The last millennium: a brief history of science leading to current infrared technology

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Pre 20th Century

Much of near infrared (NIR) science, relating to its use for quantitative measurements, is very recent and most of the people who have contributed to its history are at this meeting. Please forgive me therefore, for not mentioning names; it would take too long and I might offend by omission.

I have looked back through the history of physics, mathematics and electronics and attempted to highlight the *inventive steps* and the *enabling technology*. Our use of infrared technology is, of course, too small to direct the course of science but we shall see that we have enthusiastically embraced new, enabling, developments as they have arisen.

It is always interesting to dig into the past. Many concepts that we think are new, already exist in another guise. Likewise, many ideas and discoveries have been so far ahead of their time that they could not be exploited and have almost been forgotten.

It is interesting to observe, for example, that angles of refraction for several materials were tabulated by Ptolemaeus in AD 130 and that in 1305, the splitting of light into the colours of the rainbow was simulated by Von Freiburg, using glass spheres and water-filled flasks. He clearly understood retro-reflection by spherical water droplets.

By 1700, the laws of refraction and internal reflection had been formulated and the slide rule invented. Most interestingly, the idea that light was a stream of corpuscles was being challenged in 1678 by Huygens when he determined that apertures were a source of wavefronts. Isaac Newton, himself inclined to the corpuscular explanation, was challenged in explaining his eponymous rings.

During the next century, the speed of light had been measured by Bradley (1728), the inverse square law enunciated by Joseph Priestley (1767) and the industrial revolution was underway in Europe.

In 1757, a penniless William Herschel had moved to England, fleeing from the French at the end of the Seven Years War, when Hanover was occupied. Working as an organist and music teacher in the north of England, his reputation grew and in 1766 he was appointed organist and director of music at the prestigious Octagon Chapel in Bath. As a composer, he wrote several symphonies and chamber works (some available today on CD). Herschel was much influenced by Professor Robert Smith whose book on “Harmonics” followed by his book on “Optiks” awakened Herschel’s interest in astronomy.

Now earning £400 per year he was rich, famous and moved in influential circles. His work on constructing reflecting telescopes is legendary, as is his meticulous work on cataloguing over 2500 nebulae. He is best known for his discovery of Uranus on 13th March 1781.

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For us, however, it is Herschel's discovery of infrared radiation in 1800 that is probably of the greatest significance. His two papers[1] detailing this work describe the use of three thermometers with blackened bulbs that he was using to study the heating effect in the solar spectrum. He observed that the effect was stronger towards the red and grew even stronger beyond the red, where no spectrum was visible to the eye. Herschel referred to this as "radiant heat" and the "thermometrical spectrum". Erroneously, he considered this form of energy inherently different from light.

In a letter written to Professor Patrick Wilson, in 1800, he makes the following enigmatic and possibly prophetic statement:

"May not the chemical properties of the prismatic colours be as different as those which relate to light and heat. Adequate methods for the investigation of these may easily be found; and we cannot too minutely enter into an analysis of light, which is the most subtle of all active principles that are concerned with the mechanism of the operation of nature."

The year 1800 also saw an important first step in programming, when Jaquard used punched cards to control a weaving loom. In 1801, Young, by coherently illuminating two slits, established the wave nature of light and in 1822, computing took a major step forward with Babbage's first difference engine. In 1823, Fraunhofer constructed and used a diffraction grating to resolve the sodium "D" lines present in the flame from a Bunsen burner. By today's standards progress was slow, particularly in the NIR where a suitable detector was lacking. In 1831, the thermocouple was invented and using it in 1835, Ampere concluded that infrared energy and light were one and the same thing by demonstrating identical optical characteristics. Important concepts in logic were developed, starting around 1847 by George Boole formulating what was to become known as Boolean Algebra.

Most of the underlying theory relating to the electromagnetic spectrum was developed in the latter half of the 19th Century. Kirchoff (in 1859) enunciated the black-body radiation law, stating that the radiated energy was solely a function of the temperature of the source and frequency. It was now realised that visible light represented only part of the radiation phenomenon. Incidentally, Kirchoff also obtained atomic spectra of many elements. James Clerk Maxwell (in 1864) formulated his four equations defining the propagation of electromagnetic radiation through space. Following the contributions of Stefan (1879) and Wien (1896), the end of the century was capped with Max Plank's radiation law (1900), expressing the spectral distribution of emitted radiation as a function of some physical constants and the absolute temperature.

