## Hand-Held Vibrational Spectrometers:

**State-of-the Art Instrumentation and Novel Applications** 

UNIVERSITÄT DUISBURG ESSEN

**Open-**Minded

H. W. Siesler Department of Physical Chemistry University of Duisburg-Essen D 45117 Essen, Germany hw.siesler@uni-due.de

19èmes Rencontres HélioSPIR "La miniaturisation des spectromètres proche infrarouge" Agropolis International, Montpellier Nov. 8/9, 2018

# Foreword

Inside the molecular spectrometer market, the fastest growing segment is miniature spectrometers and Tematys (Paris) expects this market to reach \$ 300m by 2021.

This growth will be based on a wider adoption of spectrometers for in-the-field testing, on-site measurements and every-day-life consumer applications like food scanning.

Thus, spectroscopists will eventually have to accept that their scientific instruments will "degenerate" to routine tools used by non-experts at the benefit of receiving much more attention.

# Outline

- Short amendment regarding miniaturization in infrared and Raman spectroscopy
- State-of-the-art miniaturization of near-infrared spectrometers
- Discussion of selected qualitative and quantitative application examples by handheld NIR spectroscopy
- Comparative evaluation of instrument performance
- Comments on video-advertisments of "scanners"

# Outline

- Short amendment regarding miniaturization in infrared and Raman spectroscopy
- State-of-the-art miniaturization of near-infrared spectrometers
- Discussion of selected qualitative and quantitative application examples by handheld NIR spectroscopy
- Comparative evaluation of instrument performance
- Comments on video-advertisments of "scanners"

### **Miniaturization in Vibrational Spectroscopy**







**Raman Spectrometer in the 1980s** 

**Examples of Miniaturized Vibrational Spectrometers in 2017** 



Raman





### **Raman Spectra are Frequently Inundated by Fluorescence**

To minimize this problem, Rigaku Raman Technologies have introduced handheld Raman analyzers with 1064 nm excitation.



### New Instrumental Features in Raman Spectroscopy

#### Suppression of Fluorescence, Inclusion of v(CH) Region



SSE<sup>TM</sup> – Sequentially Shifted Excitation

Duo LASER<sup>TM</sup> excitation (3200 – 300 cm<sup>-1</sup>)

**Compensation of Heterogeneity by Orbital Raster Scanning** 



strongly focused: problems with heterogeneity

expanded laser focus: lower spectral resolution

orbital raster scanning: complete acquisition and retention of spectral resolution





### **Bruker BRAVO: Duo LASER<sup>TM</sup> – Excitation**

The spectrometer measures with two lasers with different excitation energy

- > each laser images a different range of wavenumbers on the detector
- ➤ two Raman spectra cover the spectral range from 300 3200 cm<sup>-1</sup> (C-H region)
- > two SSE processed spectra are merged to one Raman spectrum



### Metrohm Mira-M3: Orbital Raster Scanning (ORS)



### **Test Measurements During GDCh Workshop September 2018**

#### Supression of Fluorescence + Duo-Laser Excitation



#### Discrimination of Rutile/Anatase Made Easy



### Hand-Held FT-IR for Road Construction Work?



Can FT-IR/ATR be used for this purpose and can we use a hand-held system for "on the road" analysis ? For road construction work bitumen is blended with different polymers in order to adjust the rheological and adhesional properties (PmB).

The rapid quantitative analysis of this admixture is an important quality control issue.



bitumen sample

#### Analysis of Polypropylene/Maleicanhydride in MBW 10-25 Bitumen

FT-IR/ATR calibration spectra were measured with 60 scans, 4 cm<sup>-1</sup> res., data pretreatment: 3250-2500 cm<sup>-1</sup>, 1490-1130 cm<sup>-1</sup>, 930-680 cm<sup>-1</sup>, SNV Based on these spectra a crossvalidated PLS calibration was developed and good predictions were obtained for test samples.



On the sideline: the spectra have also been successfully correlated with physical bitumen properties : e.g. needle penetration.

# Outline

- Short amendment regarding miniaturization in infrared and Raman spectroscopy
- State-of-the-art miniaturization of near-infrared spectrometers
- Discussion of selected qualitative and quantitative application examples by handheld NIR spectroscopy
- Comparative evaluation of instrument performance
- Comments on video-advertisments of "scanners"

### 2012: So Far Largest Step in NIR Miniaturization





LVF is a one-dimensional array of vapor deposited layers with wedge geometry and no moving parts.

Transmitted wavelength depends on linear position along the filter and is detected by a 128 pixel InGaAs array.

Materials used for the mirror and spacer layers: thin, vacuum-deposited films of SiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, Ge, ZnS.

