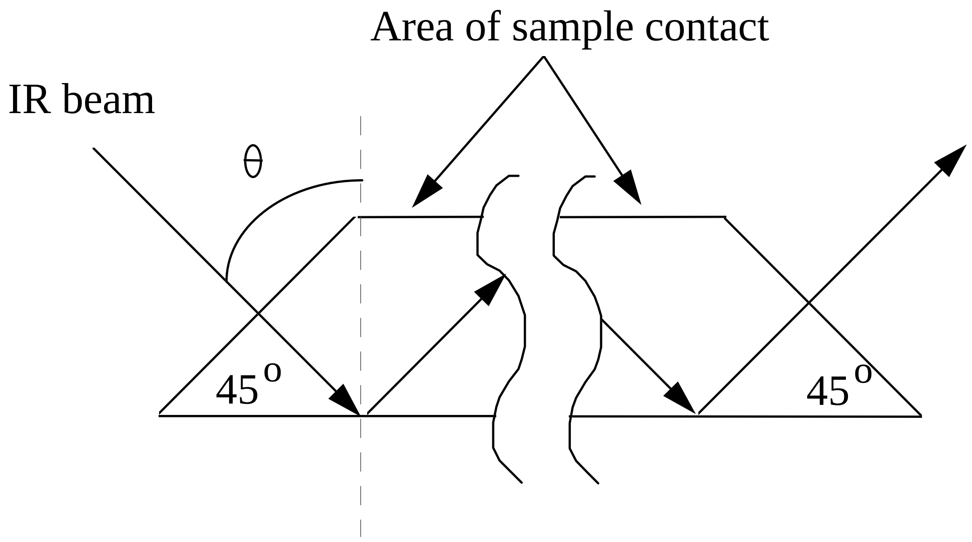

FIGURE 1. ZNSE CRYSTAL USED IN OUR DESIGN.

spectrum decreases with decreasing sample area. This becomes a more serious issue when solid samples are used instead of liquid samples. The refractive index of the ATR crystal, the angle of incidence, and the ATR crystal material all affect the number of times the infrared radiation is internally reflected [11, 12]. The intensity of the absorbance spectrum increases with the number of internal reflections. Usually, a material with a high index of refraction is chosen as crystal material.

ATR Cell Design

Our ATR cell design was centered around the ultimate objective of obtaining an accurate spectrum for a liquid sample. Obtaining this goal required consideration of several key design aspects, the first of which was the size of the cell. The cell was to fit inside an FTIR spectrometer (Nicolet Magna 550) compartment measuring 210 × 250 × 150 mm, and was to be easily removed when the instrument was used for other student experiments. An equally important consideration was to protect the delicate ATR crystal, while allowing for easy sample loading. Finally, the total cost of the ATR cell was to be kept as low as possible.

