

Miniature near-infrared spectrometer for point-of-use chemical analysis

Copyright 2014 Society of Photo-Optical Instrumentation Engineers.

This paper was published in SPIE Proceedings Vol 8992 899203-1, and is made available as an electronic reprint with permission of SPIE. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper are prohibited.

Photonic Instrumentation Engineering, edited by Yakov G. Soskind, Craig Olson,
Proc. of SPIE Vol. 8992, 899203 · © 2014 SPIE · CCC code: 0277-786X/14/\$18
doi: 10.1117/12.2040669
Proc. of SPIE Vol. 8992 899203-1

Miniature near-infrared spectrometer for point-of-use chemical analysis

Donald M. Friedrich, Charles A. Hulse, Marc von Gunten, Eric P. Williamson,
Christopher G. Pederson, Nada A. O'Brien*,
JDSU Corporation, Santa Rosa, California, USA 95407

ABSTRACT

Point-of-use chemical analysis holds tremendous promise for a number of industries, including agriculture, recycling, pharmaceuticals and homeland security. Near infrared (NIR) spectroscopy is an excellent candidate for these applications, with minimal sample preparation for real-time decision-making. We will detail the development of a golf ball-sized NIR spectrometer developed specifically for this purpose. The instrument is based upon a thin-film dispersive element that is very stable over time and temperature, with less than 2 nm change expected over the operating temperature range and lifetime of the instrument. This filter is coupled with an uncooled InGaAs detector array in a small, rugged, environmentally stable optical bench ideally suited to unpredictable environments. The resulting instrument weighs less than 60 grams, includes onboard illumination and collection optics for diffuse reflectance applications in the 900-1700 nm wavelength range, and is USB-powered. It can be driven in the field by a laptop, tablet or even a smartphone. The software design includes the potential for both on-board and cloud-based storage, analysis and decision-making. The key attributes of the instrument and the underlying design tradeoffs will be discussed, focusing on miniaturization, ruggedization, power consumption and cost. The optical performance of the instrument, as well as its fit-for purpose will be detailed. Finally, we will show that our manufacturing process has enabled us to build instruments with excellent unit-to-unit reproducibility. We will show that this is a key enabler for instrument-independent chemical analysis models, a requirement for mass point-of-use deployment.

Keywords: near infrared, miniature spectrometer, portable, linear variable filter, handheld spectrometer

1. INTRODUCTION

The optical and infrared spectroscopy industry is undergoing a major transformation akin to the computer industry. The size and weight of the instruments are shrinking from bench-top size to pocket-size. The cost is decreasing, and the performance continues to improve beyond just being acceptable. These miniature handheld spectrometers such as near infrared (NIR) spectrometers are creating new populations of users taking measurements in the field by nontechnical workers that were previously conducted in the laboratory by technical personnel. The tests are non-destructive and fast, taking only a few seconds to complete. This capability allows for obtaining real-time results that, in turn, lead to more efficient decision making. Users include farmers who would use their handheld NIR analyzers for a whole host of applications from analyzing the nutritional content of their forage for animal feed optimization to analyzing the nutritional content of their crop for determining the value of their yield, or for analyzing the soil for fertilization optimization [1]. Police officers, border patrol agents, or military personnel would use NIR spectrometers to analyze suspicious substances that may be illegal or lethal. Applications may even include inspectors from the Food and Drug Administration authenticating the types of fish imported [2]. NIR spectroscopy has been widely accepted for use in quality control in the manufacturing processes of pharmaceutical products, yet not sufficiently employed due to the high capital costs associated with the large instruments [3]. Miniaturization and affordability should enable wider proliferation of the NIR spectroscopy technology in the pharmaceutical industry [4].

*Corresponding author: nada.obrien@jdsu.com

The advancements that have enabled this exciting transformation in spectroscopy include improved detector technologies, MEMS and high-precision optical components for light dispersion, as well as other innovations in optical and electromechanical designs. Miniaturization of the optical system often faces technical challenges in thermal, stray light, and ruggedization management thus requiring careful consideration of the optical and mechanical design. In this paper, we report on the world's smallest NIR spectrometer sharing some of the systems engineering challenges that were overcome that resulted in a very rugged system with excellent spectral performance suitable for many on-the-go field applications.

2. SYSTEM DESIGN

We set out to make a miniature spectrometer for point-of-use NIR chemometrics applications. Key requirements for this application, in addition to optical fit-for use, are compactness, measurement speed, ruggedness, stability, portability and power consumption. We arrived at a Linear Variable Filter (LVF)-based optical train on top of an InGaAs array detector. The enabling element of our optical train is the LVF component that works by physically tapering the optical filter thickness with position, which results in a change in the center wavelength of the filter with position. A schematic of the effect is shown in Figure 1.