### Texas Instruments Digital Mirror Device (DMD) → Technology for Miniaturized NIR Spectroscopy

Each DMD contains up to 2 million individually controlled micro-mirrors built on top of an associated CMOS memory cell.

Electrodes are used to hold the micromirrors in the operational positions +12° / -12°.



### Texas Instruments Digital Mirror Device (DMD) → Technology for Miniaturized NIR Spectroscopy



## Texas Instruments DLP® NIRscan<sup>тм</sup> Nano Evaluation Module (EVM)(2016)

#### **Design Considerations**



#### NIRscan Nano EVM Selected Design Specifications

PARAMETER Slit Slit dimensions Spectral range Spectral resolution Detector diameter Detector type DESIGN VALUE *f*-number 2.5 1.8 × 0.025 mm 900 to 1700 nm 10 nm 1 mm Uncooled InGaAs

Optical Engine Dimensions 33 × 29 × 10 mm

## **A New FT-NIR Spectrometer**





## **Food Scanner Award Winner at CeBIT 2017**



Source: Monochromator:

Detector: Wavelength range: 2 tungsten vacuum lamps MEMS Fabry-Perot Interferometer single-element InGaAs 1.35 – 1.65 μm (NR1.7-W) 1.55 – 1.95 μm (NR2.0-W) 1.75 – 2.15 μm (NR2.2-W) 1.95 – 2.45 μm (NR2.5-W)



#### **Typical applications**

- Moisture analysis of solid and powder materials
- Ethanol concentration in biorefineries
- Fat and protein in food and agriculture
  - **Polymer sorting**
  - Chemical compounds in
  - pharmaceutical industry

# Outline

- Short amendment regarding miniaturization in infrared and Raman spectroscopy
- State-of-the-art miniaturization of near-infrared spectrometers
- Discussion of selected qualitative and quantitative application examples by handheld NIR spectroscopy
- Comparative evaluation of instrument performance
- Comments on video-advertisments of "scanners"

### Examples of What Has Been Done Already (mostly in feasibility studies)

- Identification and discrimination of chemicals and materials Raman, IR, NIR
- Authentication of pharmaceutical formulations, polymers, textiles Raman, NIR
- Authentication and characterization of food NIR
- Recycling of polymers NIR
- Qualitative/quantitative determination of bitumen IR
- Qualitative/quantitative determination of hydrocarbon contaminations (diesel, oil, gasoline) in soil NIR, IR
- Quantification of geological samples NIR
- Spectra transfer between benchtop and handheld spectrometers Raman, IR, NIR

### **Comparison of 4 Mini-NIR Spectrometers for Identification and Quantitative Analysis**

#### **Pharmacutical Formulation**



### **Carpet Authentication by Handheld NIR Spectroscopy**



In regular time intervals carpet shops announce closing down sales .....

.... with huge price reductions.

fake or genuine ?



## **Authentication of Carpets**

### Silk or Mercerized Cotton ?



## **Authentication of Carpets**



## **Authentication of Carpets**



#### **Polymer Recycling** Polymer waste has become an issue of global concern Spectra of the 5 most important commodities: PE, PP, PET, PS, PVC (b) 1.5 2 (a) PE PET 1.5 log(1/R) log(1/R) 0.5 0 0 10000 6000 10000 8000 8000 4000 6000 4000 Wavenumber (cm<sup>-1</sup>) Wavenumber (cm<sup>-1</sup>) Si-Ware Spectral Engines DLP NIRscan Nano EVM Viavi MicroNIR 1700

### **Polymer Recycling**



### **Polymer Recycling**

Spectra of the 5 most important commodities: PE, PP, PET, PS, PVC





# Outline

- Short amendment regarding miniaturization in infrared and Raman spectroscopy
- State-of-the-art miniaturization of near-infrared spectrometers
- Discussion of selected qualitative and quantitative application examples by handheld NIR spectroscopy
- **Comparative evaluation of instrument performance**
- Comments on video-advertisments of "scanners"

### **Performance Ranking**

To rank the capability of discrimination for different spectrometers a chemometric parameter was applied.

In PCA, the status of clustering greatly affects the capability of identification. Generally, the larger the Euclidean distance between the clusters of two classes, the better the performance in discrimination.

To rank the performance of different spectrometers for quantitative analysis we used different chemometric parameters such as the RMSEP/RMSECV and RPD taking into consideration several other properties such as the wavelength/wavenumber range and the S/N of the spectrometer.

