Hand-held near infrared spectrometry: status, trends and futuristic concepts

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Status

Increased interest in hand-held (HH) technology is reflected in the growing number of HH meters exhibited at PITTCON in just the last five to ten years (see Figure 1). It appears that no instrument manufacturer is exempt from the pressure to place their technology in the hands of customers.

Near infrared (NIR) spectrometers are more compact than they were five years ago. So called *portable* NIR instruments do exist, but truly hand-held NIR (HHNIR) meters have not yet appeared in the market place. The lack of commercial HHNIR meters is due, largely, to three problems: (1) Profit margins for HHNIR meters are small compared with portable units, (2) HHNIR meters furnished with calibrations may require additional resources to maintain and (3) NIR energy sources draw considerable power—too much for battery operation.

It is true that HHNIR meters do not command the profits enjoyed from laboratory and process analysers. Yet, interests in HHNIR meters will not go away. Millions of growers need an instrument to

Figure 1. Illustrating the trend in hand-held technology. Hand-held exhibits at the Pittcon meeting have increased several fold in the last five years.

monitor environmental abuse due to the misuse of farm waste and chemical fertilizers. Pharmaceutical manufacturing would like to have HH meters to test incoming raw materials and monitor processes. Clinical medicos are calling for pocket analysers to measure bioparameters related to patient health. This continued interest in HHNIR technology seems to indicate that the number of units required to satisfy needs would tend to offset the profit disparity.

Furnishing instruments with calibrations is not foreign to the NIR instrument laboratory. Infrasoft International does this on a routine basis, calibrations that involve both complex samples and complicated instruments. Research results[1,2] seems to indicate that calibrations for HHNIR meters would be no more of a problem than for laboratory instruments. Data seems to imply that calibration development, transfer and maintenance could be facilitated *via* the world wide web.

Finally, components for HHNIR technology are improving all the time. Recently, with a no-moving parts HHNIR meter costing less than $300 US, McClure and his associates[3] demonstrated that unfiltered light emitting diodes can be used to measure chlorophyll plant tissue and moisture in paper. Morimoto[2] developed a filter-based derivative spectrometer that utilised a low power Halogen lamp. Long life batteries provide adequate power to operate the Gmeter for up to 12 hours of continuous operation. Hence, HHNIR meters can be made to operate for long periods of time.

Though not approved for commercialisation as of this date, several companies are working feverishly to be the first to market a noninvasive hand-held blood–glucose meter.[4] Pushed by an annual $780 million financial incentive from invasive technology, a noninvasive blood-glucose meter would be a welcomed change to the more than 5 million diabetics in the USA alone. One of the first to attack the blood-glucose problem was Rosenthal.[5] His approach was to transmit NIR energy through the index-finger/nail to determine sugar content of the blood in the optical path. That work, conducted by a company called Futrex, was terminated in 1998 due to extenuating circumstances.[6]

Trends

McClure and his associates[2,3,7,8] have developed four NIR meters for measuring: (1) Nicotine and moisture in tobacco (Nmeter), (2) Vanillin and moisture in vanilla beans (Vmeter), (3) chlorophyll in growing plants and moisture in paper (Twmeter) and (4) protein and nitrogen in sugar/protein mixtures and grass tissue (Gmeter), respectively. This article will address the design and performance of these instruments.

Nmeter

Figure 2 shows the Nmeter mounted in a *laboratory caddy*. The Nmeter was initially intended to measure only nicotine in tobacco. However, the design permitted the incorporation of eight filters (1759, 1940, 2139, 2190, 2230, 2250, 2270 and 2310 nm) to the filter wheel, a feature which permitted the expansion of measurements to include total sugars and moisture. The filter-wheel was continuously driven by a stepper-motor. One reading was taken for each filter per revolution of the wheel.

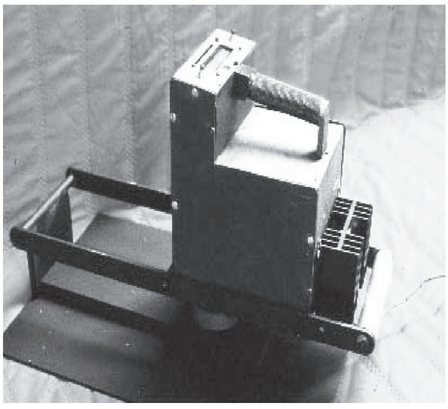

Figure 2. The Nmeter (nicotine meter) mounted in a laboratory caddy. The Laboratory caddy is used when acquiring data in the laboratory for the purpose of developing calibrations.