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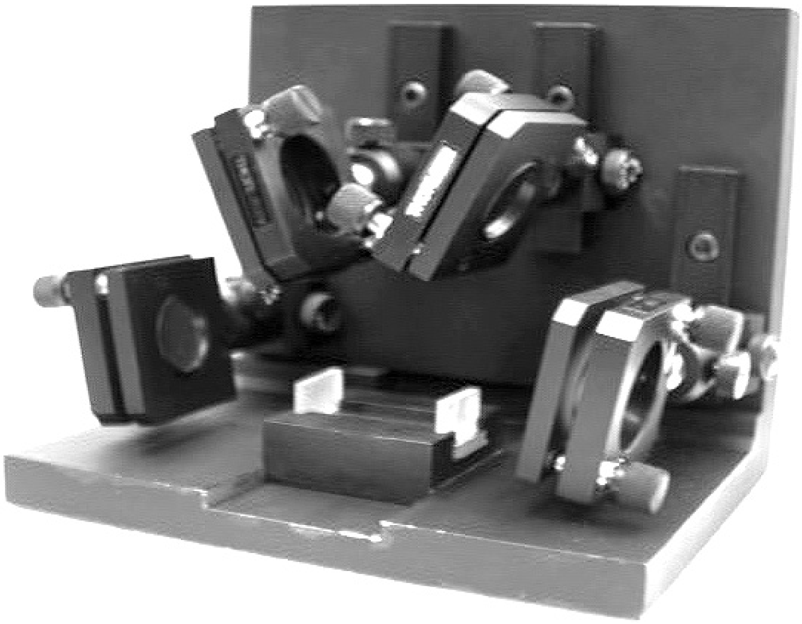
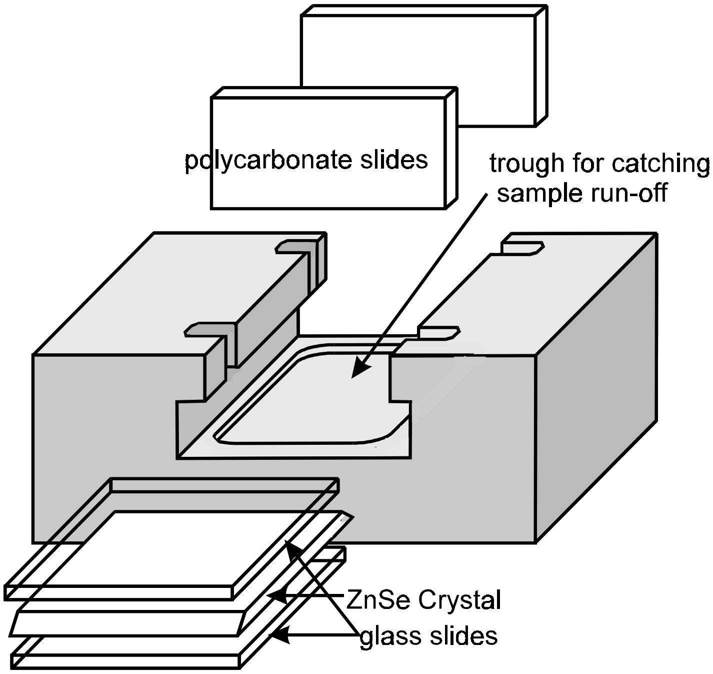


FIGURE 2. PHOTOGRAPH OF THE COMPLETED ATR CELL.

A picture of the completed design can be seen in Figure 2. The ATR crystal holder, as shown in Figure 3, protects the crystal and allows for easy sample loading. The ATR crystal is a 45° zinc selenide trapezoid (50 × 20 × 2 mm) [12]. Both angled ends of the crystal are left exposed to allow the IR beam to enter the crystal and exit after internal reflection. Two glass slides reinforce the crystal, protecting both the top and bottom surfaces, while holding the sample in contact with the crystal surfaces. The latter feature maximizes the area of sample contact, thus maximizing the amount of the IR attenuation into the sample. It allows more-volatile samples to remain in the liquid phase for the duration of the analysis. Two polycarbonate slides fit tightly into vertical grooves above the top slide, holding both slides, the crystal, and the sample in place. Finally, a shallow trough cut into the holder just below the bottom slide can catch any sample that may seep out from between the slides and the crystal. Assembly of the sample holder is shown in a movie clip (download from the abstract page).

It should be noted that the physical properties of the crystal material, ZnSe, impose some sampling restrictions. Acids and strong alkalis attack ZnSe and therefore cannot be used as samples or for cleaning. The design, however, is compatible with any trapezoidal crystal of similar thickness. Any crystal that meets the particular sampling needs can therefore be easily substituted for the ZnSe crystal.



Zinc Selenide Crystal Properties [12]

- density -------------------5.27 g cm^{-3}
- transmission range ----20,000 to 454 cm^{-1}
- total transmission -----20 to 40%
- refractive index --------2.4 at 1000 cm^{-1}
- hardness -----------------150 (Knopp #)
- max. temp. in air ------ 300 °C

FIGURE 3. ATR CRYSTAL HOLDER.