The LVF is a thin-film filter deposited with an energetic physical vapor deposition process, which makes it inherently stable with temperature and time. Filters deposited with similar processes are routinely used in undersea telecommunications applications, on deep space probes, and in other analytical instrumentations. An LVF-based instrument can have a very short optical train, because the dispersive element directly translates position to wavelength at the plane of the filter. To ensure ruggedness, we chose to mate the LVF directly to a detector array, rather than incorporate moving parts, which could increase size, decrease ruggedness, and increase power consumption. The overall optical bench is therefore very nearly the size of the detector array.

The key tradeoff in our design approach is light efficiency vs. resolution. The downside of an LVF approach is that the light efficiency is reduced compared to a Fourier transform-based instrument. Light that hits the LVF at the wrong wavelength is simply reflected. We improve this by lengthening the input area of the optical train and exploiting a non-imaging recirculation component. However, the overall light efficiency of the system is still inversely proportional to resolution.

To maximize LVF throughput, we chose an optical resolution that was well-suited to NIR spectroscopy, but not overly restrictive. In the NIR region, typical absorption band widths are around 1-2% of wavelength. Therefore, we targeted an optical resolution consistent with this need (e.g., the sharp talc bandwidth is about 0.6%). We also chose an InGaAs detector array which responds to light from approximately 900 nm to 1700 nm. By matching the LVF wavelength range to the detector range and utilizing a 128-pixel detector array, a geometric resolution of <1% is achieved.

One of the advantages that an LVF has in optical throughput compared to grating-based devices is the ability to easily handle a cone of light. To enhance throughput, we exploited this by designing the collection optics to collect as wide a field of view as we could without sacrificing resolution. For the current MicroNIR, the LVF filter is designed to accommodate a field of view of $\pm 14^\circ$. To allow as much light as possible, in as wide a cone as possible to enter the spectrometer, we chose a solid light pipe over a fiber bundle, and set the detector back from the diffuse input spot to optimize the field of view to the LVF.

For the detector we chose to use an InGaAs detector array, which is unmatched in the NIR wavelength range for sensitivity. The base range of 900-1700 nm is useful for moisture applications. Realizing some applications demand a longer wavelength, we also designed an instrument around an extended wavelength (1100-2200 nm) detector. For both situations, we opted to go with an uncooled detector, avoiding the increased size and power budget of a cooler that we felt was detrimental to our applications. The TE cooler alone would have far exceeded the 2.5W allowable power budget of a USB-powered device which has been our target for portability.

This approach resulted in an optical bench that would meet the requirements for optical fit-for-purpose, ruggedness, compactness and stability. To field a self-contained portable instrument, the spectrometer contains an onboard

illumination source and electronics. For maximum usability, we designed the electronics as a standard USB device, and added lamps that would provide as much broadband light as possible while keeping the overall power budget under the requisite 2.5W of a high-power USB device. Two small tungsten lamps provided the perfect tradeoff between electrical power consumption and optimal broadband light output in the 1000-2000 nm range.

The resulting handheld spectrometer that we refer to as the MicroNIR™ Spectrometer is shown in Figure 2. A cross-sectional view of the optical train is shown in Figure 3.

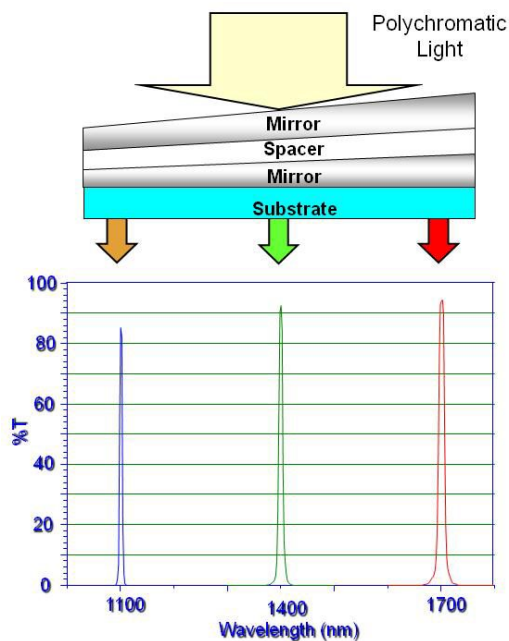


Figure 1: Working principle of a linear variable filter (NIR) component. The wedge in the thickness is applied to all layers comprising the bandpass filter design.



