On-Site Quality Control and Protection against Product Counterfeiting by Handheld Near-Infrared Spectrometers

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Open-Minded

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Handheld Vibrational Spectroscopy

Market research institutions have predicted miniature spectrometers to reach a business volume of approximately \$ 300m by 2021.

This growth is based on a wider adoption of spectrometers for:

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Short Historic Review of Miniaturization in Vibrational Spectroscopy



FT-IR Spectrometer in the mid-1970s

Raman Spectrometer in the 1980s



Short Historic Review of Miniaturization in Vibrational Spectroscopy



External Reflection

Diamond ATR

Bruker ALPHA



2005 ~7 kg

High Modularity

Mini-Laboratory for Vibrational Spectroscopy



Handheld Vibrational Spectroscopy

Examples of Miniaturized Vibrational Spectrometers in 2020







FT-IR

Raman

FT-IR + Raman

Raman (785/1064 nm excitation, ORS, SERS) IR (as FT-IR for ATR and diffuse/regular reflection) NIR (LVF, DMDTM, FP-TF, FT-NIR, Grating) (for diffuse reflection and transflection) weight: > 1kg
prize: >> 10 K US\$
weight: < 100 g
prize: < 10 K US\$
(high-volume: ~ x00 US\$)</pre>

Raman, IR: due to the high prize \longrightarrow restriction to industrial, military, homeland security applications and public use by first responders, law-enforcement and environmental institutions

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Short Summary of Practical NIR Applications

On-Site Law Enforcement illicit drugs, customs investigations

Industrial

sensor implementations in processes (e.g. real-time control of blend homogeneity) identity control of pharmaceutical formulations exploration of geological test samples (e.g. bauxite) remediation/exploration of soil (TPH) identification/discrimination of polymers (recycling)

Public and Non-Expert Interests

authentication of a broad range of products: textiles, carpets, pharmaceuticals food testing/authentication: sea-food, spices, oil, milk powder nutritional parameters (fat, protein, energy, carbohydrates, fiber)

Regarding the Selectivity of NIR



J. Workman Jr., L. Weyer, Practical Guide and Spectral Atlas for Interpretive Near-Infrared 2nd ed. CRC Press, Boca Raton, USA (2012)

H.W. Siesler, Near-Infrared Spectra, Interpretation: J.C. Lindon, G.E. Tranter, D.W. Koppenaal (eds.) The Encyclopedia of Spectroscopy and Spectrometry. Oxford: Academic Press, p 30-39 (2017)

Regarding the Selectivity MIR versus NIR







NIRscan Nano EVM, TI, DMD™





900 – 1701 nm SR 10 nm S/N ~ 3500 : 1

Spectral Engines FP Tunable Filter



1100 – 1350 / 1350 – 1650 1550 – 1950/1750 – 2150 2000 - 2450 nm SR 14 / 15 / 18 / 19 / 23 nm S/N 15000 : 1 - 1500 : 1

Si-Ware Systems MEMS FT-NIR



1298 – 2606 nm SR 8 nm / 1550 nm S/N ~ 2800 : 1 (2017) S/N ~ 2100 : 1 (2020)

Hamamatsu Photonics MEMS FT-NIR



1100 – 2500 nm SR 5.7 nm / 1533 nm S/N 10000 : 1

Southnest Technology MEMS FT-NIR





800 – 2600 nm SR 2.5 nm / 1000 nm – 13 nm / 2400 nm S/N 9000 : 1

Senorics SENOCORDERInsion NIR GratingOtO Photonics NIR16 solar cells as detectorsMicrospectrometerGrating Spectrometer



1170 – 1675 nm S/N ~ 4500 : 1 (for 1339 – 1509 nm)





900 – 1700 nm SR <16 nm S/N ≥ 5000 : 1

900 – 1700 / 900 - 2500 nm SR 8.5 nm / 18 nm S/N > 5000 : 1 / 2000 : 1

Announcement by BASF (Ludwigshafen, Germany)

BASF founded (2015) startup trinamiX has developed the Hertzstück[™] PbS infrared sensor (wavelength range 1000–3000 nm).

HertzstückTM can be installed as a sensor chip on the circuit board of a smartphone.

First spectrometers will be available in 2019 for industrial/semi-professional applications. BASF hopes that consumers will have access by 2022.



Selected Industrial Applications: Determination of TPH in Soil

The on-site analysis of soil for the exploration of TPH (total petroleum hydrocarbons) is an important industrial issue.

