Near infrared history: near infrared instrumentation—the history and lessons learned

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The history of Near Infrared began in 1800 with Herschel. Herschel was the discoverer of the planet Uranus in 1767. He was a well-known astronomer, and the builder of elaborate telescopes for his day. He conducted experiments to find a way to transfer heat from his telescope lens that he felt distorted the image. By trying to determine which wavelengths of light contributed to the heat changes he demonstrated that there was light-energy radiation beyond what we know as the visible spectrum.

Herschel published his work in three landmark papers.[1–3] However, the history of optical instruments began almost two centuries earlier, with the invention of the telescope by Galileo in 1609. While not a spectrometer, Galileo's telescope gathered reflected light from a sample (like the rings of Saturn) and focused it onto a detector, in this case Galileo's eye. Throughout the next two centuries many scientists conducted experiments with telescopes, electricity, and material properties. Their observations laid the foundations for the early prism instruments.

In the mid-1950's Wilbur Kaye with Beckman Instruments published three papers, two of which put NIR spectroscopy on a firm footing.[4–6] One of these papers described the specifications for the construction of an NIR spectrometer and the expected performance.[4] The second paper contained the spectral data for most di- and tri- atomic molecules.[5] Kaye used the fundamental IR spectra and symmetry rules and force constants to calculate the wavelengths for the combination and overtone bands observed. In this way he was able to establish rudimentary anharmonicity constants for NIR active functional groups.

My history with NIR began in 1964 when I took my first NIR spectrum on a Cary14 as a graduate student. This was followed by employment at the USDA/ARS for 37 years, and starting the National NIR Research Project in the late 1970's. The original project included six locations, the Beltsville, MD, USA laboratory of Karl Norris; the Pennsylvania State University laboratory of John Shenk; my laboratory in Athens, GA; USA, Sam Coleman's in El Reno, OK, USA, Gordon Marten's in St Paul, MN, USA and Dave Clark's in Logan, UT, USA. From these beginnings the project grew into a collection of scientists, that developed into a worldwide network of collaborating laboratories. By the time the project was ended in the late 1980's there were over 80 scientists from more than 15 countries involved. This research project's efforts culminated in the publication of handbook #643[7] and two AOAC International Official Methods.[8,9] From this point NIR Spectroscopy flourished and expanded well beyond the agricultural realm into

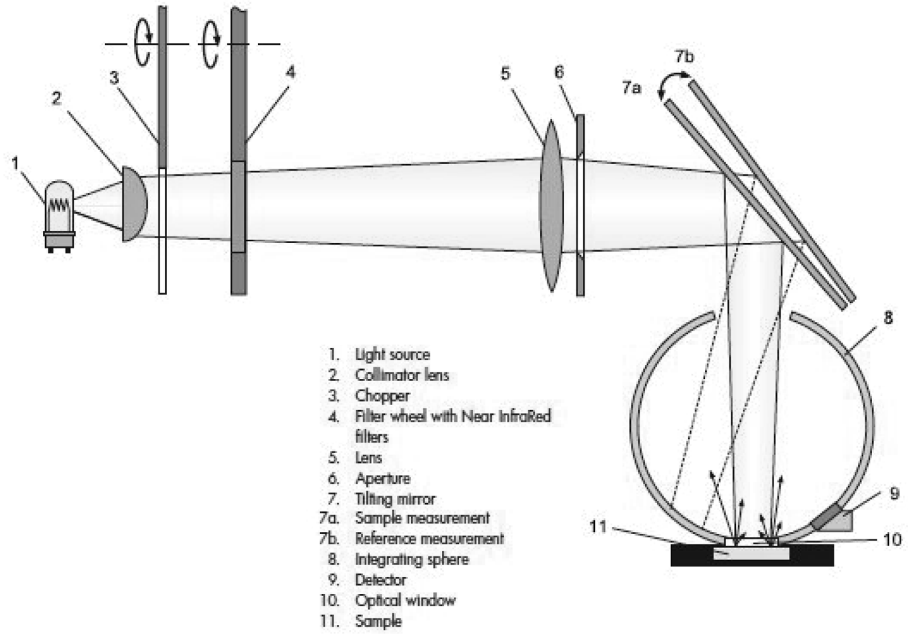

Figure 1. Schematic of Filter Instruments.

pharmaceuticals, industrial, process control, food-processing, remote imaging spectroscopy and other diverse applications.