Figure 2: The MicroNIR spectrometer.

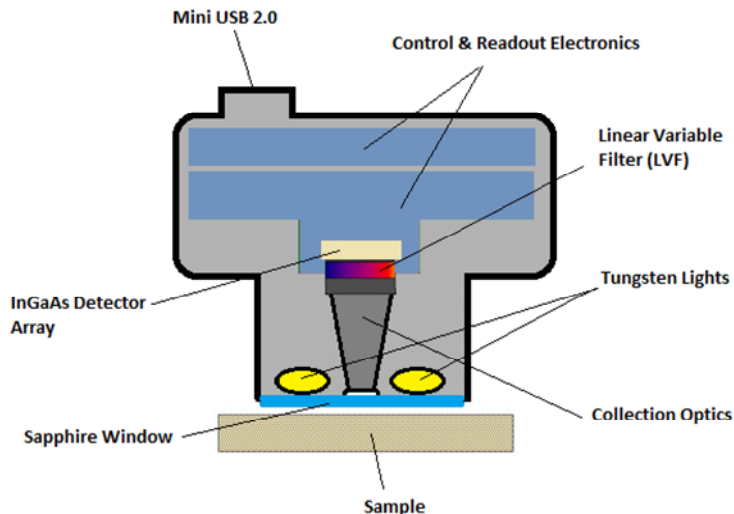


Figure 3: An illustration of the optical design of MicroNIR in diffuse reflection mode.

3. PERFORMANCE ATTRIBUTES

Key attributes of the MicroNIR spectrometer are summarized in Table 1. For applications in point-of-use and process analytical technology (PAT), measurement reproducibility among multiple MicroNIR spectrometers as well as repeatability of measurements on each MicroNIR must be well understood in order to be designed optimally into each application. Measurement reproducibility and repeatability involve determination of both wavelength calibration and photometric stability.

Table 1: Key performance attributes of the MicroNIR spectrometer.

Weight	60 grams
Dimensions	45mm diameter x 42mm height
Spectral Range	MicroNIR 1700: 950-1650nm
Number of pixels	128 pixels
Optical Resolution	<1.25% of center wavelength, i.e. at 1000nm wavelength, resolution is <12.5nm
Geometric Resolution	MicroNIR 1700: 6.25nm per pixel
Wavelength Accuracy	< 3 nm, as compared to NIST SRM-2036
Wavelength Repeatability	< 1 nm, as compared to NIST SRM-2036
Power Requirement	USB powered, <500mA at 5V
Operating Temperature	-20°C to 40°C

Calibration of the wavelength scale of LVF-based spectrometers differs from that of FTIR interferometers and diffraction grating based spectrometers. In the MicroNIR spectrometers, wavelength calibration reproducibility and

consistency among multiple units is achieved in two steps. First, the LVF is precisely aligned over the detector array. The wavelength scale (λ_{nm} vs. pixel) is determined using select absorption bands of a NIST traceable wavelength reflectance standard (Avian WCR 2066, equivalent to NIST SRM-2036) (Figure 4). The standard deviation of wavelength placement in a group of 32 MicroNIR 1700 spectrometers was determined to be ~ 1 nm across all pixels of all spectrometers. This small variation does not affect the accuracy of the individual wavelength calibration of each spectrometer. However, the variation does produce wavelength -vs.- pixel calibration scales that are slightly different for each spectrometer and has therefore necessitated a second step. An algorithm is applied to interpolate reflectance spectra of all spectrometers to a standard grid of 125 data points. This interpolation is effective in presenting the spectra from multiple units onto a common wavelength scale (MicroNIR Standard Grid) and enables spectrometer-to-spectrometer photometric calibration transfer for chemometric analysis involving multiple spectrometers. Both the original 128 pixel spectrum (“native grid”) and the interpolated 125 point spectrum (“standard grid”) are available to the user in the MicroNIR output.

Photometric reproducibility is demonstrated by the variation of reflectance values of the WCR-2066 standard across the 125 pixels of the MicroNIR standard wavelength grid for 32 spectrometers. Standard deviation is on the order of 0.5% across the central wavelength range 1000 – 1600 nm. In the shorter and longer wavelength ranges, photometric variation increases somewhat due to rapidly decreasing detector responsivity in those regions. Figure 4 shows the reflectance spectra of a WCR-2066 standard scanned by 32 MicroNIR spectrometers. These spectra were scanned and automatically converted to the standard wavelength grid. Figure 5 shows how the standard deviation varies with wavelength across the detector array.