Furthermore, contamination of soil by hydrocarbons due to accidents or leakages is a potential health risk and an issue of environmental and industrial concern \implies assessment of remediation measures that have to be taken (excavation, biotechnical method).

Diffuse-reflection NIR spectroscopy with handheld instruments proved a powerful tool for this analytical problem.

Handheld versus Benchtop Measurements

Handheld NeoSpectra **Benchtop** Scanner quartz cup with soil sample quartz cup with soil sample **Perkin-Elmer** benchtop FT-NIR spectrometer (with integrating sphere)

Handheld versus Benchtop Measurements



Handheld versus Benchtop Measurements



On-Site NIR Spectroscopy of Geological Test Samples

In exploration studies of the mining industry a fast evaluation of geological test samples in remote areas regarding the content of relevant minerals is of utmost importance.

In this respect handheld NIR spectrometers could in the near future play an important role because they can be used on-site to quickly analyze milled geological samples with reference to a possible exploration of the investigated site (e.g. for bauxite).



customized brass sample cup **Gibbsit** (Hydrargillit) γ-Al(OH)₃ **Böhmit** γ-AlO(OH) **Diaspor** α-AlO(OH)

NIR Spectra of Geological Test Samples



Benchtop Instrument

Handheld MicroNIR

The spectroscopic footprint of the minerals is also retained in the spectrum of the handheld instrument.

Handheld NIR is a potential tool for geological exploration studies.

PLS Model for Al-Content



Data Pretreatment: 8000 – 6150 cm⁻¹, 2nd derivative, elimination of 8 outliers, 2 principal components.

Test Sample	T1	T2	Т3	T4	Т5	T6	T7	T8	Т9	T10
Actual	0.0	5.1	10.3	15.5	20.2	25.0	30.3	35.6	40.4	43.0
%(w/w)										
Predicted	-4.2	13.9	15.6	15.1	18.0	24.9	34.9	39.1	41.0	35.7
% (w/w)										

Selected Applications of Public Interest: Rapid Test of Silk Quilts

The extraordinary chemical and physical properties have made silk one of the most versatile and comfortable fiber fabric for a multiplicity of customer and industrial applications. This development has led not only to extremely high prizes for silk products, but also to fraud and adulteration attempts for a multiplicity of consumer goods.

Silk quilts are extremely popular in China, but they are frequently adulterated with cotton or polyester. The consequence: variations in price from 55 to 3980 (\$ 8,50 and \$ 610,00).

Thus a rapid test for the quantitative determination of cotton in silk/cotton blends by handheld NIR spectrometers was developed.

The Silk/Cotton Calibration Samples



Statistical Parameters	Total	Calibration Set	Test Set		
n	101	81	20		
Mean (% w/w))	49.99	50.12	49.49		
Max (% w/w)	100.00	100.00	96.92		
Min (% w/w)	0.00	0.00	1.93		
Range (% w/w)	100.00	100.00	94.99		
Std Dev (% w/w)	29.26	29.37	29.54		

101 samples 0-100% (w/w) silk content

The NIR Spectrometers and their Pure Silk/Cotton Spectra

Thermo Antaris Neo Spectra

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Viavi MicroNIR Spectral Engines Senorics Scanner





Raw and Pretreated Spectra of the Different Instruments



Statistical Data of the PLS Calibrations Developed with the Different Spectrometers

Instruments	Pretreatment	Factors		RMSE (%(w/w))			DDD		
			Cal	CV	Test	Cal	CV	Test	
Thermo Antaris	SNV	2	0.9959	0.9953	0.9958	1.87	2.04	1.88	14.40
NeoSpectra	EMSC	2	0.9895	0.9891	0.9904	2.99	3.11	2.85	9.44
Viavi MicroNIR	SNV	4	0.9936	0.9923	0.9898	2.34	2.60	2.91	11.30
Spectral Engines	1st derivative	5	0.9904	0.9854	0.9768	2.87	3.60	4.39	8.16
SenoCorder	1st derivative	5	0.9858	0.9826	0.9787	3.48	3.92	4.12	7.49

Authentication of Carpets

Silk or Mercerized Cotton ?



Authentication of Carpets



Authentication of Carpets



Selected Application of Public Interest: Detection of Seafood Fraud

The largest survey conducted to date about seafood fraud revealed that 1/3 of seafood species purchased at restaurants and grocery stores in cities of the US were mislabeled (Oceana, non-profit international advocacy group). More than 1200 samples were collected from 674 retail outlets in 21 US states. Based on DNA testing the fish species were identified and mislabeling was uncovered.