### **Parameters for Performance Comparison**

#### Signal/Noise Ratio

- 1) Measure the 100% line for the available wavelength range
- 2) Calculate the mean intensity value for all wavelengths
- 3) Calculate the standard deviation for the intensity values under 2
- 4) S / N = 2 / 3

### S/N and Available Wavelength/Wavenumber Range

Si-Ware	<b>TI NIRScanNano</b>	Viavi MicroNIR	<b>Spectral Engines</b>
~ 2900	~ 4400	~ 5100	~ 9000
1298–2606 nm	900–1701 nm	908–1676 nm	1550–1950 nm
<b>Performance Ranking Qualitative Calibration</b> (Polymer Discrimination)			
Si-Ware >	<b>TI NIRScanNano</b>	Viavi MicroNIR	> Spectral Engines
Performance Ranking Quantitative Calibration			

(Pharmaceutical Formulation)

Viavi MicroNIR > TI NIRScanNano > Spectral Engines > Si-Ware

## A Word of Caution: Tellspec was Food Scanner Award Runner-Up at CeBIT 2017



**Based on Texas Instruments DLP®** 

#### **The Claims Continue:** TellSpec's AI sensor detects fish fraud in real-time: 'This technology is disruptive,' says CEO By Niamh Michail 🗗 POST A COMMENT 08-Oct-2018 - Last updated on 08-Oct-2018 at 13:37 GMT US009316628B2 (12) United States Patent US 9,316,628 B2 (10) Patent No.: (45) Date of Patent: Apr. 19, 2016 O'Brien et al. SPECTROSCOPIC CHARACTERIZATION OF (2013.01); G01N 21/27 (2013.01); G01N (54)21/359 (2013.01); G01N 21/3563 (2013.01); SEAFOOD G01N 21/55 (2013.01); G01J 2003/1234 Applicant: Viavi Solutions, Inc., Milpitas, CA (US) (2013.01); G01J 2003/2873 (2013.01); G01N (71)2201/0221 (2013.01); G01N 2201/061 Inventors: Nada A. O'Brien, Santa Rosa, CA (US); (2013.01)Charles A. Hulse, Sebastopol, CA (US); (58) Field of Classification Search Heinz W. Siesler, Essen (DE); CPC ...... G01N 21/359; G01N 21/3563 Changmeng Hsiung, Redwood City, CA See application file for complete search history. (US)

## **Authentication of Fish**



## **PCA Analysis of the Mullet Spectra**



Spectra of the skin can be clearly separated.





### A Word of Caution: "Scanner of the Future" demonstrated at IFA 2017

#### **Bosch X-Spect Scanner**



### **Calibrating Nutritional Facts Based on PLS Models**

3500+ NIR spectra of different pasta/sauce meals were recorded (5 spectra/plate).



averaged spectra (EMSC) of 700+ plates for calibration development of nutritional parameters (fat, energy, protein, carbohydrates, sugar, fiber) log (1/R) wavelength (nm) 900 1400 Slope Offset RMSE R-Square **10 factors** 0.4118676 0.7851678 0.5155271 0.411867 0.8218948 0.5381283 0 3843894 Fiber Predicted Reference

### **Detection of Contaminations on Textiles ?**



### **Potential Future Applications for Handheld Spectroscopy**

- handheld Raman spectroscopy of body fluids for forensic evidence at crime scenes (I. Lednev, University of Albany, NY)
- wider adoption by first responders, law enforcement and environmental authorities (detection of contaminations)
- wider adoption in industry because miniaturization facilitates sensor implementations in processes
- identification/authentication of pharmaceutical formulations
- authentication of gemstones (Raman libraries are available), ivory, amber, cultural heritage investigations
- rapid identification of polymers, textiles (carpets)
- rapid fuel quality assessment by portable NIR in combination with chemometric evaluation routines
- food testing and authentication (by public) given that solid calibrations are provided

# Conclusions

- State-of-the-art hand-held Raman, IR and NIR spectrometers showed good performance for a multiplicity of case studies.
- Generally, handheld instruments have launched vibrational spectroscopy into a new era of "on-site" analysis.
- New instrumental developments will further promote the use of handheld spectrometers by a new user community.

# Acknowledgements

Hui Yan, Jiangsu University of Science and Technology, Zhenjiang, China

Frank Pfeifer, Lars Herberholz, Sylvia Iwaszek, Laima Thimm, Damir Sorak University of Duisburg-Essen, Germany

Uwe Hoffmann (nir-tools), Essen, Germany

Nada O'Brien (now with Oculus (Facebook) formerly with VIAVI Solutions (formerly JDSU), USA

Armin Gembus, Felix Fromm, Bruker Optik GmbH, Germany

Stefan Geisler, P. Krebs Deutsche METROHM GmbH & Co. KG, Germany

Anette Fey, Sebastian Ziewer-Arndts, Analyticon Instuments GmbH, Germany

Ahmed Korayem, Scott Smyser Si-Ware Systems/NEO SPECTRA, Egypt

Janne Suhonen, Spectral Engines, Finland