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Review Paper

Species authentication and geographical origin discrimination of herbal medicines by near infrared spectroscopy: A review ☆

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ABSTRACT

Near infrared (NIR) spectroscopy as a rapid and nondestructive analytical technique, integrated with chemometrics, is a powerful process analytical tool for the pharmaceutical industry and is becoming an attractive complementary technique for herbal medicine analysis. This review mainly focuses on the recent applications of NIR spectroscopy in species authentication of herbal medicines and their geographical origin discrimination.

Contents

1. Introduction

As one of the most traditional forms of health care, herbal medicine has been worldwidely used for over hundreds of years. The World Health Organization (WHO) estimates that about 65%–80% of the world's population, particularly in the developing countries, has limited access to modern medical care, and herbal medicine is still their primary source of health care [1]. Certain botanicals have been widely used in some societies, such as turmeric (*Curcuma longa* L.) and *Curcuma xanthorizza* Lam [2]. Active components like morphine, digitoxin, cocaine and taxol contained in herbal medicines are used in standard allopathic medicine, and related quality standards regarding the purity, safety and efficacy are carried out by the United States Food and Drug Administration (USFDA) [2,3]. In fact, it is estimated that over a quarter of modern medicines are directly or indirectly derived from higher plants [4].

Herbal medicine can be represented either as a single-herb or a multi-herb formula, and it is reported that about 92% of herbal medicine formulas are a combination of less than thirteen herbal medicines [5]. Traditionally, the identification of herbal medicine is carried out according to the differences in morphology, and/or thin layer chromatography (TLC) identification or content determination of one or two marker constituents [6,7]. The characteristics of systematism, multi-target and synergistic actions of traditional Chinese medicines (TCMs) originate from their multiple constituents, which can vary significantly in contents. The

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chemical compositions in herbs may vary depending on the species, location of growth, age, harvesting season, drying processes and some other factors [8]. Consequently, to ensure the reliability and repeatability of pharmacological and clinical researches and to guarantee the consistency of the final product quality, the determination of all bioactive constituents of a herbal material is necessary [9,10]. However, elucidating all of the herb bioactive compounds is time-consuming, arduous and unsuitable for clarifying the synergies between herbal medicines. Thus, it is of utmost importance to formulate quality control protocols based on entire metabolome, which can be regarded as a 'pattern-oriented' method, especially for species authentication and geographical origin discrimination [6].

For herbal medicine species authentication, the WHO, the USFDA and the European Medicines Agency (EMEA) have updated their regulations and state that the identification of herbal medicines is one of the first assays that should be conducted to ensure their quality and discriminate from related species or adulterated samples [11–14]. However, species authentication is still not sufficient for quality control of herbal medicines. It is reported that, for herbal medicines even from the same species, the quality and efficacy are somewhat different according to their growing conditions such as cultivation soil and climates based on the geographical origins [15–17]. Therefore, rapid and accurate analytical approaches are essentially required the estimation of correct value and the prevention of illegal distribution.

Due to its capability of fingerprinting analysis, the modern vibrational spectroscopies [mid-infrared (mid-IR) and near-infrared (NIR) and Raman] fulfill the common requirements such as speed of analysis and ease of use, especially in combination with chemometric techniques, and are highly efficient in distinguishing types or species as well as geographical origins of herbal medicines [3,18]. Among these, NIR spectroscopy is widely applied owing to its high analytical speed, low cost and reliability for qualitative and quantitative analysis of various types of samples such as soil [19], food [20] and beverages [21]. Thus, NIR spectroscopy serves as an excellent candidate for herbal medicine analysis [15].

During the last few years several review articles dealing with NIR spectroscopy and its applications to analysis of natural products have been published [3,22,23]. With the aim of providing an up-to-date overview of the applications of NIR spectroscopy on medicinal plant analysis, the present review summarizes the recent applications of NIR spectroscopy to herbal medicine species identification and geographical origin discrimination during the past 15 years.