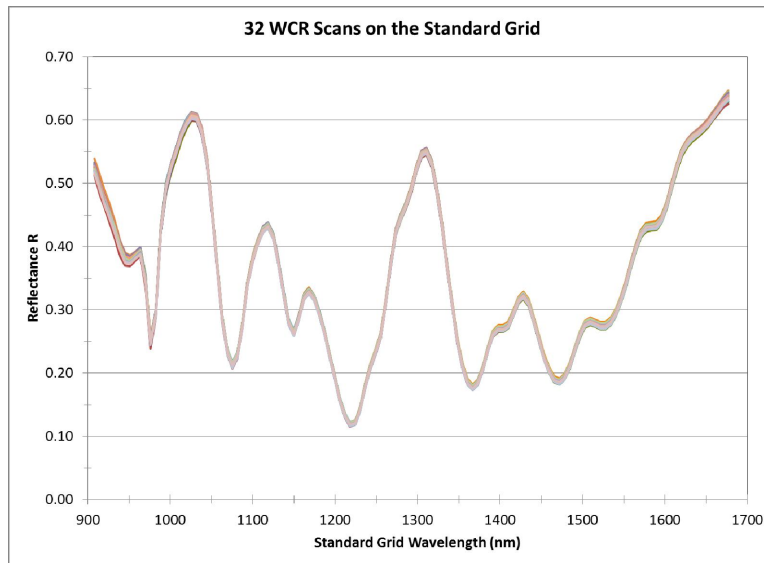


Figure 4. Wavelength reflectance standard WCR-2066 scanned by 32 MicroNIR 1700 spectrometers and displayed on the MicroNIR standard wavelength grid.

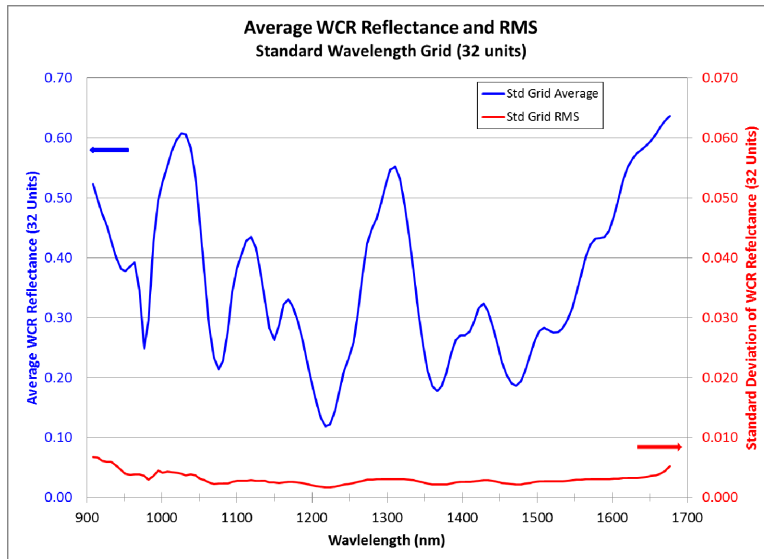


Figure 5. Standard deviation of the reflectance values of WCR-2066 scanned by 32 MicroNIR 1700 spectrometers and displayed on the MicroNIR standard wavelength grid. The upper trace is the wavelength standard (WCR-2066) averaged over 32 spectrometers.

Stability of wavelength calibration is a key concern in spectrometer deployment over time and into environments with large temperature variations. A single MicroNIR 1700 was initially wavelength-calibrated with the WCR 2066 standard. Then wavelengths values of absorption peaks of another standard, NIST SRM 1920, were measured by the spectrometer and tabulated for 160 days. Figure 6 shows the variation of the SRM1920 wavelengths reported by the spectrometer. The variations are less than 0.2 nm, except for one short wavelength peak (1013.8 nm, 0.4 nm rms across 160 days) which was subject to measurement error due to its small amplitude and location in the low responsivity short wavelength range of the spectrometer. Thus, the MicroNIR wavelength calibration is stable, with variation over time much less than the specified wavelength repeatability.

Stability of the MicroNIR was evaluated by environmental testing including temperature/humidity cycling (MIL-PRF-28800F Class 3 Temperature and Humidity); shock/vibration (MIL-PRF-28800F Class 2 Shock and Vibration); and package drop tests (ISTA 2A). Wavelength calibration varied less than ± 0.7 nm during the temperature and humidity tests, including operation at $+50^{\circ}\text{C}$ and -20°C , and varied less than ± 0.2 nm when compared to before and after the shock and vibration tests. Temperature and humidity profiles are shown in Figures 7 and 8.