The FTIR instrument has a beam diameter of ~10 mm, and the entrance face of the ATR crystal is 2 mm wide. For maximum throughput, the beam therefore has to be focused onto the entrance of the crystal. For this purpose, the ATR cell uses two spherical mirrors (25-mm diameter, 50-mm focal length; Edmund Scientific Company, 101 East Gloucester Pike, Barrington, NJ 08007) to focus and direct the IR beam. Two 25-mm gold-coated flat mirrors (Edmund Scientific) provide additional directional control of the beam. The order of the mirrors, from source to detector, was flat to spherical (focuses beam on crystal face) to spherical to flat. The first spherical mirror focuses the beam onto the entrance, while the other spherical mirror focuses the exiting beam onto the detector (see Figure 4 for the IR beam path). Our choice of 25-mm diameter mirrors is based on the premise that more accurate reflection can be

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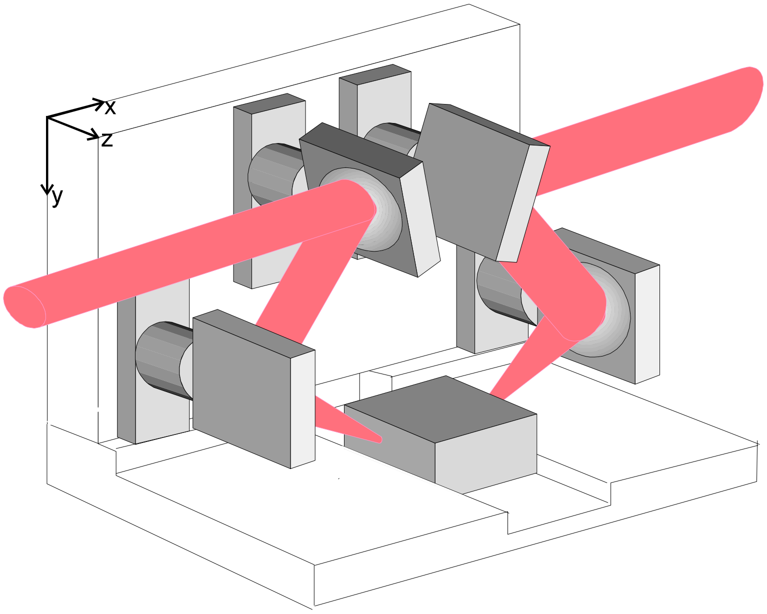

FIGURE 4. IR BEAM PATH IN THE ATR CELL

achieved with a mirror similar in size to the beam being reflected. The mirrors also need to be large enough to tilt at a considerable angle and still reflect all of the incident beam. Fifty millimeters was the longest focal length available for 25-mm spherical mirrors. Longer focal lengths provide a greater freedom for the spacing of optical components.

The sample holder with the ATR crystal is oriented horizontally for simplicity and ease of changing samples. A vertical optical-component mounting plate followed from this design so as to limit the beam adjustment to two major dimensions (*y* and *z* in Figure 4). The schematics for the base plate and back plate can be seen in Figure 5a. Mirrors are mounted in mirror mounts attached to posts held by post holders (Thorlabs Inc., P.O. Box 366, Newton, NJ 07860) [6]. This setup allows the mirrors to be rotated about the *z* axis, thus permitting adjustment of incidence angles. The post holders also allow for *z*-directional adjustment of the individual mirrors' positions. The vertical (*y*, Figure 4) mirror position can be adjusted through the use of rails and rail clamps onto which the post holders are mounted. This design presents a range of possible component positions. Provided the sample compartment is of similar size or bigger, our ATR cell can be configured to work with any FTIR instrument. This is a significant advantage over commercially available cells, which are built to suit specific FTIR instruments.