As typical examples, the aquaculture catfish (Pangasius, Vietnam) and the Tilapia (Victoria Lake, East Africa) have become popular, low-priced edible fish in numerous countries, but have come under criticism for their extensive treatment with pesticides and antibiotics and as ecologically harmful, belonging to the 100 most dangerous alien species.

Thus, it would be desirable if these fish can be unambiguously identified and discriminated in their whole fish or filet form from any other highquality species.

NIR-Spectroscopic Authentication of Red Mullet / Mullet



Authentication of Red Mullet / Mullet



PCA Analysis of the Mullet Spectra



Spectra of the skin can be clearly separated.

Discrimination of Samlet and Salmon Trout Measurement with NeoSpectra Development Kit

Sample Presentation for Diffuse-Reflection of Filet Measurement



Samlet (US\$ 38,-/kg)



Salmon Trout (US\$ 25,-/kg)

40 Spectra of each Fish Species were Measured (EMSC pretreatment)



Discrimination of Samlet and Salmon Trout 2D Score Plot of Principal Component Analysis



In view of the flexibility of handheld instruments, not only corporate enforcement bodies but also customers will have in the future a very fast on-site measurement tool at hand to distinguish lower quality from superior quality seafood in mislabeling attempts.

Finally, a word of caution ...

In their advertisements many "Direct-to-Consumer" companies make empty promises regarding the performance of their "Scanner of the Future". Furthermore, they oversimplify the measurement to "point-and-shoot" procedures with any deficiencies in sample presentation (distance to sample) and sample heterogeneity being taken care of by "cloud evaluation".

Some of the exaggerated claims:

- prediction of the freshness of fruits and vegetables
- identification of pesticide residues on fruits and vegetables
- identification of stains on textiles to control washing machine
 unrealistic accuracy for nutritional parameters.
- None of these can be fulfilled, because:
- NIR is not a micromethod; neither can it detect ppm levels of anthocyanin (from red wine stain) on polyester nor even ppb (!!!) residues of pesticides on fruits and vegetables.
- The problem: the unfulfilled expectations lead to a complete misjudgement of the real potential of (handheld) NIR spectroscopy.

Just an Example: Attempt to Measure Vegetable and Fruit Freshness



Contrary to what is claimed in videos, no ageing trend could be detected for almost all fruits and vegetables !!!

Monitoring the Freshness of Lemons: Storage 11 days at 20°C



3D PCA Score Plot 0.3 0.2 0.1 d1 PC3 d7 -0.1 d11 -0.2 -0.3 0.6 0.4 1.5 0.2 1 0 0.5 PC2 -0.2 -0.4 -0.5 -0.6 -1 However, no trend in this gap.

Detection of Contaminations on Textiles ?



Detection of Contaminations on Textiles ?



Conclusions

Thus, instead of getting misled by flamboyant advertisements of "direct-to-consumer" companies, focus on realistic applications of handheld NIR spectroscopy for every-day-life:

- Avoid deception by internet sale of tablets for weight loss or erectile dysfunction.
- Detect adulteration of spices, olive oil and other food products.
- **Do not get cheated with textiles, carpets or tourist articles** (e.g. ivory, amber).
- Screen nutritional parameters of food products in realistic concentration ranges for a healthy life style.

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Spectra Transfer

Laboratory Spectrometer → Handheld Instrument

For the dissemination of handheld NIR spectrometers the access of spectral data that have already been acquired with benchtop instruments is an extremely important issue. By transferring the data from the benchtop (master) to the handheld (target) instrument, one can shorten the model development time and accelerate the adoption of the handheld device for on-site/in-the-field use.

Challenge: measure only a few samples with both, the target (handheld) and the master (benchtop) instrument for the transfer.

Enabling procedure: piecewise direct standardization (PDS)

In the following publication the development of a spectra transfer tool has been described for a quantitative and a qualitative calibration case study and here only a few features will be outlined.

> U. Hoffmann, F. Pfeifer, Ch. Hsuing and H. W. Siesler Spectra Transfer Between a FT-NIR Laboratory and a Miniaturized Handheld NIR Spectrometer Applied Spectroscopy, 70(5) 852–860 (2016)

The NIR-Spectroscopy Hardware

Bruker MPA



Viavi MicroNIR

spectra transfer





Quantitative Case Study: 25 Organic Solvent Mixtures of Benzene/Cyclohexane/Ethylbenzene



Demonstration of Transfer Performance

Overlay of a spectrum of a liquid mixture of benzene/cyclohexane/ethylbenzene (40/30/30 % (v/v)) measured on the target instrument and the corresponding spectrum after transfer from master to target format.

