The history of near infrared spectroscopic analysis: Past, present and future – "From sleeping technique to the morning star of spectroscopy"

T. Davies

Norwich Near Infrared Consultancy, 75 Intwood Road, Cringleford, Norwich, NR4 6AA, UK

The history of the analytical use of near infrared (NIR) spectroscopy is reviewed and its future potential is assessed. This future is very bright if sufficient new researchers are attracted to this academically unfashionable spectroscopy.

"Glittering like the Morning Star, full of life, splendour and joy"

Edmund Burke, 1790.

In 1983 Professor David Wetzel wrote an article [1] for Analytical Chemistry in which he described near infrared (NIR) spectroscopic analysis as a "sleeping technique". At the time of the first international NIR conference held under the aegis of the International Committee for NIR spectroscopy (ICNIRS) in 1987 I referred to that paper and said that it was "Time for the Giant to wake up" [2]. A gap of a decade and the additional excitement of looking to the millennium justify a further re-assessment of the potential of NIR spectroscopy. I believe the "Giant" has woken up but that the future of NIR spectroscopy is so important that we can now see that the giant we had imagined is a pygmy compared to the potential of NIR to influence all aspects of our lives.

The past

Near infrared energy, as defined by IUPAC [3], extends from 780 – 2 500 nm (12 800 – 4 000 cm^{-1}). Fredrick William Herschel discovered it in 1 800 in an experiment [4], which should be taught to every school child. He looked for something where he "knew" there was nothing and discovered that the sun's energy was not limited to what we can see. In his experiment Herschel projected a rainbow on to a bench by the aid of a prism then he measured the relative heating effect of different parts of it (Fig. 1). As he moved from the blue to the red the heating effect increased. It was still increasing when he came to the end of the spectrum so he continued his measurements and found that the maximum heating effect was well into the black area passed the end of his spectrum. It could be said that the rest is history. But for most of the last two centuries Herschel's discovery was important as a stepping stone to the rest of the electromagnetic spectrum. There was a brief period of interest in the late 19th century, which can be summarised by the work of Abney and Festing [5] and then in the 1950's there was rather more interest, which has been recounted by Whetsel [6,7].

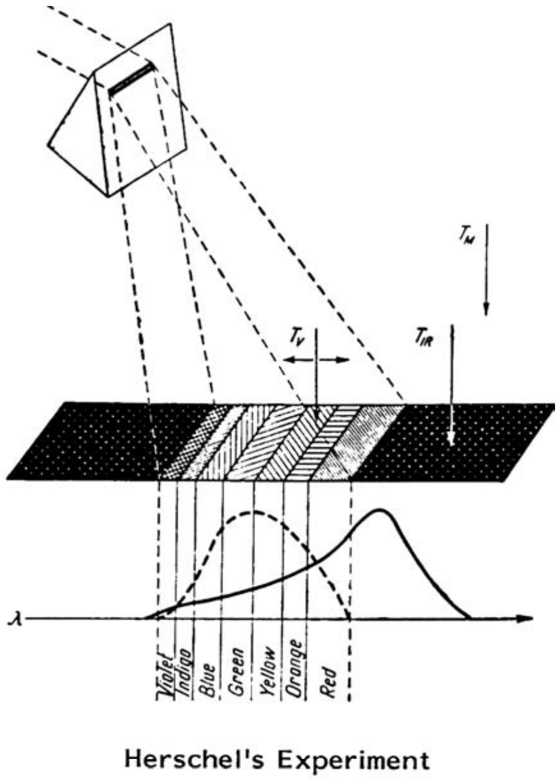

Figure 1. Herschel's experiment, which demonstrated the existence of NIR energy. Sunlight is diffracted to form a rainbow on a table, on which are placed thermometers. The thermometers can be positioned so that one is being subject to a band of radiation while the other two monitor the background temperature. The dotted line indicates the relative response of the human eye to the wavelength of radiation while the solid line indicates the relative heating effect.

© EDP Sciences, Wiley-VCH

Article available at http://analusis.edpsciences.org or http://dx.doi.org/10.1051/analusis:199826040017

The present

Almost all of the current use of NIR spectroscopy extends from the work of Karl Norris. Import contributions being made by Williams [8], McClure [9] and Shenk [10]. Norris's classical paper [11] has recently been republished in the Journal of Near Infrared Spectroscopy [12] making easily assessable for the first time for many years. It is well worth reading! This was a special volume of the journal to mark the occasion when the international NIR community made Karl Norris the "First Fellow of Near Infrared Spectroscopy" in recognition of his unique contribution to NIR spectroscopy. This award was made by the International Committee for NIR Spectroscopy during the 8th conference organised in its name, NIR-97 held at Essen, Germany in September 1997. The original work applied NIR spectroscopy to the determination of analytes in agricultural commodities the most important example being the protein content of wheat. Further work over the last twenty years extended NIR spectroscopy to the analysis of analytes in food [13], animal feeds [14], polymers [15], wool [16], textiles (natural and synthetic) [17], pharmaceuticals [18], chemicals [19], and petroleum [20]. The majority of this utilisation is in terms of quantitative analysis but in the pharmaceutical area the qualitative analysis of raw materials [21] has been the most important application. The recent work has been in environmental [22] and clinical analysis [23]. It is clear that there are few areas of analytical chemistry in which NIR spectroscopy has not been or cannot be utilised. What are the unique features that make NIR spectroscopy so versatile?