The environmental chamber test set up is shown in Figure 9.

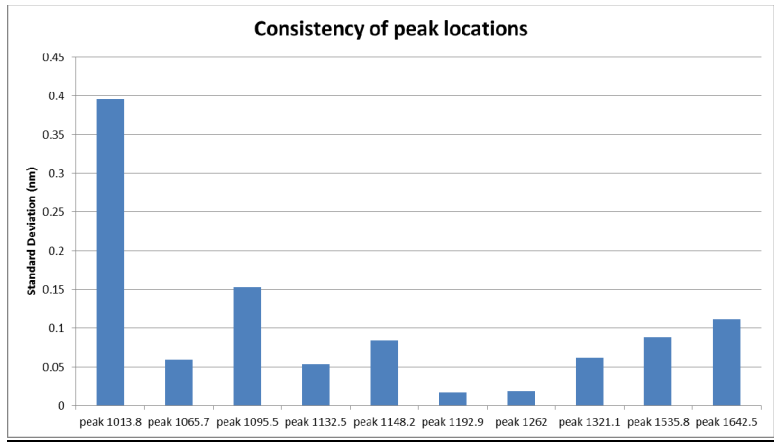


Figure 6. Variation in detected peak location over 160 day study.

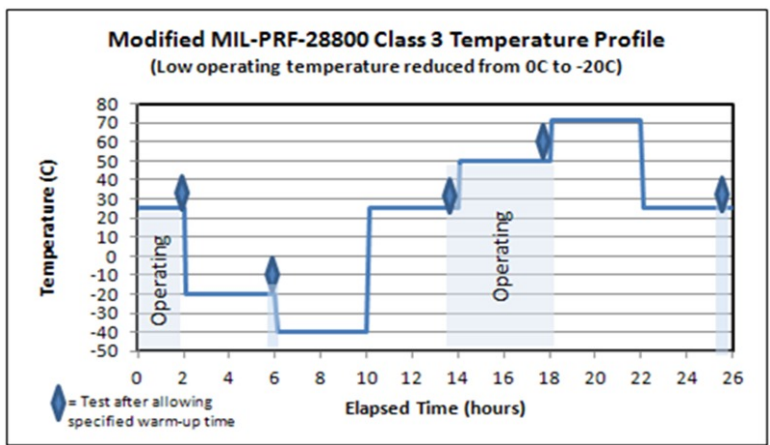


Figure 7. Temperature cycling MicroNIR 1700 with modified MIL-PRF-28800 Class 3 profile.

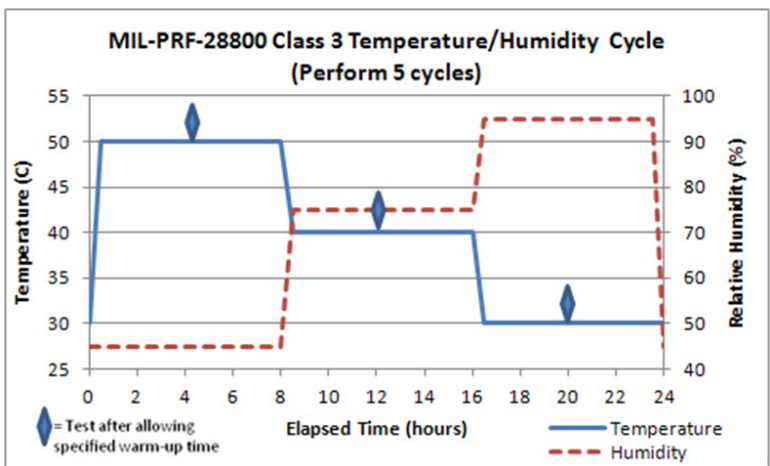


Figure 8. Humidity testing MicroNIR 1700 with MIL-PRF-28800 Temperature/Humidity cycle