Software for acquiring filter readings, downloading data to a computer and uploading calibrations to the meter was written in C. With the filter wheel rotating at 60 rpm, twelve spectra (eight readings spectrum^{-1}) were recorded in about 8 s. The twelve readings were averaged to produce an *average spectrum*. Only average spectra were used for developing calibrations and computing the composition of *unknown samples*. The meter weighed 3 kg, a bit heavy for a hand-held device that was to be used continuously on eight hour shifts.

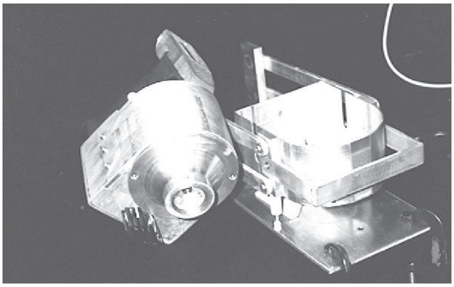

Figure 3. The Vmeter was designed to measure vanillin and moisture in vanilla beans. The meter is shown to the left of the laboratory caddy. The caddy is used to hold the Vmeter when recording data used to develop calibrations.

Vmeter

A picture of the Vmeter is given in Figure 3. It is a filter-based meter much like the Nmeter. It has a filter wheel with seven filters and a reference screen. The filter wheel is rotated with a DC motor at 640 rpm. Filter identification and position is made possible with a decoder-wheel attached to the shaft of the filter wheel. The Vmeter differs from the Nmeter in that it illuminates the sample with two lens-end Halogen lamps and filters the reflected light while the Nmeter filters the illumination and captures a portion of the reflected light. These two lamps draw 0.8 A at 5 volts and have a life of 10,000 hours. Adequate illumination was achieved by running the lamps at 3.4 V, reducing the load on the battery. The Nmeter weighs 2.6 kg without the battery and 2.9 kg with the battery.

The Vmeter was designed to opterate in two modes. In the first mode, the Vmeter is connected to a PC through an RS232 serial port. Due to added functionality, this mode is the preferred mode of operation in a laboratory environment. In the second mode, the Vmeter is disconnected from the computer for *field operation*, after calibrations have been uploaded from the computer to the meter. In this latter mode, meter measurements are displayed on the liquid-crystal display (LCD) and stored in the memory.

TWmeter

The TWmeter,[3] shown in Figure 4, was developed to minimise the cost of HHNIR technology. Dubbed the *TWmeter*, this device was conceived for use by researchers and others in *Third World* countries unable to afford more costly technology found in developed countries. Three light-emitting diodes (LEDs) were selected to measure chlorophyll and moisture in plant tissue. Centre wavelength and emission bandwidth of the LEDs (Sylonex, Inc., Plattsburg, NY, USA) were as follows: (1) 700 nm–100 nm, 880 nm–50 nm and 940 nm–50 nm. The 700 nm filter, near the chlorophyll absorption band of 673 nm, did not exactly correspond to the chlorophyll absorption maximum but the emission did provide illumination at 673 nm. The 940 nm emitter provided illumination at 960 nm, the absorption of water. The 880 nm emitter was chosen as a reference.

Figure 4. The Twmeter was designed to measure chlorophyll and moisture in situ. It has no moving parts and has a parts cost of less than US$300.00.

The TWmeter was powered with four 1.5 V alkaline batteries hooked in series to provide

Table 1. Performance of the Nmeter, Vmeter, TWmeter and Gmeter.

