

Application of a multi-wavelength near infrared diode laser array for non-destructive food analysis

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Introduction

Near infrared (NIR) spectroscopy has become a widely used method in food and beverage analysis because of its speed, accuracy and the simplicity of sample preparation. If application of NIR spectroscopy is in the transmission technique the high-energy part of the near infrared between 1100 nm and 800 nm is preferred. The advantage is the larger penetration depth into the measuring medium. In comparison with mid infrared (MIR) one registers reduced NIR absorption around the factor 100, but due to the higher energy a 1000-fold larger penetration depth in the measuring medium is achieved.¹ For the wavelength area of 700–1100 nm, layer thickness from 1.0–20.0 cm is recommended to be still within the range of acceptable extinction.² Besides, it has to be taken into account that, due to the high energy, the sample under investigation might undergo structural changes. Clearly, biological material is particularly concerned if broad-band thermal radiation produced by an incandescent filament is employed. However, there are non-thermal types of emitter, which emit radiation from a much narrower range of wavelengths like laser diodes. The principal advantage of a non-thermal source is its efficiency: power consumption is much reduced lowering thermal dissipation. Diode lasers function the same way as lasers but linewidths are not as narrow as typical lasers. Since NIR absorption bands are relatively broad and only poorly dissolved due to overlays of overtones and combination bands, even the use of only relatively few laser diodes might already supply sufficient spectral information in the frequency range from 700 to 1100 nm. The broader linewidths of diode lasers are to be seen as advantageous for this application. Currently, standard diode lasers of adequate power output are not available for every wavelength in the range of 750–1100 nm and emitters produced for non-standard wavelengths are expensive. Thus, in this work, the suitability of an array of six (seven) standard diode lasers as light source for NIR transmission measurements in fruit and vegetables was investigated. Another requirement of NIR instruments is that detection must be efficient to enable measurements to be made in a reasonably short time, as for some applications (for example, sorting of fruits on a conveyor band) short response times are essential. For this purpose a fast diode array spectrometer (integration time from 3 ms) was used as the detector. The objective of this work was to investigate the ability of this experimental set-up to satisfactorily predict Brix values, firmness and internal defects in fruits and vegetables by non-destructive NIR transmission measurements.

Materials and methods

Materials

Apples (Rubinette variety), were from Obstgut Müller, Neuwied-Oberbieber, Germany, harvest season, 2000. Peaches (Concord variety) were from Staatliche Lehr- u. Forschungsanstalt, Neustadt / Weinstraße, Germany. Tomatoes (three different varieties) were purchased from a local market. For measurement of internal defects some of the Rubinette apples were artificially damaged by storing in different high carbon dioxide atmospheres which caused internal browning of different severity. Sucrose and deuterium oxide (D_2O) were from Merck, Germany.

Reference analysis of Brix value, firmness and internal defects

Cylindrical segments of about 2 cm diameter were taken from the fruits at the positions where the NIR measurements had been performed. After squeezing, the Brix value of the juice was measured using an AR 2008 digital refractometer (Krüss Optronic, Germany). Fruit firmness was measured by a TA-XT2i Texture Analyser (Stable Micro Systems, United Kingdom), firmness given as ($kg\ cm^{-2}$), force sensor area $3.14\ mm^2$. For estimation of internal defects in apples the fruits were cut into halves and the degree of defective tissue was classified visually on a scale between 1 and 9, where the latter corresponded to the severest defects.

NIR diode laser array

A schematic view of the array is given in Figure 1. Temperature-controlled laser diode modules LGT (LG-Laser Technologies GmbH, Kleinostheim, Germany) were used. The modules fulfil the same specifications (round beam profile and high coherence length) as Helium–Neon lasers, but are available for many more wavelengths. Seven LGT for single mode laser diodes were employed with the following wavelengths and net output powers behind the focussing optics: 785 nm/40 mW, 808 nm/50 mW, 830 nm/30 mW, 850 nm/50 mW, 920 nm/50 mW, 980 nm/50 mW and 1060 nm/25 mW. The 920 nm diode laser was not yet in operation during the acquisition of the presented first results. The power stability (peak to peak, 4 h) was $< 0.5\%$ deviation, noise (peak to peak, 0 Hz–20 MHz) was $< 0.5\%$. Operating voltage: 10–12 VDC, operating current: 0–3 A. The modules

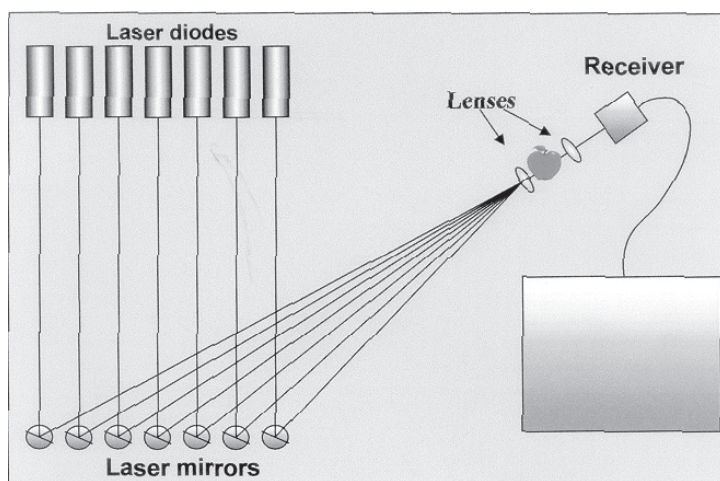


Figure 1. Schematic view of the NIR diode laser array.