Some of the special features of NIR spectroscopy

Near infrared spectra are composed of absorptions due to overtones of fundamental bond stretching or bending vibrations occurring in the infrared region, combinations of the same fundamental absorptions and electronic vibrations (such as those occurring in rare earths). Every molecule containing hydrogen will have a measurable NIR spectrum and given the ubiquitous distribution of hydrogen this means that a very large number of analytes are amenable to NIR analysis. The formation of hydrogen bonds changes bond lengths and this changes the bond strength. The result of this is an apparent shift in the expected positions of absorption peaks. The formation of hydrogen bonds is very sensitive to the presence of other ions and temperature, which makes it possible to analyse solutes with no NIR absorptions when dissolved in suitable hydrogen containing solvents. The determination of sodium chloride in water was established many years ago [24]. A combination absorption only requires one of its vibrations to be infrared active, thus NIR spectroscopy can make measurements of absorptions which would normally be thought of as being only Raman active. This is apparent from some of the applications in the polymer industry [25] and was demonstrated by the work of Barton et al. [26] in two-dimensional spectroscopy, which linked spectra from Raman and NIR measurements of the same samples. The large number of possible vibrations give rise to very complex spectra, which were thought (in some cases are still thought) to be impossible to utilise. Except for the few systems investigated in the '50s the utilisation of NIR spectroscopy had to wait for the invention of the computer and its development as the laboratory or the personal computer.

Once we had computers then the advantages of NIR spectroscopy were apparent. Absorptions in the NIR region are much weaker than those in the IR region, which means that NIR spectra can be obtained directly on samples without the need for dilution. This makes diffuse reflection of solid samples amenable to direct analysis. Silica is transparent to NIR radiation, which makes cells and windows cheap and reasonably robust. Sensitive and low noise detectors in the form of silica photocells or lead sulphide photometers, fibre optic cables that transmit NIR energy and the computer chip, are all readily available. This makes possible the construction of comparative inexpensive, robust analysers, which can be used by relatively unskilled workers. These instruments have been made to work by the development and utilisation of the mathematical techniques known as chemometrics, without which the NIR revolution would not have occurred.

The future

The present phase of the development of NIR analysis has lasted for over a quarter of a century and it might be expected that by now it would be a mature technology approaching a plateau of utilisation. However, this is not the case. The development of chemometrics, miniaturisation of instrument components and new areas of applications has extended the rapid development phase for much longer than would be thought possible. It is currently possible to build cheap and robust spectrometers, which may foresee the advent of devices, which will be in every day use in household appliances. Actually the first of such devices may soon be found in cars as detectors of ice on road surfaces; an application presented at the recent international conference on NIR spectroscopy, NIR-97, by Huth-Fehre and colleagues [27]. I propose to highlight two areas of development which I believe are of paramount importance. If our hopes are realised, life in the 3rd millennium will be greatly influenced by advances in medical applications of NIR spectroscopy and by the development of NIR imaging systems.

Medical application

The use of NIR in medical applications has been pioneered by the work of Delpy [28] and colleagues at University College London. Their work on measuring the oxygenation status of the brains of premature babies has had far reaching consequences. An international conference in London in 1996 demonstrated that other groups had extended the work to measuring brain activity in human adults. Work being done by Lodder in the USA and Mantsch in Canada is likely to result in the use of NIR in the operating theatre becoming routine. Mantsch would go much further and suggest than NIR is capable of being used for the routine monitoring of health in humans; it had already been shown to be

© EDP Sciences, Wiley-VCH

able to differentiate between benign and cancerous tumours [29].

NIR imaging

Sometime in the next century NIR vision systems will be so common that people will wonder why evolution did not equip us with NIR vision! Actually the question of NIR and evolution is quite interesting but this is not the place for that discussion.

Pioneering work on the utilisation of NIR vision has been conducted by McClure in the USA [30] and by Bertrand et al. [31] in France. McClure was working with an automated horticultural system for tobacco plants. He demonstrated that a robot arm could be trained to replace a pot containing failed seedlings from a stock of pots of good seedlings in order to produce trays of plants ready for planting, containing close to 100% good plants. The robot used an NIR vision system to detect the pots of failed plants. More recently, I have proposed a relatively simple and robust system for use in food processing [32], which is based on the use of infrared emitting diodes.

