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Short communication

Present and Future of Miniaturized NIR Spectrometers Combined with Challenging Data Management Strategies

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Introduction

The ongoing miniaturization of spectrometers creates a perfect synergy with the common advantages of NIR spectroscopy (Beć et al., 2020a; Beć et al., 2021). The combination of portability and direct on-site application with high-throughput and non-invasive way of analysis is seen as a decisive and critical advantage in various industries, in particular in the phytopharmaceutical sector. The characteristics and application potential of miniaturized NIR sensors is not entirely similar to the benchtop spectrometers regarding the performance, applicability, and optimization of methodology. These devices remarkably increase the flexibility of analysis; however, attention needs to be paid to the various factors affecting their performance in different analytical scenarios. Currently, it is a focused and very active research direction to perform systematical evaluation studies of the accuracy and reliability of various miniaturized spectrometers that are based on different technologies, e.g. Fourier transform (FT)-NIR, micro-optoelectro-mechanical system (MOEMS) Hadamard mask or linear variable filter (LVF) coupled with array detector (Beć et al., 2020a; Beć et al., 2021).

NIR spectroscopy a particularly potent tool for analyzing natural products and their constituents. The suitability of miniaturized NIR spectroscopy to determine crucial parameters related to the conditions of vegetation, e.g. quality properties of medicinal plants, optimization of the harvest time, analysis of the content of active ingredient, should be noted. These qualities directly translate to thriving development and application of UAV-mounted sensors, i.e. airborne NIR spectroscopy, which can be seen as the next-generation of this technology.

In addition to progressing technology, the importance of using combined tools, integrated into the package of a micro-NIR analytical method to improve its accuracy, reliability and applicability should be emphasized. Advanced calibration methods (e.g. artificial neural networks ANN, nonlinear regression) directly improve the performance of miniaturized instruments in challenging analysis and balance the accuracy of these instruments towards laboratory spectrometers. Two-dimensional correlation spectroscopy (2D-COS) provides insight into the relative sensitivity observed between different instruments in specific NIR bands (Kirchler et al., 2017). The quantum mechanics simulation of NIR spectra reveals the wavenumber regions where the best correlated spectral information resides, and unveils the interactions of the target analyte with surrounding matrix, to ultimately enhance the information gathered from the NIR spectra (Beć et al., 2018). This set of methods enables the intelligent design of future micro-NIR analyzes, which is especially important for samples with a complex matrix.

Novel Instrumentation, Benefits and Pitfalls Resulting from Miniaturization

NIR spectroscopy is a powerful tool for qualitative and quantitative analysis involving natural products, e.g. plant medicines. NIR spectroscopy as a rapid and high-throughput analytical method, with on-site capability, high chemical specificity, and no/minimal sample preparation offers significant practical advantages compared to the conventional methods of analysis. Novel portable NIR spectrometers further enhance the potential of this technique (Beć et al., 2020a; Beć et al., 2021).

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In recent years, remarkable advances in the field of spectroscopic instrumentation and methods of analysis have appeared. Dynamic development of miniaturized, on-site capable NIR spectrometers and new tools of spectral analysis increase the potential and reliability of NIR spectroscopy in phytonalaytical applications.

The advantages of miniaturized NIR spectroscopy are particularly exposed in the field of phytonalaysis (Beć et al., 2020b). In contrast to synthetic medicines, natural products feature chemical diversity that can vary depending on the medicinal plant cultivation conditions, geographical origin or harvest time. The content bioactive compounds and their derivatives, and thus, the quality parameters of the natural medicine need to be controlled with respect to a number of conditions. NIR spectroscopy is particularly competitive in such difficult scenarios. However, miniaturization of the instruments has a non-negligible impact on their applicability and analytical performance, as the necessary compromise to achieve their autonomy and small form factor. Therefore, attention should be given to developing appropriate analytical framework for optimal use of these instruments in practice (Beć et al., 2020a; Beć et al., 2021).

Innovative Methods and New Applications

The NIR calibration procedure based on non-linear methods, e.g. Gaussian Process Regression (GPR) and Artificial Neural Networks (ANN) have been demonstrated to offer substantially improved performance in the case of less than ideal data-sets, e.g. resulting from difficult nature of the analyzed sample (i.e. chemically complex plant matrix), reduced quality of the spectra or the limited spectral characteristics of handheld and miniaturized NIR instruments (i.e. narrow spectral region, lower resolution and poorer S/N typically accepted for the miniaturized spectrometers) (Mayr et al., 2021). The prediction performance of those calibration models constructed for miniaturized spectrometers are of comparable quality to those developed for benchtop instruments, as evaluated through the root-mean square error of prediction (RMSEP) determined on the basis of an independent test set (Mayr et al., 2021).

The complexity of the NIR spectra, which results from the intrinsic convolution of many individual overtones and combination bands, makes it difficult to interpret by conventional spectroscopic methods (Beć and Huck, 2019). We tackle this problem with anharmonic vibration analysis based on the DVPT2 scheme and the underlying optimization for less time-consuming computations (Ozaki et al., 2021). Detailed assignments of NIR bands enable us to interpret the characteristics of the PLS regression models that were built to describe the quantified chemical constituent, e.g. the example of the piperine in black pepper samples (Grabska et al., 2021). Two models were compared, which were developed for spectral data sets obtained with the benchtop laboratory instrument (NIRFlex N-500) and a miniaturized spectrometer (microPHAZIR). The sensitivity of the two instruments to certain types of piperine NIR vibrations is different, with the stationary spectrometer being much more selective.

Conclusions and Future Prospect

The ability of straightforward on-site usage, non-destructive analysis of samples featuring wide variety in chemical composition and physical form, while remaining sensitive to the chemical fingerprint is a decisive breakthrough achieved by NIR spectroscopy in the past decade. One of the most up-to-date breakthroughs is the sensor miniaturization. In general, the design principles of the NIR instrumentation (spectrometers, optics, cells, sample handling) guarantee a wide area of expansion in the currently rapidly growing and diversifying market of natural products. The progress in the sensor technology will certainly continue in the nearest future.

Currently, two major trends in further advancing NIR spectroscopy in natural product analysis are pursued in our working group. The first is the development and employment of miniaturized NIR sensors for flexible approaches in the discussed fields. The second trend is the implementation of innovative frameworks for spectra interpretation and calibration, where quantum chemistry provides deeper understanding about the performance of individual spectrometers and chemometric models, respectively. While advanced calibration methods provide essential gain in analytical prediction, the fundamental progress in interpretability of NIR spectra creates several opportunities for a better-informed design of applications tailored for specific needs.

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