were capable of modulation up to 20 MHz. A Basic-programmable interface (CIL Microsystems, United Kingdom) was used to control the lasers by TTL-pulses (+5 V: ON, 0 V: OFF) with a PC.

NIR transmission measurements

Near infrared 'spectra' were obtained using a transputer-integrated diode array spectrometer Tidas (J&M, Analytische Mess- und Regeltechnik GmbH, Aalen, Germany) containing a Zeiss MMS spectrometer module with 256 pixels. The spectral range was from 340 to 1150 nm, the minimal integration time was 1.4 ms. Measuring software was Spectralys (LabControl, Cologne, Germany). For measurements of sucrose concentrations a standard sample holder for 10 mm cuvettes was used connected to the detector via fibre-optics. For transmission measurements in fruits, using the experimental set-up shown in Figure 1, two spectra per fruit (in 90° angle) were recorded. Integration times were fixed for all measurements at three milliseconds for the reference (no sample in light path) and ten seconds for measurements of the samples. A typical spectrum of the reference is shown in Figure 2. *Quasi* absorption spectra (shown in Figure 3) were calculated by the measuring software and delivered in the format ".UVD".

Data analysis

Analysis of NIR data was performed by partial least squares (PLS) regression, using either Spectralys (LabControl, Cologne, Germany) or Opus NT (Bruker, Ettlingen, Germany). The latter automatically uses a variety of data subsets, spectral data point averaging, derivatives (1st and 2nd) and other data pre-treatments (for example, mean centring, multiplicative scatter correction and baseline correction) to determine the best data pre-treatment for each assay. The number of PLS factors used in the calibration was determined by the prediction residual error sum of squares F-statistic from the one-out cross-validation procedure. The accuracy of the developed calibration models was based on the high multiple correlation coefficient R^2 and low standard error of prediction (*SEP*) or the root mean square errors of prediction (*RMSEP*). In view of the fact that the NIR laser transmission measurements were done with varying path-lengths (diameters of the fruits) the data received from the reference method analytics were corrected for the manually determined path-lengths before entering them into the calibration process leading to unusual units like 'Brix per mm'.

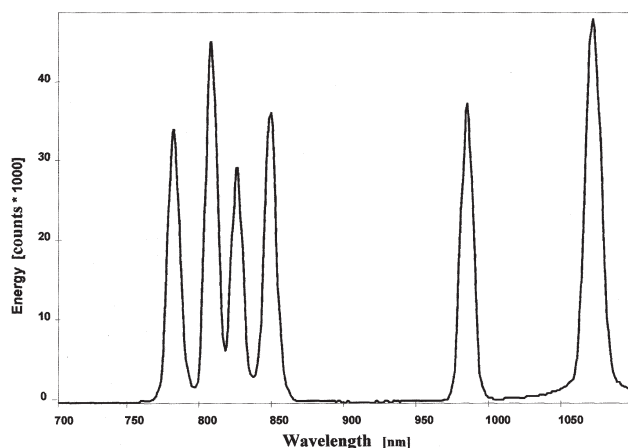


Figure 2. Typical reference spectrum (no material in the light path) of the laser diode array.

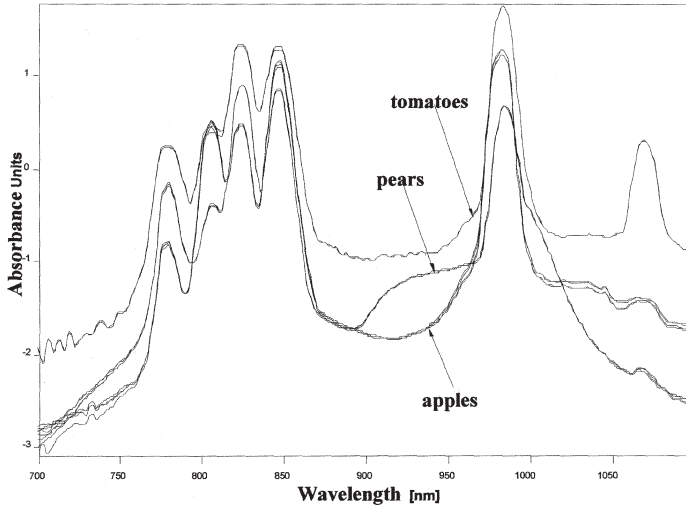


Figure 3. Typical 'absorbance spectra' of different fruits, recorded with the experimental set-up.