Meter	N	$R^{2\,a}_C$	*SEC*	*SEP*	$CV_P^{\,b}$
Nmeter					
Nicotine	327	0.933	0.226	0.228	8.1
Sugars	327	0.923	1.367	1.373	9.2
Moisture	327	0.728	0.794	0.976	8.1
Vmeter					
Moisture	60	0.977	0.710	0.857	5.8
Vanillin	60	0.865	0.324	0.672	17.4
TWmeter					
Chlorophyll	40	0.847	0.90	0.99[c]	18.1
Moisture	72	0.993	0.90	1.04[c]	1.8
Gmeter					
Protein[d]	60	0.990	2.570	2.740	6.3
Nitrogen[e]	60	0.951	0.581	0.630	17.2

[a]R^2_C = Coefficient of Determination for Calibration
[b]CV_P = *SEP*/Mean
[c]root mean square standard error
[d]in protein/sugar mixture
[e]in dry grass tissue

6.0 V that was regulated to + 5 V to power the meter. Measuring 10 cm wide, 19 cm long and 5 cm high, the TWmeter weighs 364 g and can operate continuously for more than 16 hours without changing batteries. The TWmeter has no moving parts.

Gmeter

A protype of the Gmeter[2] is shown in Figure 5. The Gmeter was designed to measure protein in protein/sugar mixtures and to measure nitrogen in plant tissue. It is unique in that it utilises 2nd derivative calculations from data obtained with narrow-band filters. The derivative is calculated according to a formula derived from the Taylor series expansion of a digital function. The filter wheel in the Gmeter can accommodate up to ten filters, however, only a single-term 2nd derivative utilising three filters has been tested so far.

Only the prototype meter has been built at this time. Calculations indicate that the Gmeter could be reduced to a cylindrical volume with di-

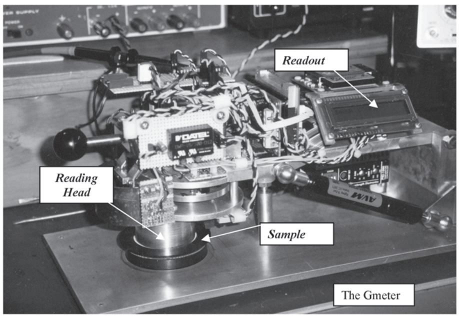

Figure 5. A prototype of the Gmeter mounted in a laboratory caddy. The Gmeter could be packaged in a cylinder 7 cm diameter by 8 cm tall and weigh less than one kilogram. It is the first meter to use filters to generate derivatives.

mensions of 7 cm diamter by 8 cm high and weigh about 1.5 kg. The Gmeter operates in the step-scan mode.

Performance

Performance data for all four meters discussed above are given in Table 1. A general rule-of-thumb, developed from experience in this laboratory, indicates that an application (calibration and prediction) is not very robust unless the coefficient of variation (*CV*) for prediction is less than 10%. Performance of all meters met this performance criteria for at least one assay. Nmeter data resulted in a CV_p of less than 10 for nicotine, sugars and moisture. The Vmeter produced a CV_p of 5.8 for moisture, but its performance for vanillin was less impressive (CV_p = 17.4%). The TWmeter did a good job of measuring moisture, but did not perform well when measuring chlorophyll. However, chlorophyll measurements are quite nonlinear[9] and the data shown is for a linear calibration. The Gmeter was designed to measure protein in protein/sugar mixtures and this calibration was robust. It was not optimised for measuring nitrogen in plant tissue, but the protein calibration did surprisingly well for measuring nitrogen (CV = 17.2%). If the filter selection was optimised for measuring nitrogen in plant tissue, the authors are convinced that the calibration would be robust.

Future prospects

Over the last 50 years, we have seen NIR instrumentation evolve into two areas: (1) The laboratory and (2) The process line. Process instruments (located *at-line, in-line* or *on-line* are designed to operate in high-temperature and dusty environments. Laboratory instrument, on the other hand, are designed to function in temperature/humidity-controlled labs.

More recently, managers of both laboratory and process analysers are finding an increasing need to make measurements remote from the line and laboratory. The ever increasing flow of products renders the falible human opinion useless. Objectivity, rendered by HH technology, enables managers to make intelligent decisions concerning the quality of both raw materials and product output.

The demand of HHNIR is here—now! The call for HHNIR will not go away. Problems facing this important contribution to spectroscopy will be overcome. HHNIR meters will appear within five years. More than likely, the first development will be the blood–glucose meter. However, HHNIR to monitor environmental abuse could be the first NIR meter on the market. Who will be the first?

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