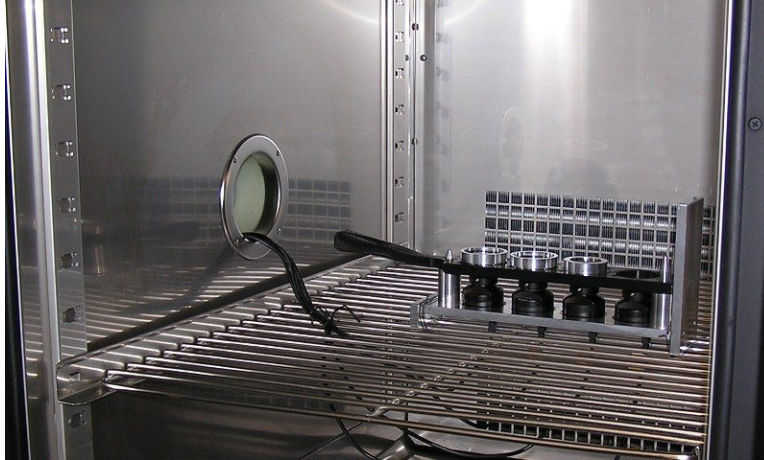


Figure 9. Temperature and humidity chamber with fixture holding MicroNIRs and measurement standards.

4. APPLICATIONS EXAMPLES

NIR spectroscopy is a highly desirable technology due to its high sample measurement flexibility. Samples ranging from liquids to powders to films and slurries can easily be measured in the NIR spectral region. Furthermore, NIR is capable of measuring through transparent sample packaging such as glass and plastic further adding to the technology's flexibility. As a result, applications of NIRS vary widely across industries, however. A common demand in many industries is rapid material qualification (identification and conformity). Having a handheld spectrometer to ascertain quickly the quality of manufacturing materials is critical to most manufacturing operations.

The World Health Organization (WHO) estimates that roughly 10 percent of the world's pharmaceuticals may be counterfeit, with far higher rates in parts of the developing world. Illegal generic imports not only threaten public safety but also erode brand owner's profit margins. Counterfeiting and illegal drug imports are global crimes with well documented consequences [5].

The MicroNIR has been demonstrated as a suitable technology to investigate the possibility of counterfeit product detection. The following plots show the 2nd derivative of the NIR spectra of known authentic drugs compared against example counterfeit products of the authentic brand.

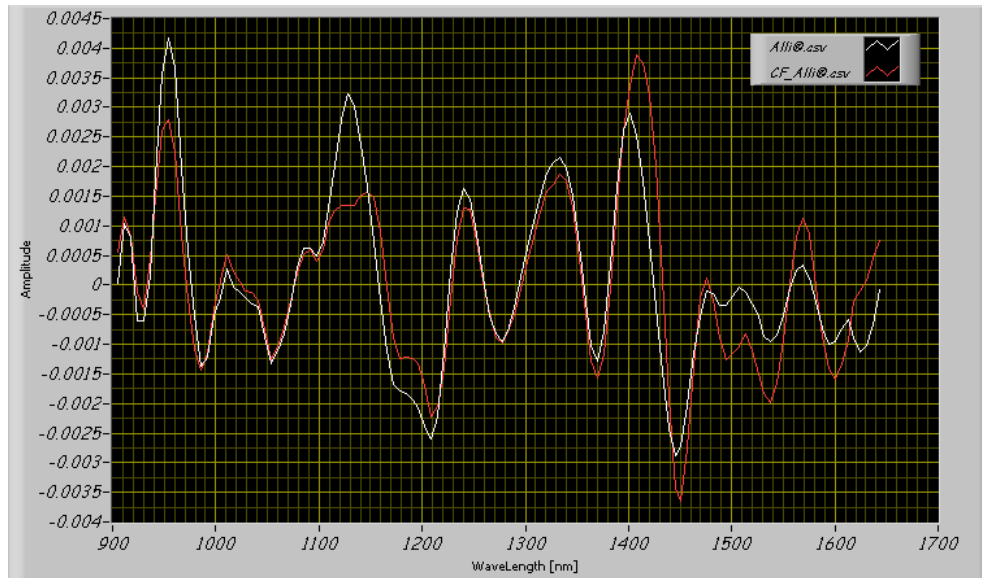


Figure 10: Authentic Alli® (white spectrum) and counterfeit Alli (red spectrum) weight loss capsule blends