There are three classes of instruments I wish to describe, as they have and will continue to have the biggest impact on NIR technology. This is not to diminish the importance or significance of AOTF (acousto-optic tuneable filter), diode array and hyper-spectral imaging instruments because each has a role to play, but the filter, dispersive and interferometer instruments perform the bulk of the NIR measurements. Filter instruments came in three types in the early days of NIR spectroscopy.

The discrete filter instruments were produced by DICKEY-John and Technicon (later Bran&Luebbe). A schematic of the Technicon instrument is shown in Figure 1.

These instruments had from 6–24 filters on a wheel and differed only in the type of detector. The Dickey-John used lead sulphide detectors at 45 degrees to the incident beam and the Technicon instruments used an integrating sphere. These instruments were very robust and some are still in service today. The tilting filter instruments were made by Neotec (later, Gardner-Neotec, Pacific Scientific, NIRSystems, Tecator, and currently Foss) and produced a segmented spectrum when the angle of incidence changed, as the filter passed through the beam. These instruments had the capability of incorporating more sophisticated chemometrics, if they had been available, but the computers of the time were not up to the task.

The early days of NIR with dispersive monochromaters began with a few pioneers who following the advice of Wilbur Kaye built their own systems. Karl Norris chose the Cary 14 and a Hewlett-Packard mini-computer. John Shenk used a Jobin-Yvon monochromator and a Digital

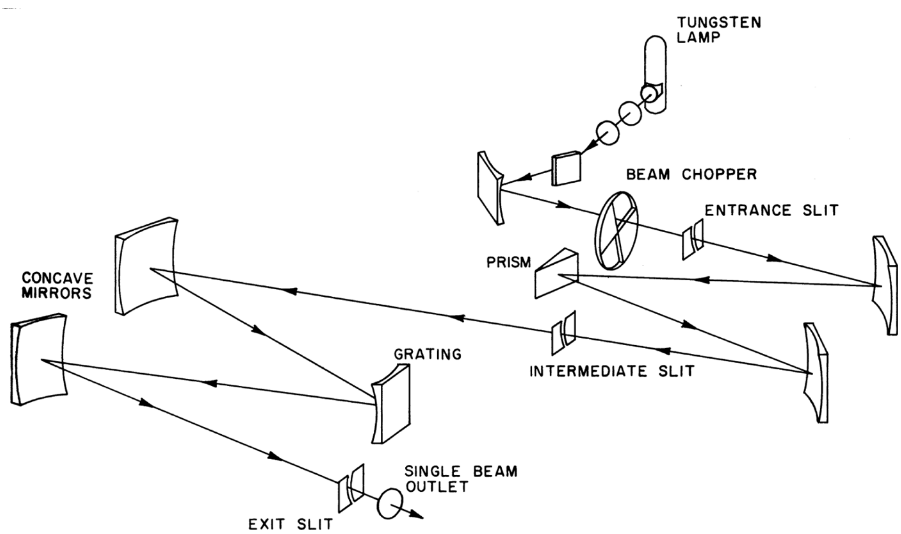

Figure 2. Schematic of the Cary 17 spectrometer.

Equipment Corporation (DEC) mini-computer. Fred McClure used a Cary 17 with a Data General mini-computer. Figure 2 is the schematic of the Cary 17.

The National NIR Research Project chose the same instrument and computer for all locations. At the time there were only two commercial choices the Technicon 500 and the Neotec 6150. The Neotec Instrument was chosen along with a DEC mini-computer. From this instrument the Neotec/NIRSystems 6350 with a PC was developed and culminated in the Foss 6500, which has served thousands of users for over 20 years. Today the Foss XDS and other variants are available, as are the new instruments from Unity Scientific called the SpectraStars. We have much improved equipment and better software today and many more options for sampling.

