Journal of Food Composition and Analysis xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Study Review

Analytical techniques combined with chemometrics for authentication and determination of contaminants in condiments: A review

Q1 Ingars Reinholds [a,*], Vadims Bartkevics [a], Isabelle C.J. Silvis [b], Saskia M. van Ruth [b], Susanne Esslinger [c]

[a] Institute of Food Safety, Animal Health and Environment, "BIOR", Lejupes Street 3, LV-1076 Riga, Latvia
[b] RIKILT Wageningen UR, Akkermaalsbos 2, BP 6708WB Wageningen, Netherlands
[c] Federal Institute for Risk Assessment BfR, Max-Dohrn Street 8-10, 10589 Berlin, Germany

ARTICLE INFO

Article history:
Received 17 February 2015
Received in revised form 6 May 2015
Accepted 14 May 2015
Available online xxx

Keywords:
Food analysis
Targeted and non-targeted methods
Food safety and quality
Spices
Herbs
Multivariate analysis
Contaminants
Food fraud

ABSTRACT

Spices and herbs play an important role as flavorings, colorants, and also as bioactive compounds used in medicine and cosmetics. The presence of common contaminants, e.g., mycotoxins, pesticide residues, heavy metals, and the adulterants, e.g., azo dyes, filth and extraneous matter have been permanently monitored in condiments in order to control their quality, compliance to market, and safety to human health. The present paper shows a comprehensive overview of the analytical methods, based on the modern instrumental techniques and the most perspective statistical tools, based on univariate and multivariate (chemometrics) statistics, used for qualitative and quantitative determination of contaminant levels and for the authentication issues of different spices and herbs, discriminated by their geographic or biological origin. The review comprises more than sixty studies covering the last decade, describing the benefits of different analytical methods including multidimensional (non-targeted and targeted) approaches combined with multivariate chemometric techniques for the assessment of contaminants in spices and herbs in relation to research of their safety and quality issues. The methods based on multivariate data description and regression techniques are among the most promising techniques for the authentication of spices/herbs and determination of their contamination or adulteration risks with potential hazards.

Abbreviations: AAS, atomic absorption spectrometry; AF/AFs, aflatoxin/s; AMWFA, alternative moving window factor analysis; ANNs, artificial neural networks; ANOVA, one-way analysis of variance; CA, cluster analysis; CCA, canonical correlation analysis; CDA, canonical discriminant analysis; CVA, canonical variate analysis; DA, discriminant analysis; DART, direct analysis in real time; DFA, discriminant function analysis; DON, deoxynivalenol; DRIFTS, diffuse reflectance infrared Fourier transform; EMA, ecological momentary assessment; FA, factor analysis; FAAS, Flame atomic absorption spectrometry; FAES, flame atomic emission spectrometry; FB/FBs, B-type fumonisin/fumonisins; FID, flame ionization detection; FIMS, flow injection mass spectrum; FS, fluorescence spectrometer; FT-IR, Fourier transform infrared; FT-MIR, Fourier transform mid-infrared; FT-NIR, Fourier transform near-infrared; FT-Raman, Fourier transform near-Raman; GFAAS, graphite furnace atomic absorption spectrometry; GC, gas chromatography; GC–MS, gas chromatography–mass spectrometry; GSA, gas sensor arrays; HCA, hierarchal cluster analysis; HG-AFS, hydride generation atomic fluorescence spectrometry; H NMR, proton nuclear magnetic resonance; HPLC, high performance liquid chromatography; HPLC-DAD, high-performance liquid chromatography with diode array detector; HPLC-DAD-MS, high-performance liquid chromatography with diode array – mass spectrometry detector; HPLC-FLD, high-performance liquid chromatography with fluorescence detector; HPLC–MS/MS, high-performance chromatography with tandem mass spectrometry detector; HPLC-PCD-FLD, HR-ICP-SFMS, high resolution inductively coupled plasma sector field mass spectrometry; HSD, honestly significant difference test; HSI, hyper spectral imaging; ICP, inductively coupled plasma; ICP-AES, inductively coupled plasma-atomic emission spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; ICP-OES, inductively coupled plasma-optical emission spectrometry; KNN, k-nearest neighbors; K–S, Kolmogorov–Smirnov test; K–W, Kruskall–Wallis one-way analysis of variance; LA-ICP-TOF–MS, laser ablation inductively coupled plasma time of flight mass spectrometry; LDA, linear discriminant analysis; LIBS, laser-induced breakdown spectroscopy; LRA, linear regression analysis; MDA, multiple discriminant analysis; MDS, multidimensional scaling; MIR, mid-infrared; MLR, multiple linear regression; MPLS, multivariate partial least square; NAA, neutron activation analysis; NIR, near-infrared; OTA, ochratoxin A; PARAFAC, parallel factor analysis; PCA, principal component analysis; PCA-ANN, principal component analysis-artificial neural networks; PCR, principal component regression; PLS, partial least square; PLS-DA, partial least-square discriminant analysis; SANN, self-associative neural networks; SERS, surface enhanced Raman spectroscopy; SIMCA, soft independent modeling by class analogy; SVR, support vector machine; S–W, Shapiro–Wilk test; TOF, Time of flight; *t*-test, Student's distribution null test; UHPLC, ultra high-performance liquid chromatography with tandem mass spectrometry detection; UV–vis, ultraviolet–visible; XRF, X-ray fluorescence; *z-test*, *z*-score test.