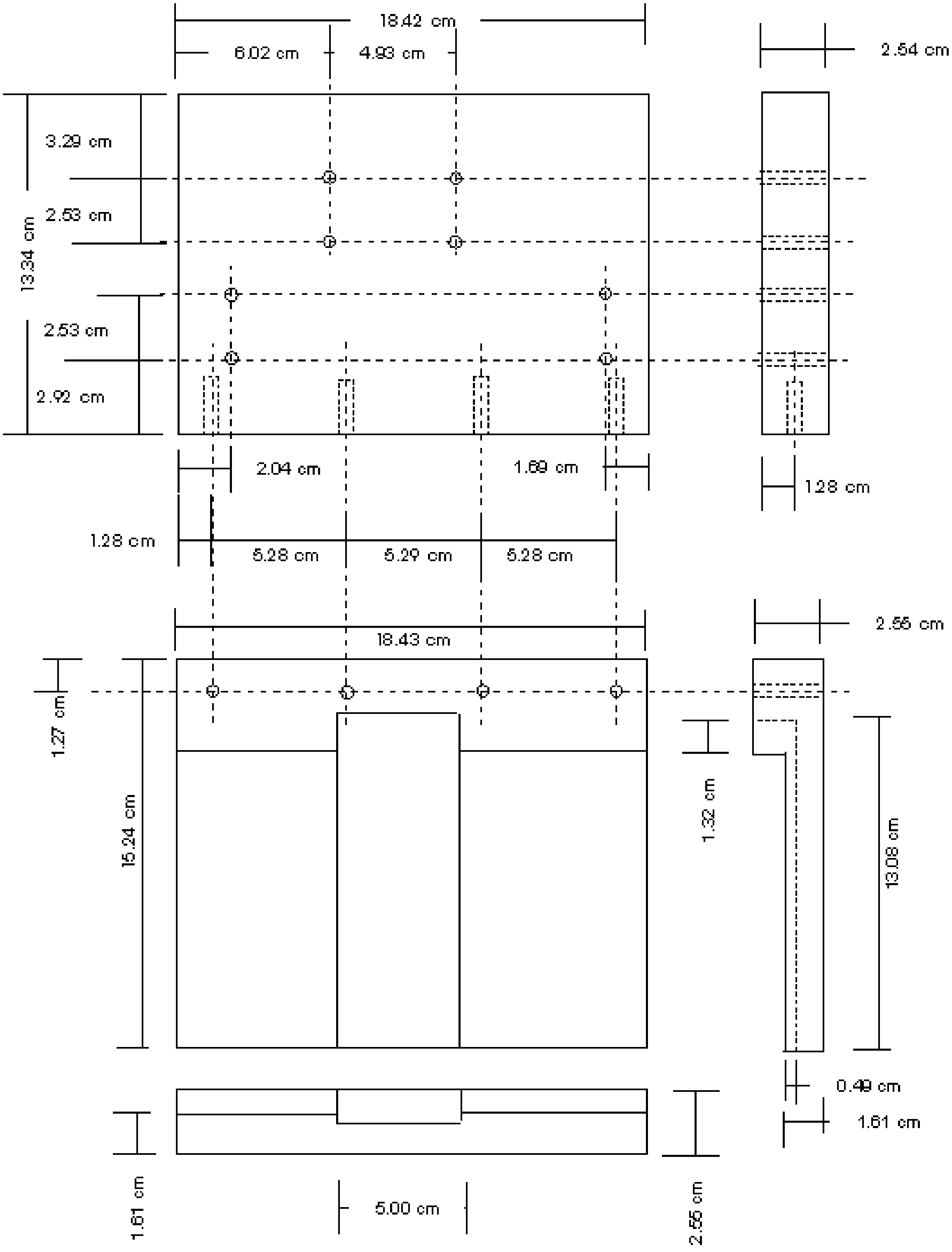

Figure 5b: Bottom and Mounting Plate Design

FIGURE 5. A) SCHEMATICS OF REAR MOUNTING PLATE AND BASE PLATE.

