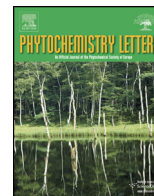




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Selected latest applications of molecular spectroscopy in natural product analysis

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ABSTRACT

The field of molecular vibrational spectroscopy applied to natural products is advancing extremely fast. Traditionally applied separation techniques (LC-, μ -LC-MS, GC, CE-MS) offer the advantages of high selectivity/sensitivity, but their application for routine quality control is limited due to long analyses times. Therefore, molecular spectroscopy in combination with multivariate analysis (MVA) enjoys excellent reputation, because of the fast and non-invasive measurement enabling the analysis of several physical and chemical parameters simultaneously. Near infrared (NIR; 4.000–10.000 cm^{-1}), attenuated total reflection (ATR; 400–4.000 cm^{-1}), Raman and far ultraviolet (FUV; 120–200 nm) spectroscopy have permanently increased their efficiencies for quality control of predominantly food stuff, but also of other natural products including mainly medicinal plants. All four techniques enable not only a quantitative analysis of potent ingredients, but also qualitative fingerprint analysis for the discrimination of, e.g., species and/or geographic origin, respectively. Thereby, each individual spectroscopic technique possesses its specific strength. Powerful miniaturized portable spectrometers based on linear variable tuneable filter (LVTf) or micro-electro-mechanical systems (MEMS) are helpful in order to prevent consumers from deception on one hand, on the other hand they represent powerful analytical instruments for measurements in the field. 2-Dimensional correlation spectroscopy (2DCOS) represents a powerful technique for monitoring the dynamics of a system including temperature stability, extraction procedures etc. Imaging and mapping spectroscopy using infrared radiation and/or Raman scattering are not only suitable for classification of food stuff including e.g. maize kernels and/or coffee beans, but also for localizing the distribution of ingredients down to a resolution of 4 μm .

In the present contribution, the latest progresses of the different techniques are introduced and their applicability in the fields of natural product analysis will be discussed in detail by distinct selected applications.

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1. Introduction

Infrared (IR) is the electromagnetic region between the visible (VIS) and the microwave wavelength (Herschel, 1800). It is divided

into near- (NIR, 750–2.500 nm, 4.000–13.000 cm^{-1}) (McClure, 2004), mid- (2.500–25.000 nm, 400–4000 cm^{-1}) (Chalmers and Griffiths, 2002) and far-infrared (400–10 cm^{-1} , 25.000–106 nm) (Griffiths et al., 2006) sub-regions, from which mainly NIR and MIR are applied to natural products analysis (Huck, 2015).

From a general point of view, NIR spectroscopy is concerned with the absorption, emission, reflection and diffuse-reflection of light (Siesler et al., 2008). NIR is electronic as well as vibrational spectroscopy dealing with overtones and combination modes being described by the model of the an-harmonic oscillator. MIR is vibrational spectroscopy dealing with fundamental modes following the harmonic oscillator principle. In comparison to the MIR, NIR spectra are usually crowded containing a manifold of

Abbreviations: ATR, attenuated total reflection; CA, cluster analysis; CE, capillary electrophoresis; CEC, capillary electro chromatography; DR, diffuse reflection; FPA, focal plane array; FT, Fourier transform; LC, liquid chromatography; MCT, mercury cadmium telluride; MEIRS, material enhanced infrared spectroscopy; MIA, multivariate image analysis; MLR, multiple linear regression; MVA, multivariate analysis; NIR, near infrared spectroscopy; PCA, principal component analysis; PLSR, partial least square regression; TCM, Traditional Chinese Medicine; Vis, visible.

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information extracted from overlapping peaks. NIR intensities are 10–1000 times lower and therefore highly sensitive spectrometers must be designed (Lutz et al., 2014). The design and further optimisation of portable and hand able NIR spectrometers based on micro electro mechanical systems (MEMS) (Schuler et al., 2009) and linear variable tuneable filters (LVTF) (Wetzel et al., 2006) are recently supporting NIR spectroscopy becoming very popular.

For MIR studies the application of attenuated total reflection (ATR) is most suitable benefiting from the evanescent field which can penetrate at least a few micro-meter into the sample of interest providing high signal-to-noise (S/N) ratio (Schönbichler et al., 2014). NIR, MIR and Raman spectroscopy were also called the three sisters of vibrational spectroscopy (Huck et al., 2016a,b). The principle of Raman spectroscopy is based on an inelastic scattering process in which photons incident on energy transfer to or from molecular vibrational modes (Šašić and Ozaki, 2010). This gives rise to a change in frequency of the emitted photon, hence the term “inelastic”. As energy levels are unique for every molecule, Raman spectra are chemical specific.

Far-UV (FUV, 120–200 nm) is concerned with the electronic transitions of a molecule (Morisawa et al., 2013). Recent developed FUV spectrometers are based on the attenuated total reflection (ATR) technique that enables the measurement of liquid and solid samples at least in the 240–280 nm region.

