Agilent Cary 630 FTIR Spectrometer Supporting Organic Synthesis in Academic Teaching Labs

Application note

Academic

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Introduction

As it has been for the past half century, IR spectroscopy is a fundamental analytical technique that undergraduate organic chemistry students must understand and have the opportunity to use. The demands of the undergraduate labs require that FTIR spectrometers possess certain design attributes associated with the multiuser environment. The spectrometer must be easy to use, rugged, reliable, compact and cost attractive.

The recently introduced Cary 630 system (Figure 1) meets and exceeds these requirements and is an excellent choice for the undergraduate organic lab. In addition, it is equally at home in graduate level and research labs where organic chemists determine the identity and structure of synthesized compounds via a rapid IR analysis.

Figure 1. The Agilent Cary 630 FTIR spectrometer (all photographic elements shown in context)

Agilent Cary 630 FTIR Spectrometer – features and benefits for academic organic synthesis applications in teaching and routine research support

Overall System Design

- Most compact, superior performing FTIR available - ultracompact design preserves valuable bench top space
- Light weight allows system to be relocated, as needed
- Completely sealed optics and compact size enables use in standard fume hoods
- Broad range of sampling interfaces available, handling liquids, solids and gases
- Overall performance and ease of use advantages translate into virtually all analyses requiring less than a minute to execute

Optomechanical Components

- Permanently aligned interferometer and optical system results in an extremely reliable, everyday “workhorse” system
- Interferometer and optics are exceedingly rugged – Cary 630 uses the same optomechanical components as those used in Agilent’s portable and handheld industrial systems, which require the highest level of robustness
- Large aperture optics and short internal optical paths provides class-leading performance

Sampling Interfaces

- No-alignment, interchangeable sampling accessories allow students to understand and readily practice different experimental methods – transmission, ATR etc.
- Sampling interfaces available include: diamond ATR, diffuse reflectance, solid, liquid and gas transmission as well as Agilent’s innovative, exclusive DialPath technology for liquids analysis
- Diamond ATR sampling interface is ideal for analysis of reaction starting materials, reagents and product – impervious to scratching and highly chemically resistant (pH 1 -14)
- ATR sampling interface enables grab sample, neat reaction mixture analysis – no sample dilution necessary
- Powder press, which ensures good optical contact of solids with ATR crystal, cannot be overtightened, i.e. diamond window cannot be damaged by overpressure
- Sample interface RFID ensures that methods are matched with appropriate sampling technologies

Software and User Interface

- Highly visual, intuitive software allows data acquisition with essentially no training required.
- Real-time spectrum display works in conjuction with ATR powder press to ensure adequate contact between solid samples and diamond ATR crystal.
- Experimental results can be stored under individual student's name or other identifier
- Student can verify identity of starting materials, isolated intermediate compounds and final products by comparison with spectra in on-board IR spectral library
- For more advanced experiments or analysis, data is readily transferrable to commercially available data analysis package.
- On-board diagnostics ensure peak operating efficiency

Application example: Syntheses of esters of o-hydroxybenzoic acid

A classic undergraduate organic chemistry experiment, which is also ideal for FTIR analysis, is the synthesis o-hydroxybenzoic acid esters, i.e.the condensation reaction of salicylic acid with methanol to form methyl salicylate (oil of wintergreen), and the esterification of salicylic acid with acetic anhydride to form acetylsalicylic acid (aspirin). This lab synthesis is particularly useful as a teaching tool because the synthesis is associated with product isolation, purification and the analysis of final product for purity and yield. Melting point, FTIR analysis and proton NMR are often employed in support of this teaching experience, so the student receives an understanding of how synergistic analysis provides a better overall understanding of chemistry. With respect to FTIR analysis, these reactions allow the student to measure solids, liquids and slurries using a variety of IR sampling methods.