During the second half of the century, the interaction of light with matter began to receive serious attention. Atomic absorption features were observed in solar spectra (Fraunhofer absorption lines) and Lord Rayleigh published his λ^{-4} electron resonant scattering law.

The evolution of spectrographic instruments was underway, the diffraction grating (initially produced by winding a thin wire round a pair of fine threads) had been developed and the prism was well established. Christiansen and Rayleigh both produced relatively narrow-band optical filters, using index-matching and dyes. In 1882 Professor Rowland gave the fledgling industry of spectroscopy a major boost by producing large ruled gratings and inventing the concave diffraction grating, which became the mainstay of spectrograph and spectrometer design.

In 1890 Hermann Hollerith applied Jaquard's programming principles and developed a tabulation machine to help with the US census. He then formed the Tabulation Machine Company, later to become IBM.

Just as Plank rounded off the century with his radiation law, in 1891, A.A. Michelson[2] published a paper describing the two-beam interferometer. Hence, we entered the 20th century with much the same range of optical techniques that we use today.

The observations mentioned above were made by eye, the infrared still lacked a suitable detector. However, around 1829 Niepce and Daguerre joined forces and invented the photographic plate. [The word photography was coined by Sir John Herschel (William's son) in 1839!]. By the mid to late

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1800's, it was noted that the photographic plate had some infrared sensitivity and in 1881 Abney and Festing[3] photographically recorded the spectra of organic liquids in the range of the Herschellian spectral domain, 1000–1200 nm. This work was of great significance because they realised the importance of atomic grouping in the NIR spectrum and the hydrogen bond in particular.

The 20th Century

At the beginning of the 20th century the early NIR industry was just underway. Still lacking was a suitable NIR detector and the need for computation had not yet arisen. However, the optical technology required was almost fully in place. Even the principle of the Laser was postulated by Einstein in 1917.

Stimulated by the work of Abney and Festing, Coblentz,[4] around 1905, produced a series of papers extending these measurements to many compounds over the spectral range 800–2800 nm. He identified the characteristics of C–H bonds and speculated on the existence of an harmonically related series.

During the first half of the 20th century many workers systematically extended the "spectral database" of organic compounds, assigning spectral features to functional groups. Industry was waking up to this new and exciting technology.

It is interesting to speculate on the date of the first quantitative measurement by infrared absorption. Perhaps it was made by F.E. Fowle in 1912,[5] at Mount Wilson, where he made line-of-sight measurements of atmospheric water vapour.

Electronics, too, was beginning to develop; in 1900 Fleming invented the vacuum tube and in 1919 the flip-flop bi-stable (Eccles & Jordan) had made its appearance. Interestingly, in 1926 Lilienfield (way ahead of his time) patented the NPN junction as a current amplifier. Two years later the cathode-ray tube made its debut. By 1936 Buracle had constructed the first electrical data logging machine.

The 1930's saw major developments in statistical science, spurred on by the study of populations. Notably, in 1933, Hotelling[6] wrote a classic paper on Principal Components Analysis and Mahalanobis formulated statistical criteria for defining the extent of and measuring the distances between data clusters in multi-dimensional space.

The rise of computing

In 1937/38, there were to be two events that changed the face of computing. Claude Shannon published his thesis on information theory and digital communication and Alan Turing created the first programmable computer. He went on to design "Colossus", a programmable computer using vacuum tubes dedicated to code-breaking the "Enigma" machine. By 1944, Maunchley and Eckert had developed "ENIAC" a computer with 18,000 tubes and consuming 150 kW. (There was a replacement bill for 19,000 tubes per annum). The first, truly commercial computer was "UNIVAC" produced during 1948/51.

William Shockley of Bell Laboratories patented the point-contact germanium transistor in 1947—one that could be manufactured this time—the technical revolution was really underway.

A very significant development in NIR was also in progress. Lead-sulphide (PbS), a compound semiconductor, had been studied for academic interest in the 1930's. It was recognised as a potentially sensitive near-infrared detector and for strategic reasons development was funded by both the German and British governments. Work started before the Second World War and continued through into the late 1950's. Because much of this was classified, the entry of PbS into the commercial arena was slow and discrete. However, in the late 1950's Mullard in the UK were offering a vacuum deposited PbS detector.

During the pre- and post-war periods, Von Neumann evolved the principles of modern computer architecture and stored programs. FORTRAN, developed from 1954 to 1958 by John Backus at IBM

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became the first, structured, scientific language, although Von Neumann originally dismissed it as a derivative of Turing's code.