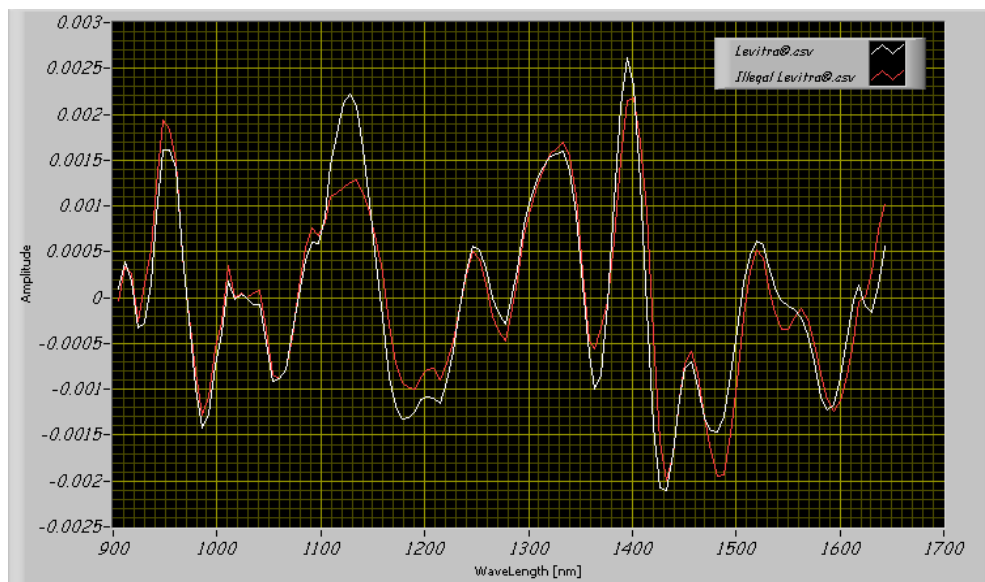


Figure 11: Authentic Levitra® (white spectrum) and illegal generic (red spectrum) tablets

Clear spectral discrepancies are seen in both of the above examples demonstrating NIR spectroscopy's ability to easily distinguish fakes and illegal generics from the branded authentic products.

Counterfeit detection is not limited to the pharmaceutical industry, but rather more instances of fraud are occurring in the food industry as well. A recently published report on one of the largest surveys conducted to date about seafood fraud revealed that one-third of seafood species purchased at restaurants and grocery stores in cities across the United States were mislabelled [6].

The following photos show a winter codfish next to a typical codfish. Visually the samples are quite similar, but the market value is substantially different.

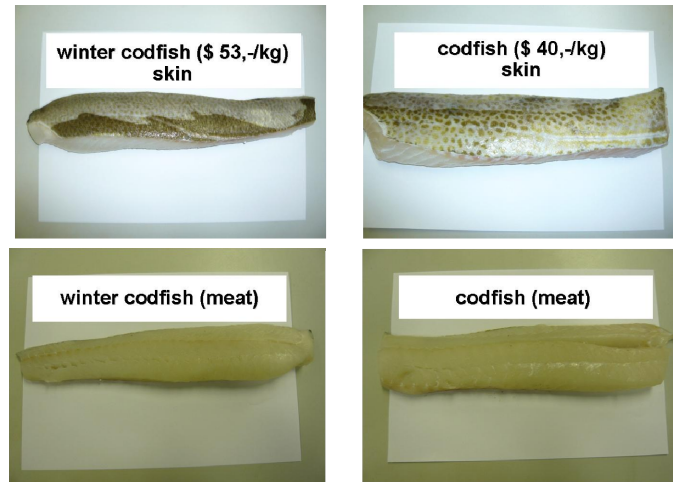


Figure 12: Winter codfish meat and skin samples

NIR spectra were collected on samples from each fish type and spectrally compared. The following plots demonstrate the MicroNIR's ability to discriminate between similar species of fish fillets. Figure 13 shows a 3-dimensional score plot result from a Principle Component Analysis (PCA) of a spectral set containing both winter codfish and codfish. The different spectra from the respective classes group with each other creating a cluster effect. The separation of the clusters indicates the presence of significant spectral characteristics of the two classes.

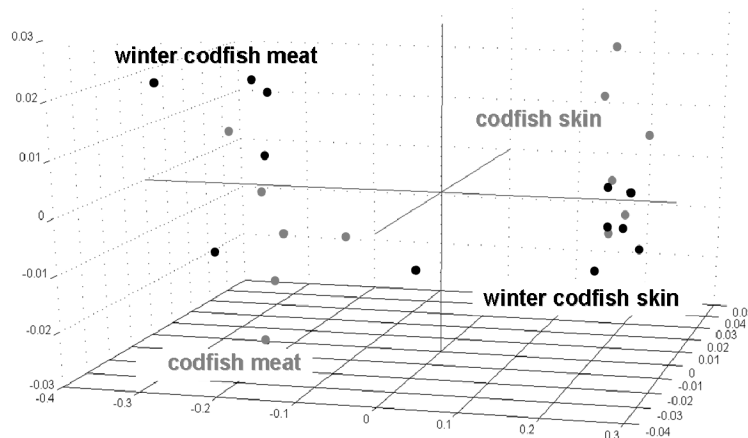


Figure 13: 3D score plot of the PCA model (1 factor, no outlier) for the discrimination of the different codfish.