Two-dimensional (2D) spectroscopy, first proposed by Noda in the 1980s (Ozaki and Noda, 1996), has been further developed (Li et al., 2011) and has gained considerable popularity in various application fields including food and agricultural products (Fudge et al., 2013). Defined by two independent spectral axes, the 2D correlation spectrum is generated by applying correlation analysis to the dynamic fluctuations of spectral signals caused by external perturbations, e.g., chemical, thermal or mechanical stimulations. One notable feature of 2D correlation spectroscopy (2D-COS) is that the cross-peaks can potentially be used to characterize intermolecular interactions. So the advent of 2D-COS brings about a new avenue for the investigation of intermolecular interactions.

Vibrational spectroscopic imaging and mapping can in principle be understood as the coupling of a microscope to an NIR, MIR, or Raman spectrometer, respectively (Salzer and Siesler, 2009; Šašić and Ozaki, 2010). Microscopes consist almost of the same parts as their optical analogues using mercury cadmium telluride (MCT)

and charged-coupled devices (CCD) detectors for IR and Raman. The advantages of this technique can be summarized as micro spatial imaging (resolution down to 6 and 1 micro-meter using IR and Raman) of highly complex samples, high sensitivity and selectivity (Pezzei et al., 2010).

In many applications it is impossible to correctly assign the corresponding vibration bands. Vibrational spectroscopy in combination with multivariate statistical analysis (MVA) is a powerful synergistic combination enabling the extraction of the required information from the spectrum in the first step (Blanco and Villarroya, 2002; Kessler and Kessler, 2006). In the following, clustering methods such as principal component analysis (PCA), hierarchical cluster analysis (HCA), fuzzy-C-means clustering and others enable the reduction of numbers of variables enabling qualitative analysis (Huck and Huck-Pezzei, 2014). For the establishment of quantitative regression models, partial least square regression (PLSR, (Petter et al., 2009)) is the preferred method, correlating spectral data with those obtained from reference methods, e.g., liquid chromatography (LC, (Huck et al., 1999)) even hyphenated to mass spectrometry (LC-MS, (Stöggel et al., 2005)) including solid-phase extraction (SPE, (C. Huck, 2016; Huck and Bonn, 2000)), gas chromatography (GC, (Valtiner et al., 2008)), capillary electrophoresis (CE, (Huck et al., 2002)) and chromatography (CEC, (Stöggel et al., 2006)), mass spectrometry (MS, (Najam-ul-Haq et al., 2006)).

As in the previous contribution the fundamental principles and applicability of NIR and MIR was described (Huck, 2015), it is the intention of the present contribution expanding to novel vibrational spectroscopic methods. Therefore, in the next chapter the main principles of the new methods are described and in the following one selected applications are discussed.

2. Methods

In the following the main trends of the different vibrational spectroscopic methods applied to natural product analysis will be discussed.

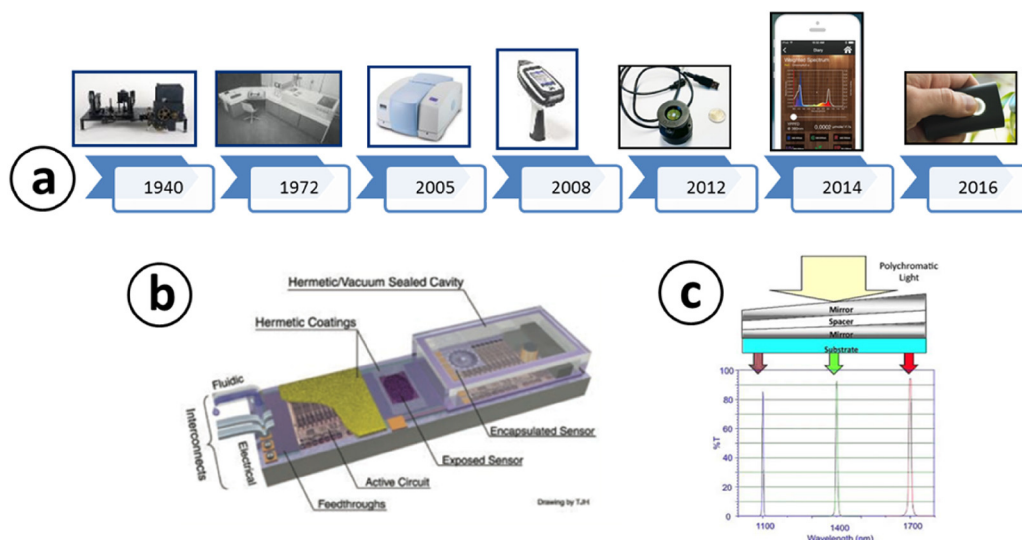


Fig. 1. (a) Trend of miniaturisation in NIR spectroscopy over time; (b) micro-electromechanical system (MEMS) and (c) linear variable tuneable filter (LVTF).

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