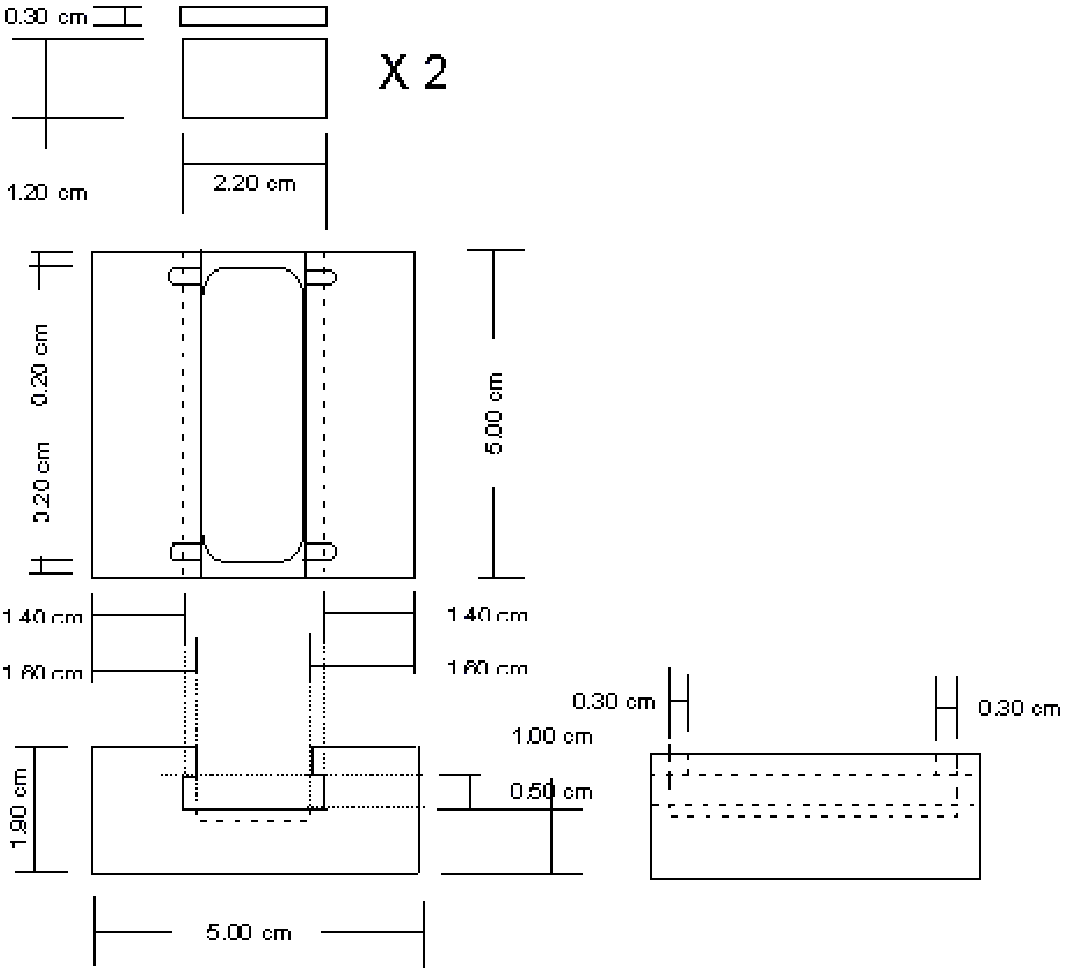

Fig.A2: ATR Crystal/Sample Holder

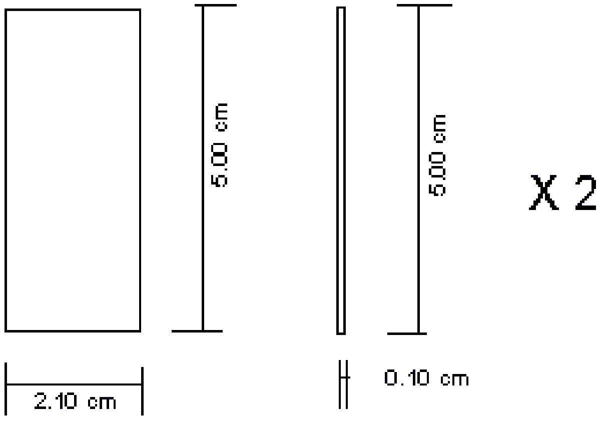

Fig. A3: Slide Dimensions

FIGURE 5. B) SCHEMATICS OF SAMPLE HOLDER.