In the preparation of methyl salicylate, the starting materials and final product have highly characteristic infrared spectra (Figure 2). The diamond ATR sampling

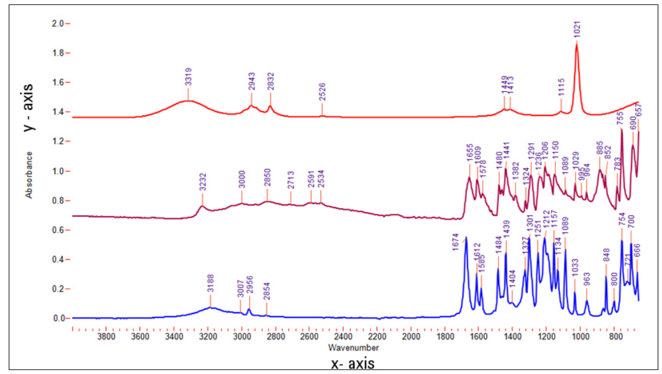

Figure 2. The IR spectra of methanol (red), salicylic acid (maroon), and methyl salicylate product (blue).

interface is ideal for the measurement of these compounds, which are solids and liquids. For methanol reagent, the student simply puts a drop of the liquid on the diamond sensor and initiates analysis. A high quality spectrum only requires 2 seconds to collect and the system's rapid analysis capability is useful when volatile solvents or reagents are analyzed. For the solid salicylic acid starting material, a few grains are placed on the diamond sensor; the powder press is rotated downwards until enough contact is made so that a spectrum appears in the real-time spectrum display (Figure 3). After the reaction is complete, a drop of the oily product is placed on the diamond sensor

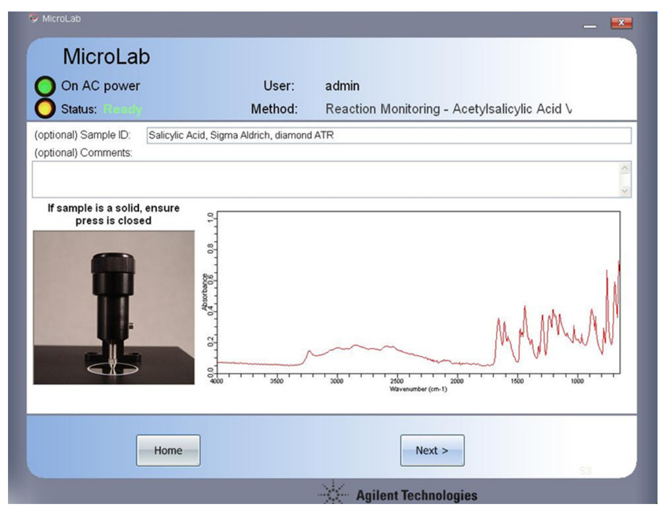

Figure 3. Powder press ensures that solid sample is in contact with diamond ATR crystal to obtain high quality IR spectrum. Powder press design eliminates overtightening. Instantaneously refreshed spectra obtained in real-time analysis window shows that solid sample is in contact with the Diamond ATR crystal.

for IR analysis. If the instructor wishes, a sample of the reaction mixture can be taken periodically and the overall IR spectrum can show the progressive loss of reagent and formation of product as a function of reaction time. To enable the students to experience other methods for analyzing compounds by FTIR, the transmission module can be quickly mounted on the Cary 630 and a drop of the methyl salicylate product sandwiched between two IR sample windows can be analyzed for comparison to the data obtained via ATR.

Acetylsalicylic acid is formed by the reaction of salicylic acid and acetic anhydride. Since acetic anhydride is a corrosive, irritating chemical, the Cary 630 FTIR should be placed in a fume hood. The student will also observe the chemical resistance of the diamond ATR, since a by-product of the reaction is acetic acid and a few drops of sulfuric acid are added to act as a catalyst. The IR spectrum (Figure 4) of these reagents and products are very indicative of their structure and composition. The student will be readily able to see the