Following the PCA analysis, unknown samples of the two classes were then classified using a SIMCA classification method. SIMCA is Soft Independent Modelling Class of Analogy, is a statistical method for supervised classification of data. The method requires a training data set consisting of samples (or objects) with a set of attributes and their class membership [7].

Figure 14 shows the visual result of the SIMCA analysis where the test fish were compared against the training data and the test samples were correctly classified.

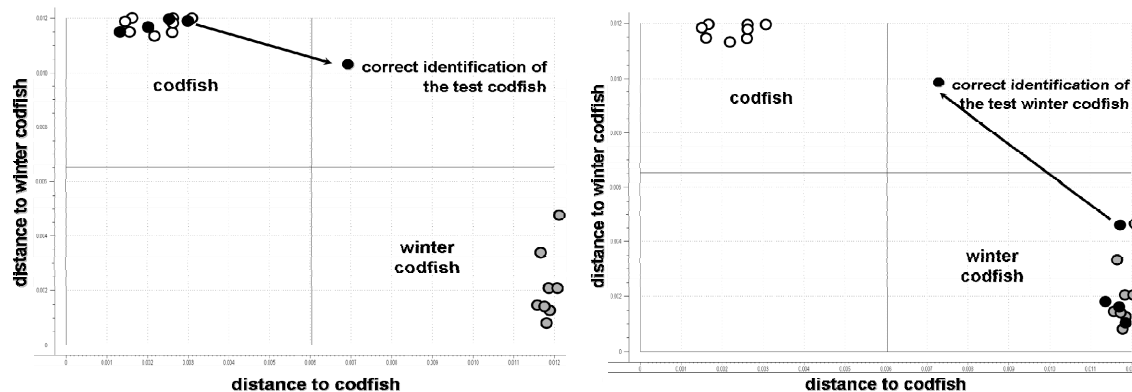


Fig. 14: Coomans plot of a SIMCA analysis (5% significance) demonstrating the correct identification of a test codfish file (top) and a test winter codfish file (bottom) measured on the skin and meat.

Implementing a handheld spectrometer such as the MicroNIR enables a company (or an industry) to help protect its brand and the possible safety of its customers.

5. CONCLUSIONS

We have shown that an LVF-based spectrometer can achieve excellent performance in terms of system to system reproducibility, measurement repeatability, and environmental stability. The ultra-compactness, low-cost, and the low-power consumption, along with the ability to leverage cloud computing, and operate the MicroNIR through a smartphone or a small tablet computer, will enable ubiquitous real-time analysis in a wide range of applications in the food, agriculture, and healthcare industries. Other wavelength ranges are possible with the proper selection of detector, optical elements and LVF materials.

REFERENCES

- [1] Shenk, J. S., Workman, J. J., Westerhaus, M. O., [Handbook of Near-Infrared Analysis], Burns, D. A and Ciurczak E. W. (editors), 3rd Edition, CRC Press, Boca Raton, USA, 347-386 (2008).
- [2] O'Brien, N., Hulse, C.A., Pfeifer, F., Siesler, H.W., "Near infrared spectroscopic authentication of seafood," J. Near Infrared Spectroscopy, 21, 299-305 (2013).
- [3] Anderson, C.A., Drennen, J.K., Ciurczak, E.W., [Handbook of Near-Infrared Analysis], Burns, D. A and Ciurczak E. W. (editors), 3rd Edition, CRC Press, Boca Raton, USA, 585-611 (2008).
- [4] Alcalà, M., Blanco, M., Moyano, D., Broad, N., O'Brien, N., Friedrich, D., Pfeifer, F., Siesler, H., "Qualitative and Quantitative Pharmaceutical Analysis with a Novel Handheld Miniature Near-Infrared Spectrometer." J. Near Infrared Spectroscopy, 21(6), (2013). doi: 10.1255/jnirs.1084
- [5] T. Mackey and B. Liang, Journal of Pharmaceutical Sciences, Vol. 100, No. 11, November 2011
- [6] K. Warner, W. Timme, B. Lowell, and M. Hirshfield, "Oceana Study Reveals Seafood Fraud Nationwide", February 2013 report, written by Oceana
- [7] Wold, Svante, and Sjostrom, Michael, 1977, SIMCA: A method for analyzing chemical data in terms of similarity and analogy, in Kowalski, B.R., ed., Chemometrics Theory and Application, American Chemical Society Symposium Series 52, Wash., D.C., American Chemical Society, p. 243-28