But for an unfortunate accident we would by now be receiving data from the most recent development of this line of research. The satellite hosting the Hyper Spectral Imager (HSI) failed after a few days of flight. This spectrometer was designed to view the earth with a vision system that extended from 400 – 2500 nm (a visible and NIR vision system) to produce data arrays containing nearly 100 000 pixels. Although the project had quite modest agricultural aims such as detecting the type of crop being grown at any location, researchers hoped that it would be possible to detect part of a large field showing signs of stress (nutrient shortage, microbiological or insect infestation). Thus the system would be capable not only of monitoring the earth's agricultural production but also of controlling the quality of that production. The computer network required to realise this structure will be very large but the possibility is clear. And this is only one of the uses of the data! Others are pollution detection and control, mineralogy and of course military

Conclusion

In this brief article I hope I have alerted those who had previously not given serious consideration to NIR spectroscopy that this is a technique of value. It is important that this is achieved because the full potential of NIR analysis will only be realised if sufficient numbers of new graduates are attracted to NIR research and turn the possibilities into realities. This is not likely to happen if their teachers tell them that NIR is a region of overlapped absorbencies beyond human comprehension. If this downgrading were to continue, then the Morning Star will have a false dawn.

References

1. Wetzel, D. L. *Anal. Chem.* **1983**, *55*, 1165A-1176A.
2. Davies, A. M. C. *European Spectros. News* **1987**, *73*, 10-16.
3. Sheppard, N.; Willis, H. A.; Rigg, J. C. *Pure Appl. Chem.* **1985**, *57*, 105-120.
4. Herschel, W. *Phil. Trans. Roy. Soc. London* **1800**, *Part II*, 284-292.
5. Abney, W.; Festing, E. R. *Phil. Trans. Roy. Soc. London* **1881**, *172*, 887-918.
6. Whetsel, K. B. *N.I.R News* **1991**, *2*(3), 4-5.
7. Whetsel, K. B. *N.I.R News* **1991**, *2*(5), 10-11.
8. Williams, P. C. *Cereal Chem.* **1975**, *52*, 561-576.
9. McClure, W. F.; Norris, K. H.; Weeks, W. W. *Beitr. Tabakforsch. Int.* **1977**, *9*, 13-18.
10. Norris, K. H.; Barnes, R. F.; Moore, J. E.; Shenk, J. *J. Anim. Sci.* **1976**, *43*, 889-897.
11. Norris, K. H.; Hart, J. R. Proceedings of the 1963 International Symposium on Humidity and Moisture, Vol. 4; pp 19-25.
12. Norris, K. H.; Hart, J. R. *J. Near Infrared Spectrosc.* **1996**, *4*, 23-29.
13. Davies, A. M. C.; Grant, A. *Int. J. Food Sci. Technol.* **1987**, *22*, 191-207.
14. Murray I, Hall PA, *Anal. Proc. (London)* **1983**, *20*, 75-79
15. Davies, A. M. C.; Grant, A.; Gavrel, G. M.; Steeper, R. V. *Analyst (London)* **1985**, *110*, 643-647.
16. Connell, J. P.; Norris, K. H. *Text. Res.* **1980,** *50*, 371-380.
17. Ghosh, S.; Rodgers, J. in: Handbook of Near-Infrared Analysis, Burns, D.A.; Ciurczak, E. W. Eds., Marcel Dekker, New York, 1992; pp 495-526.
18. Ciurczak, E. W. in: Handbook of Near-Infrared Analysis, Burns, D. A.; Ciurczak, E. W. Eds., Marcel Dekker, New York, 1992; pp. 549-563.
19. Weyer, L. G. *Appl. Spectrosc. Rev.* **1985**, *21*, 1-43.
20. Workman, J. *J. Near Infrared Spectrosc.* **1996**, *4*, 69-74.
21. Rose, J. 2nd Annual Symposium on NIRA, Tarrytown, USA, 1982.
22. Malley, D. F.; Hauser, B. W.; Williams, P. C.; Hall, J. in: Near Infrared Spectroscopy: the Future Waves, Davies, A. M. C.; Williams, P. Eds., NIR Publications, Chichester, 1996; pp 691-699.
23. Hall, J. W.; Pollard, A. *J. Near Infrared Spectrosc.* **1993**, *1*, 127-132.
24. Hirschfeld, T. *Appl. Spectrosc*. **1985**, *39*, 740-1.
25. Miller, C. E.; Eichinger, B. E. *Appl. Spectrosc*. **1990**, *44*, 496-504.
26. Barton, F. E. II, Himmelsbach, D. S.; Archibald, D. D. *J. Near Infrared Spectrosc.* **1996**, *4*, 139-152.
27. Beard, J. *New Scientist* **1997**, 7.
28. Cope, M.; Delpy, D. T. *Med. Biol., Eng. Comput.* **1988**, *26*, 289-294.
29. Wallon, J.; Yan, S. H.; Tong, J.; Meurens, M.; Haot, J. *Appl. Spectrosc.* **1994**, *48*, 190-198.
30. Taylor, S. K.; McClure, W. F. in: Proceedings of the 2nd ICNIRS conference, Iwamoto, M.; Kawano, S. Eds., Korin Publishing Company, Tokyo, 1990; pp 393-404.
31. Robert, P.; Bertrand, D.; Devaux, M. F.; Sire, A. *Anal. Chem.* **1992**, *64*(6), 664-667.
32. Davies, A. M. C. *Proc. Cont. Qual.* **1997**, *9*, 139-142.

© EDP Sciences, Wiley-VCH