The development of mainframe computers evolved rapidly but they were not to make their mark in infrared technology. Instead, developments at the opposite end of the scale were to dominate. In 1959 Kulb and Noyce (to be a co-founder of Intel in 1968) produced the first integrated circuit, working at Texas Instruments. It took until 1971 to produce the first microprocessor, the 4004. It had 256 bytes of ROM, a 60 KHz clock and 2300 transistors. By 1974 we had the Intel 8080 and the Motorola 6800. The first PC was probably the Altair in 1975 followed closely by the Commodore "PET" in 1977 (the same year that saw Bill Gates and Paul Allen found Microsoft).

IBM were late into the field with their first PC in 1981 but soon their designs defined the formats for compatibility.

Annual sales of PC's were around 300,000 in 1981 and over 3 million by 1982!—then third party software boomed—ask Bill Gates. The PC rapidly became the driving force behind NIR technology.

Following a few quiet years after the Second World War, the study of infrared absorption picked up with Wilbur Kaye's[7] and Whetsel's[8] work but most contributions were essentially academic; a really strong industrial need had not yet developed and instrumentation consisted of conventional spectrometers with some home-built modifications.

The analogue era

In America, during 1949, the US Department of Agriculture initiated an egg-grading program and Karl Norris was involved in making visible spectral measurements. By the mid-50's he had drifted into the very-near-infrared but was limited by detectors to < 1000 nm The excellent Cary 14 spectrometer was first produced in 1954 and Norris' group acquired one and substantially customised it. The dielectric interference filter was developed at the beginning of the 1950's by several workers following wartime work on antireflection coatings. They were not to be commercially viable until the 1960's.

The growing need for fast, quantitative determinations of moisture, protein and oil provided the impetus for developing reliable calibrations. The late 60's and early 70's saw the birth of what was to become the laboratory instrument sector of NIR analysis. Commercial instruments by Dickey–John, Technicon and Neotec slowly appeared and modern NIR technology was launched.

During this same post-war era Harry Willis, working at ICI in the UK, saw the need for the characterisation of polymers by NIR as early as 1945. Initially he worked with a pre-war instrument which scratched spectra on a drum covered with carbon–black. During the 1960's Willis was influential in the design of the Grubb–Parsons industrial spectrometer and began looking at ways of using NIR absorption for the on-line measurement of polymer film thickness. Here began the on-line school.

The first dedicated on-line NIR analyser appears to have been produced by Pier-Instrument in Germany in the late 1960's. It was vacuum-tube based and employed two interference filters for the measurement of moisture. Roger Edgar and I just might have been first; we delivered a two-filter instrument in 1968 to the IPC Research Laboratories. It employed the 2950 nm–OH absorption band to measure the thickness of the water-film on litho printing plates. We were both lecturers at Imperial College, London at the time. Perhaps the instrument should have been called "Moonlight 1".

At about this time Brun Sensor Systems produced an overly ambitious 3-component web analyser. It employed a 1 kW light source and approached melt-down if halted.

By 1970, Anacon in the US and Infrared Engineering in the UK were manufacturing instruments using up-to-date technology which gave reliable and, importantly, stable measurements. They were joined by Moisture Systems Inc. a few years later and rapid, competitive development was underway.

Laboratory and on-line technologies evolved along separate paths and to this day (sadly) there has been little interaction. However, both schools have evolved along similar lines, principally because they have both responded quickly to new technology.

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In the early 1970's analogue electronics was well established and formed the basis of practically all data reduction for NIR instruments. However, this very much limited the scope of the mathematical model employed to convert absorptions into quantities. Effectively, the data reduction was limited to a few additions, subtractions, multiplications, divisions and logarithms. Whilst regression on coefficients to perform initial calibration could be done, "off-machine" models were effectively limited to simple ratios or log ratios. The Beer–Lambert absorption law, as a model, reigned supreme. One thing all models at the time had to have in common was that the measured values had to be entered into the calculation to obtain a result. In other words, iterative techniques were beyond the scope of the electronics.

The Beer–Lambert law is strictly only true for plane parallel radiation and the absorption coefficient is assumed constant. It is unsuited to scattered light and wide illumination and collection angles. However it is simple—and it inverts:

$$I_t = I_0 \exp(\ \mathrm{kt}) \quad \text{becomes} \quad \log\left({}^{I_0}\!/_{I_t} \right) = kt$$

hence t (quantity) can be expressed as the input and absorbed intensities I_0 and I_t which can be measured. The absorption coefficient k is constant.