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The base plate, back plate, and ATR crystal holder are solid aluminum. It is unnecessary to secure the cell to the compartment floor, as the ATR cell's weight is sufficient to hold the cell safely in place. This also makes it easier to remove and replace the cell. Marking the final position of the ATR cell inside the compartment facilitates subsequent realignments.

Optical components are typically black to prevent light scattering and reflection that could interfere with a measurement. Typically, the black finish is imparted by an anodization process. Time constraints on this project did not permit sending the cell away to be anodized, since the turnover time of the closest facility was 2–3 weeks plus shipping. Thus we opted for black spray paint. However, this cannot be recommended as spray-painted layers are thicker than anodized layers, which brings about size complications due to the increased thickness. In addition, some sample solvents may dissolve the paint, and paint is not as durable as an anodized surface.

Optical Alignment and Testing of the ATR Cell

The alignment procedure begins by placing the ATR cell into the sample compartment. Most commercial interferometers emit a visible He:Ne laser parallel to the IR beam. The He:Ne laser has a small diameter relative to the IR beam, and has a slightly different index of refraction through the various media of the ATR cell. However, initial alignment of this laser through the ATR cell serves as a starting point in the optical alignment. The intensity of the IR beam reaching the detector is then monitored via the FTIR software (OMNIC by Nicolet). The mirrors can now be adjusted until the maximum intensity is reached. The mirrors' positions are then fixed and the ATR cell is ready for use. Following the initial mirror alignment for a given interferometer, the ATR cell can be easily removed and replaced in the spectrometer with little additional alignment necessary.

The intensity of the IR beam was measured with an empty sample compartment to determine the maximum possible beam intensity. This maximum was found to be ~25 volts (readout value provided by the software), whereas the maximum intensity measured with the ATR cell in the IR compartment was ~2.8 volts. The IR beam, after striking all four mirrors, should theoretically still possess $(0.96)^4$, or 85%, of its original intensity. One can expect an additional 60% to 80% drop in the IR beam intensity upon passing through the ZnSe crystal. This results in the beam exiting the

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ATR cell with ~20% of the original beam's intensity. After careful optical alignment, the beam intensity with the ATR cell was ~10% of the maximum beam intensity. This means the ATR cell was operating at ~50% of its maximum theoretical efficiency. The additional intensity loss may be caused by the facts that the IR beam is not fully captured by the mirrors, and that it may not be entirely focused on the point of entry of the ZnSe crystal. A commercially available ATR cell in the same spectrometer, adjusted by the manufacturer's sales representative, achieved a maximum detector signal of 2.1 volts, i.e., the home-built cell has similar or even better throughput than the commercially available cell. In addition to the Nicolet Magna 550 spectrometer, the cell will also work with a Perkin Elmer Spectrum 2000 spectrometer. Other manufacturers have similar sample-compartment dimensions; thus the cell design can easily be adapted to fit a variety of FTIR spectrometers.

Cost of the ATR Cell

The itemized and total cost of the ATR cell are shown in Table 1. The total cost for the ATR cell with two 1-inch-thick base plates, including labor, was ~$1300. Anodizing the base plate and sample holder would add ~$100 to the total cost. A market survey revealed that similar commercial ATR cells cost between $2000 and $7000. In comparison, our ATR cell is about half this price or less. Additionally, our portable ATR cell's optical configuration can be adjusted to fit different FTIR spectrometers while commercial cells often are sold in a configuration only suitable for specific spectrometers. This extra flexibility enables users to upgrade their spectrometers without the need to purchase another ATR cell.