In the early 1990's NIR interferometers began to be marketed. FT-IR interferometers have been around for some 40 years, but in the mid-infrared wavelength region, where their advantages are best exploited. The original experiment which led to the invention of the interferometer, was the measurement of the speed of Light by Michelson in 1899. This type of interferometer is still the benchmark for FT-IR and FT-NIR instruments and the schematic is shown in Figure 3.

Early instruments offered for use in the NIR region came from Buchi and ABB. These were followed by instruments such as the FT22N from Bruker Optics, which allowed both reflectance and transmission measurements of the same sample. This instrument was followed by Bruker's Matrix series and the M, and the Thermo Nicolet Antaris system. These instruments are capable of much higher and variable resolution than the dispersive monochromator, and have found adherents in the pharmaceutical and fine chemicals sectors. The higher resolution is best for small molecules in matrices at lower concentrations.

Along the way we learned many things that we never expected, and we discovered that there are no true research projects, only the journey.

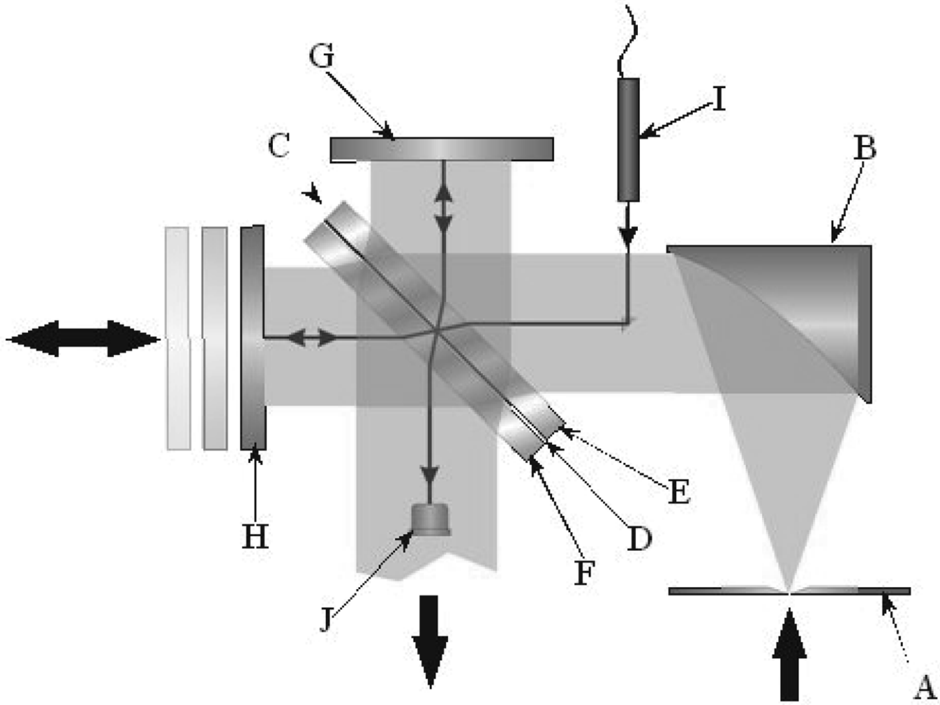

Figure 3. Schematic of an Interferometer. Legend: A: Jacquinot stop; B: fixed mirror; C: beam-splitter; D, E, and F are features of the beam-splitter; G: flat mirror; H: moving mirror; I: positioning laser; J: detector.

Lessons

1. The principles that we use in NIR research have not changed, but the equipment that is available to us today is better.
2. Each new application is a puzzle where the analyst must determine the best instrument, optical geometry and sample handling. This means deciding what kind of instrument (filter, Diode array, dispersive, interferometer, etc.) what sampling geometry (spinning cup, fiber optic probe, standoff reflectance, etc.) and chemometrics should be used.
3. It helps to read the literature. The history of instrument development has many lessons that need to be passed on to new users. It also helps to reread the classic papers to obtain new foci for research.
4. NIR spectroscopy is more than a technique. It is a means of improving our world. We have improved our world with NIRS and will continue to do so in the future.
5. The Exhibition at NIR 2009 contained many of the best instrument offerings available today. I hope we all learned something new from it.

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