However, the following equation, a model for the transmission of an optically flat, absorbing film, cannot be inverted.

$$T = \frac{8 n_0 n_2 (n_2 + k_2)}{E \cosh\alpha + F \sinh\alpha \quad G \cos\beta + H \sin\beta'}$$

where $\alpha = 4\pi kt / \lambda$ and $\beta = \pi nt$. E, F, G and H are constants. In this case we wish to express t in terms of the measured transmission T. This model can only be used by trying values of t until the calculated and measured transmissions, T, match. This model had to wait until low-cost embedded microprocessors were available.

During the 1970's, NIR instruments found their way into many diverse applications. Foodstuffs, notably grain, (for the estimation of moisture, oils and proteins), formed the backbone of laboratory applications. On-line measurements were dominated by moisture (with tobacco being very important), paper, polymer film and coating thickness. Several thousand instruments were delivered.

Calibration, its maintenance and its transfer became a growing problem. The pioneering days were over and users wanted value, reliability and consistency.

Digital instruments and PC's

By 1985, instruments had embedded microprocessors, memory was still expensive but there was a new versatility. Sets of calibrations could be stored, input data could be powerfully manipulated and results could be analysed. Several new manufacturers appeared on the scene and a new group arose; the third party software vendors.

With PC's rapidly dropping in price and massively increasing in performance, powerful data analysis software became available for smoothing, curve-fitting, regression etc. At last, principal components analysis and cluster analysis, with their origins in the 1930's, could be harnessed. Chemometrics, the name given to this expanding field by Svante Wold, had been born. Full wavelength instruments challenged wavelength pre-selection and the relative merits of the two methods have been the subject of much controversy.

New optical techniques have also arisen with wavelength selection by non-linear optical crystals, acousto-optically-tuneable-filters (AOTF's) and wavelength specific emitting diodes and laser diodes. It remains to be seen how wide the appeal will be. Instruments based on diodes can be of low power

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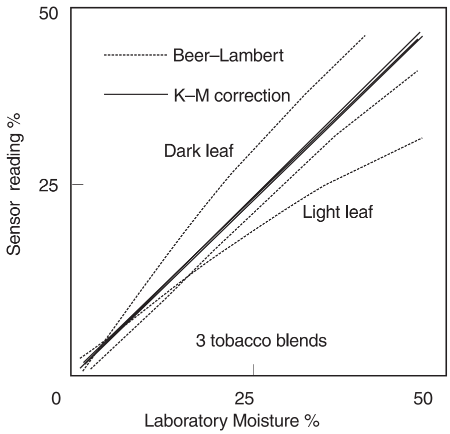
consumption and need not contain moving parts, lending themselves to portability. Likewise, the use of fibre-optical delivery means that in some applications (so far mainly pharmaceutical) a laboratory instrument can operate in the production environment or in hazardous areas.



Perhaps the 90's will be remembered for increasingly sophisticated data treatments attempting to ease the ever present burden of calibration. This burden has been imposed by the diversity of instruments, difficulties with reference standards and the lack of suitable mathematical models. Concerning the latter, Figure 1 shows the dramatic effect of incorporating a Kubelka–Munk approximation into a calibration for moisture in tobacco. Note the blend sensitivity of the Beer–Lambert calibration. The explanation for the improvement is simple. The higher the reflectivity of the blend the weaker is the corresponding moisture absorption band. The K–M approximation takes some account of reflectivity changes. The better model not only improves but simplifies calibration. Has too much been expected of chemometrics? Time will tell.

Over the last 20 years, much attention has been given to instrument design and data manipulation but little on the modelling of real scattering media. At last, there is new hope. Dahm and Dahm[9] have approached the problem of scattering from finite media and have formulated some new equations. Some of this work was revealed at the last Chambersburg conference and looks very promising. Perhaps others will be stimulated into developing modelling as the new field of infrared development?

Conclusions

Over the last two decades, NIR technology has gained wide acceptance, deepening market penetration and maturity. Over the last half century, workers in the field have been quick to exploit emerging technologies. The success of the technique is evident from the wide diversity of applications and in some industries, its acceptance as the reference method.

The implementation of more powerful processors, better algorithms representing improved NIR modelling will lead to easier and more robust calibrations. The next millennium holds great promise.

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