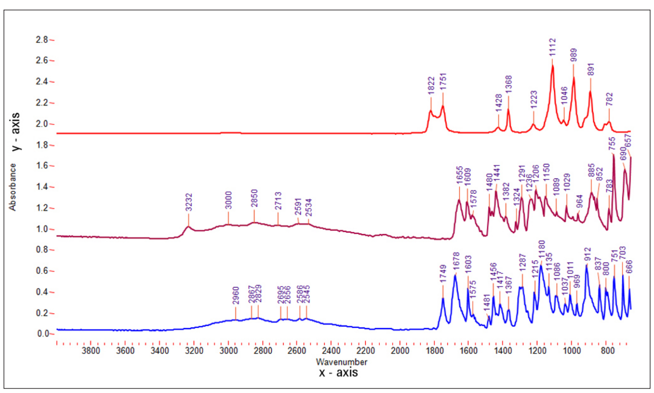

Figure 4. IR spectrum of reagents salicylic acid (maroon), acetic anhydride (red) and product acetylsalicylic (blue)

loss of the 1820 cm^{-1} acetic anhydride carbonyl bands with the concurrent formation of the characteristic 1745 cm^{-1} ester carbonyl vibration in the product. Periodic sampling of the reaction mixture shows the reaction progress as a function of time. As in the previous example, solid materials are analyzed using the powder press and liquids by placing a drop of the solution on the diamond window. For reaction mixtures that are either a slurry or where the solubility of the product is such that solids and liquids maybe present, the student will observe that the liquid phase of the reaction yields the strongest IR absorbances, and the powder press is required to ensure good optical contact between the solid components of the reaction mixture and the diamond window. Moreover, the student can determine the effectiveness of product purification by observing if the IR spectrum of starting material is still present in the isolated product.

Conclusion

The Cary 630 FTIR spectrometer has superior capabilities for the analysis of organic syntheses as either part of undergraduate teaching courses or as a routine spectrometer in support of graduate research. The unique combination of versatile sampling, ease of use, robust system components, combined with attractive pricing and low cost of long term operation meets the needs and requirements of the multiuser academic environment.

Synthesis of o-hydroxybenzoic acid esters – Use of infrared spectroscopy and analysis of spectra

If the mixture that is formed from the reaction of salicylic acid and methanol is dried down and analyzed without purification, the students will observe the methyl CH stretch absorbance band at 2956 cm^{-1} (see Figure 2) for methyl salicylate, along with bands from the unreacted salicylic acid starting material. Bands that the students should watch for is the loss of the salicylic acid broad OH---O stretch absorbance in the region from 2800-2200 cm^{-1} and the OH---O wag absorbance at 885 cm^{-1}. If the reaction mixture is not dried down, but rather further heated on a hot plate at 100°C , methyl salicylate will condense on the sides of the vial. This clear oily condensate can be collected with a swab or plastic pipet for measurement on the diamond crystal for IR analysis. Very little of the liquid is necessary, the 1.5 mm diameter diamond only needs a thin film on its surface, to produce an excellent infrared spectrum of the product.

The carbonyl region of the IR spectra of salicylic acid, methyl salicylate, and acetylsalicylic acid makes for an interesting study on how IR can be used to characterize hydrogen bonding influences on carbonyl group frequencies. Hydrogen bonding lowers the carbonyl group frequency in the IR spectrum and under normal conditions, the carboxylic acid group forms a H-bonded dimer at 1710-1700 cm^{-1} The carbonyl frequency can shift as high as 1750 cm^{-1} when analyzed in the gaseous state (no H-bonding is possible) or in very dilute solution in a non-polar solvent. The carboxylic acid carbonyl band (COOH) for salicylic acid (Figure 4) is lower in frequency (1655 cm^{-1}) than that in acetylsalicylic acid (1678 cm^{-1}). This is due to the slight very weak hydrogen bonding influence from the phenolic OH group present in the salicylic acid and not in the aspirin, which is enough to disturb the dimer found in normal non-influenced aromatic COOH. Benzoic acid which has no phenolic OH group has the carboxylic acid dimer absorbance at 1678 cm^{-1}, nearly identical to that in acetylsalicylic acid. Interestingly, the methyl ester in methyl salicylate (Figure 2) is at the same frequency (1678 cm^{-1}) as the carboxylic acid groups. This is due to the slight hydrogen bonding from the phenolic OH group, which is either intramolecular, intermolecular, or a mix of both H-bonded states, since the normal aromatic methyl ester without a phenolic OH group should be much higher at ~1730 cm^{-1}, such as in orthophthalates.

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