2. Near infrared technique

The American Society of Testing and Materials (ASTM) defines the NIR region from 780 to 2526 nm (12821–3959 cm^{-1}), located between the red band of the visible light and the mid-IR region [24]. The most prominent absorption bands are a consequence of the absorbance of light due to molecular vibrations (overtones and combinations of the fundamental mid-IR bands) of hydrogen bonds like –C–H, –S–H, –N–H, and –O–H functional groups [25]. The NIR region was discovered by Herschel more than 200 years ago, and it has become a popular technique since 1960. The current triumph of NIR spectroscopy is attributed to Norrisr et al. who recognized the immense capability of NIR spectroscopy as a potential process analytical technology tool in industrial practice for measurements of certain types of food, agricultural components and product quality control [26].

NIR spectroscopy has gained wide acceptance in various fields since it has several advantages over other analytical techniques with respect to fast acquisition, low cost, and nondestructive character towards the analyzed sample, while the most noticeable feature of NIR spectroscopy is its ability to acquire spectra for solid, semi-solid, and liquid samples without or with only minimal sample preparation [27–30]. On the one hand, the interest in NIR has increased owing to the improvements of instrument and the advancement of intrinsically safe measurement probes and fiber optics which make the delocalization of the measurements a reality. On the other hand, the fast growing applications of NIR spectroscopy also have been stimulated by the advance in computer technology and the progress in new mathematical methods which make large-scale data processing possible [28]. However, like every scientific technique, NIR spectroscopy has its own disadvantages. For instance, in comparison to mid-IR spectra whose absorbance bands can be directly interpreted due to the specific absorption of organic functional groups, NIR spectra are more complex owing to the nature of NIR bands (overlapping overtones and combination bands for hydrogen bonds). Besides, the physical state of the sample and the testing environment also influence the spectra, which make the data interpretation more complicated [31]. In summary, it is particularly hard to discern 'relevant' information about the characteristics of target analytes from the raw spectra.

Therefore, for qualitative or quantitative NIR analysis, mathematical and statistical methods are required to extract 'relevant' information (i.e. spectral variables related to properties of the analyte) and reduce 'irrelevant' information (i.e. interfering parameters), which belongs to the research field of chemometrics [32]. Chromemtrics regroups several related topics including design and optimization of experimental procedures, information extraction strategies (modeling, classification and hypothesis validation) and techniques for obtaining knowledge about chemical systems [33]. Owing to the development of chromemtrics, NIR spectroscopy has found applications in a broad range of domains during the past decades, such as in the petrochemical [34,35], environmental [36,37], pharmaceutical [31,32,38], clinical [39,40], agricultural [41,42], food [40,43], biomedical [44], and herbal medicinal [22,23,45] sectors.

3. Selected applications of herbal medicine species authentication

Although some herbal medicines are of different species, the morphological characteristics are similar to each other, especially, among closely related species. Therefore, the rapid and sensitive recognition of herbal species plays a decisive role in herbal medicine quality control. The traditional test mainly depends on naked-eye inspection or TLC. These test methods are either subjective in nature or require operative skills and experience which are not efficient enough for screening huge volumes of herbal medicines [46]. Over the past decade, a large number of publications have been available in the literature, which are dedicated to the classification of herbal medicines based on their species using NIR spectroscopy.

Paris, which belongs to the Liliaceae family, contains about 24 species and is mainly distributed in Europe and Eastern Asia. However, only the rhizomes of *Paris polyphylla* var. *chinensis* and *P. polyphylla* var. *yunnanensis* are officially listed in Chinese Pharmacopoeia. It is hard to discriminate dry rhizomes of the same genus by traditional morphological identification methods, especially for the original powder form. Zhao et al. [47] used NIR spectroscopy in combination with partial least squares discriminated analysis (PLS–DA) to give a preliminary overview of the similarities and differences among the species, and the results indicate that wild *Paris* species exert a significant effect on the NIR