Test Experiments

In order to verify the ATR cell was working properly, several samples with well-established spectra were tested. The spectrum of acetone, for example, is shown in Figure 6. These samples served as demonstration objects for students to learn about major frequency ranges for vibrations of certain chemical functional groups. Table 2 shows a comparison of the major IR peaks from both an IR atlas [13] and our experimental results. The difference between the established and experimental values falls within experimental error. The peak locations are determined manually while the spectrum is viewed on the computer screen. Therefore, an error of approximately ±10

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TABLE 1. Cost of the ATR cell.

Item	Cost
ZnSe crystal	$ 400
2 spherical mirrors	60
2 flat mirrors	40
Posts and post holders	55
Rails and rail carriers	136
4 Mirrors and mounts	228
2 Al base plates + labor (1" thick)	225
Sample cell + labor	144
2 glass slides	17
Spray paint	5
Total	1,310

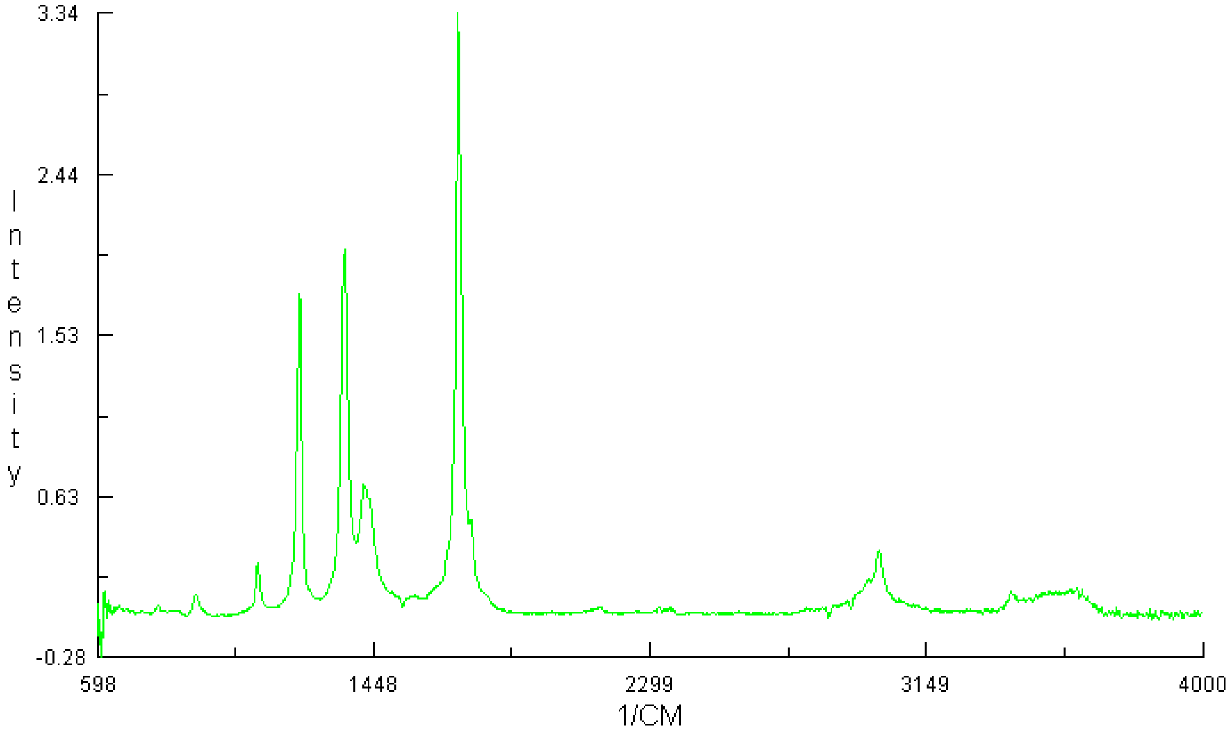

FIGURE 6. IR SPECTRUM OF ACETONE OBTAINED WITH THE HOME-BUILT ATR CELL.