* Corresponding author. Tel.: +371 26802448.
E-mail address: ingars.reinholds@bior.lv (I. Reinholds).

http://dx.doi.org/10.1016/j.jfca.2015.05.004
0889-1575/

Contents

1. Introduction

Since ancient times, spices and herbs of various types (i.e., berries, seeds, roots, fruits, bark, and leaves) have been used as substantial additives in culinary, medicinal, cosmetic and other compositions (Schweiggert et al., 2007). The differences of spice quality characteristics, e.g., color, odor, and flavor are based mainly on their biological and geographic origin. High-quality condiments, especially the most expensive spices like saffron, vanilla, and cinnamon, belong to high price products due to their rare sources and the complicated production or harvesting conditions (Bythrow, 2005; Melnyk et al., 2010). Almost every stage of condiment production, i.e., growing, storage, transporting, and distribution may be under the risk of contamination by biogenic or chemical environmental pollutants, e.g., mycotoxins, pesticide residues, heavy metals, accidental adulterants such as floral wastes or ashes, and fraudulent components, such as artificial colorants, dense materials, or plants of foreign species (Amate et al., 2010; Karadaş and Kara, 2012). Besides many economical circumstances including the issue of added value (brand, quality characteristics) and commercial gain, there are internal and external consequences of possible health hazards of spices, herbs and their products, as many of the contaminants can cause acute and chronic health disorders in humans (Chan, 2003; Škrbić et al., 2013). Various analytical methods have been used in recent years for the monitoring of contamination levels in commercial spices, herbs, and their products. The present review summarizes the latest approaches used with analytical methods such as liquid and gas chromatography (LC, GC), nuclear magnetic resonance, near and mid-infrared, Raman, ultraviolet–visible, X-ray fluorescence spectroscopy (NMR, NIR, MIR, Raman, UV–vis, XRF), as well as inductively coupled plasma, atomic emission, and atomic absorption spectrometry (ICP, AES, AAS), and the techniques of artificial simulation applied in the recent investigations. Over the last decade, several statistical methods of multivariate analysis have been applied for quality control and authentication of spices and herbs. Despite the overall tendency of decrease in contamination cases compared to previous centuries, a pronounced problem of contamination has remained. The methods of counterfeiting have become more deliberate and increasingly difficult to detect by the most common analytical methods. Thus, work should be continued on the development of more effective (rapid, affordable, portable, and on-line) instrumental techniques of high sensitivity and selectivity for the detection and prevention of these offenses. It is important to expand the integration of spectrometric/spectroscopic techniques coupled with multivariate chemometric tools, in order to monitor the already known hazards and also to assess possible novel contaminants. The functional groups of unidentified contaminants could be determined, comparing their structural, chemical, and biochemical characteristics to already known compounds, depending on possibly predictable factors.

An objective of the present review is to summarize the studies evaluating the origin and environmental contamination of commercially available spices and herbs, employing the latest analytical methods combined with chemometrical analysis.

The latest investigations reported in prominent scientific peer-reviewed journals over the last decade discussing the application of multivariate statistics, based on chemometric viewpoint in authentication of spices and herbs and control of contamination levels and the possibility of adulteration in condiments of culinary, pharmaceutical, and cosmetic value are summarized in this review.

2. Application of chemometrics in condiment analysis

The corresponding approach of chemometrics discipline is based on application of mathematical, statistical, and other methods in order to obtain an objective evaluation of results by gaining essential, i.e., meaningful information from the results of related and unrelated sets of chemical data. Based on multivariate analysis, several chemometric methods find application in quantitative or qualitative measurements of chemical data, the possible changes of product quality under the definable factors or under the influence of fraudulent practices and various pollutants. Chemometrics shows invaluable benefits in calibration analysis of spectrometric/spectroscopic data, applied in targeted as well as non-targeted techniques to identify the contamination/fraud of spices or authentication of their geographic and biological origin.

The most common multivariate methods and principles for hazard determination in spices and herbs are described shortly, to better explain the analysis of literature from 2003 to 2014, and can be divided according to purpose in the following three categories (Eriksson et al., 2006; Miller and Miller, 2010), whereas their application strongly correlates with the respective investigated objective:

- data description and visualization,
- discrimination and classification,
- regression and prediction.

Excellent scientific publications present and discuss the applicability of these approaches in more detail (e.g., Trygg et al., 2006; Brereton, 2009, 2014; Bro, 2003; Oliveri and Downey, 2012).

Please cite this article in press as: Reinholds, I., et al., Analytical techniques combined with chemometrics for authentication and determination of contaminants in condiments: A review. J. Food Compos. Anal. (2015), http://dx.doi.org/10.1016/j.jfca.2015.05.004