First results and discussion

Figure 2 shows a typical reference spectrum of the laser diode array. Note that the 920 nm diode laser was not yet in operation during the acquisition of the presented first results. The shown spectrum was recorded using a spectrometer module with 256 pixels over the spectral range from 340 to 1150 nm which means, dependent on the large spectral bandwidth of that detector (> 3.2 nm per pixel) the peaks appear broader than they actually are. Using a detector with a spectral resolution of < 0.8 nm

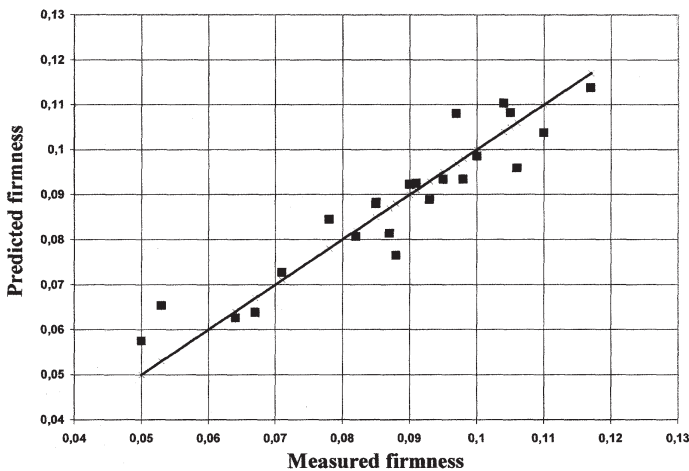


Figure 4. Correlation between fruit firmness obtained by the destructive mechanical method and that predicted by NIR.

Table 1. Comparison of calibration results of different assays.

Assay	R^2	$RMSEP$	R^2 for single laser					
			785 nm	808 nm	830 nm	850 nm	980 nm	1060 nm
Apples Internal defects (scale 0–9)	94	0.41	–02	59	66	64	91	77
Apples Firmness (range 3–9 kg cm ²)	88	0.43	47	58	74	35	52	61
Apples Brix (range 13–19%)	90	0.53	02	13	25	06	03	50
Pears Brix (range 10–18%)	93	0.49	03	10	12	21	31	33
Tomatoes Brix (range 4–7%)	97	0.24	36	36	65	66	29	15
Sucrose in D ₂ O (range 0–15%)	99	0.42	92	88	75	42	95	86

the peaks appear more narrow (data not shown): They cover about 5 nm at half height and about 10 nm at the basis. That means that fruits are illuminated by the laser diodes with light that usefully covers about 2–5 nm.

Typical ‘absorbance spectra’ of different fruits, recorded with the experimental set-up are shown in Figure 3. Note that they are only *quasi*-absorption spectra as they are calculated from spectra recorded with different—but fixed—integration times (see materials and methods). Differences between the ‘absorption’ spectra of tomatoes, pears and apples in the invisible range from 700 to 1100 nm can to be recognised.

The spectra of apples seem to contain enough spectral information to make possible calibrations for non-destructive measurements of fruit firmness. Figure 4 shows the correlation between fruit firmness obtained by the destructive mechanical method and that predicted by NIR. The $RMSEP$ was 0.43 (range 3–9 kg cm^{–2}). Good agreement between the conventional method and NIR was observed with $R^2 = 88$.

Table 1 lists the calibration results of further experiments carried out with apples, pears, tomatoes and sucrose solutions that were assayed for Brix values or sucrose content. Apples were also assayed for internal defects and firmness (see also Figure 4). In all cases good or acceptable values for $RMSEP$ and R^2 were achieved. In rows 4 to 9 of the table the correlation coefficients for calibrations using only the spectral range of a single laser are listed. For the determination of Brix values the wavelengths 830, 850 and 1060 show the highest correlation. The measurement of sucrose in heavy water relies mostly on the absorption at 980 and 785 nm which has to be expected from conventional absorption spectra. Wavelengths of 980 and 1060 nm give the best information on internal defects in the investigated apples. There might be a correlation with the water content (peak at 980 nm). Apple firmness correlates

best with absorption at 830 nm. The most valuable laser wavelengths of this investigation seem to be 830 and 1060 nm. Unfortunately, these laser diodes were commercially available only with about half of the output power of the residual used laser diodes. Some further improvement is to be expected from the 920 nm laser that was not yet in operation during the acquisition of the presented first results. This laser should be very suitable for transmission measurements in fruits containing much water since the high and broad water absorption around 980 nm is avoided.

Conclusions

Non-destructive food analysis (Brix value in apples, pears and tomatoes; Brix, firmness, internal defects in apples) using an array of NIR laser diodes in transmission mode, in combination with a fast diode array spectrometer as the detector, seems to be feasible. First calibration results are promising with respect to correlation coefficients and standard errors of prediction.

References

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2. L. Liekmeier, *Schwingungsspektroskopie im nahen Infrarotbereich*. Firmenschrift Perkin/Elmer Bodenseewerk, Überlingen, Germany (1984).