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TABLE 2. Comparison of experimental and literature values [13] for major IR absorption peaks of acetone.

Acetone Established (cm^{-1})	Experimental (cm^{-1})
902.4	904.4
1092.6	1095.2
1222.2	1220.0
1363.0	1359.7
1421.7	1418.1
1715.1	1711.7
3004.6	3007.1

cm^{-1} can be expected. As can be seen from Table 2, the experimental values agree well with those found in the literature.

The cell was used by the student group to take spectra of gasoline samples, which were collected from four local gasoline stations. This project, which will not be further described here, showed that the cell is capable of performing qualitative and quantitative analyses of liquid samples. The project will be expanded for the upcoming laboratory course.

Future Projects

The design and construction of the cell has been a very rewarding project for the students. It can be performed in one semester, if the instructor orders the ATR crystal well in advance (delivery time for our crystal was 6 weeks). Once the cell is completed in the present form, further design projects can include, for example, the construction of a solid-sample holder, which ensures good contact between the sample and the crystal without putting too much mechanical stress on the crystal. Once the cell is completed and tested, instructors for laboratory courses have the opportunity to design a variety of experimental projects. Those can include the analysis of wastewater samples, different grades of gasoline from different manufacturers, and different grades and ages of motor oils and other lubricants.

Educational Aspects

This paragraph will describe some of the “feelings” and experiences the student group had during the semester. The group consisted of two chemical engineering juniors, one first year chemical engineering graduate student, and one third-year chemistry graduate student. The instruction given to the group at the beginning of the semester was to build an ATR cell for liquid IR sampling. The students had no knowledge of ATR spectroscopy, nor had they seen an ATR cell before. Although student progress was closely monitored by the instructor during the course, the cell design was almost completely developed by the students.

The following comments were compiled from the students and may help other instructors to identify possible problems with this project:

> “It was scary at first, but this is what research is about—the unknown! The first thing we did was to go to the library to find out what exactly is ATR spectroscopy.”
>
> “We had to learn how to search for information in the library. There was not much under the heading of ATR, but we knew there must be more, we finally found more information under other headings, such as internal reflection spectroscopy, FTIR....”
>
> “We looked through a variety of schematics of different cells. Many were too fancy or too big, but we figured out what components were required to make our own.”
>
> “We then needed to define our tasks:
>
> I. Cell needed to fit into compartment
> II. Cell needed to be portable
> III. IR beam from source was too big, need to focus it down and into the crystal
> IV. Needed to direct exit beam from crystal into detector
> V. Design an easy-to-load and unload sample holder for both crystal and sample.”

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> "We had to make the decision on lenses vs. mirrors from their advantages, disadvantages, and cost, then we had to figure out what kind of mirrors were appropriate and order them."
>
> "We estimated the positions and the dimensions of the cell and the sample holder. We made several drawings and then *communicated* with the machine shop about the viability of our ideals, choice of materials, and finish coating."
>
> "We learned to align and test the cell."
>
> "We also came up with our own project to study after the cell was built—observe the difference (e.g., additives, composition changes...) between three grades of gasoline from the same company and also between different companies in the local area."

Conclusions

The project presented in this paper was performed by two graduate students and two undergraduate students taking an advanced chemical engineering laboratory course at Purdue University. The students have demonstrated the ability to design and construct a complex ATR cell with commercially available optical elements. They gained valuable practical experience in design, construction, and implementation of optical instrumentation while the teaching laboratory gained an ATR cell, at a very low cost, that can be widely used in future laboratory courses. The cell design makes it very flexible and portable between various FTIR spectrometers. With the information provided here, it should be possible to copy the design. The authors would be happy to answer any questions from interested readers.

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