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Potential and limitations of non-targeted fingerprinting for authentication of food in official control

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ABSTRACT

The investigation of the so-called food fingerprints provides high potential with regard to the characterization and identity verification of food. Therefore, this kind of non-targeted analysis obtained increasingly importance during the recent years. These applications are usually based on spectroscopic and spectrometric data providing the capability for a comprehensive characterization of the investigated matrices. The subsequent statistical multivariate data analysis enables a general identification of many deviations from the expected product composition. Besides the classical tests of authenticity of foods, a comprehensive analysis that also allows the detection of hazardous or safety-relevant manipulations and violations of the respective laws e.g. with regard to non-authorized food additives or a prohibited use of technological processes is of urgent need in food control. In the literature, several approaches are already pursuing the non-targeted observation of abnormalities in various foods covering a broad variety of analytical methods. This review highlights a current overview of the applicability of this approach using classic spectroscopic as well as spectrometric analytical techniques on the basis of examples of the three most investigated food matrices: honey, olive oil and wine. Furthermore, difficulties as well as challenges regarding the use of food fingerprinting in official food control are discussed.

1. Introduction

The identity and authenticity of products are current topics in food and feed science for both sides: on the one hand consumer protection authorities and on the other hand producers and dealers. Since the beginning of food trade, incidents concerning adulterations of relevant products are well known. However, detection of these adulterations provides a great challenge to the analytical chemists concerning its identification because of increasing product diversity and the continuous development of new production technologies.

The term authentication (authenticity testing) used in food control describes the confirmation of all requirements regarding the legal product description or the detection of fraudulent statements (this definition is based on (Gary & Ebeler, 2011; Lees, 2003; MoniQA, 2013). Particularly in view of:

(i) the substitution by cheaper but similar ingredients,
(ii) extension of food using adulterant (e.g. water, starch including exogenous material) or blending and/or undeclared processes (e.g. irradiation, extraction),
(iii) the origin, e.g. geographic, species or method of production.

The classical authenticity assessment of food is usually based on the analysis of specific marker compounds, which are indicative for a certain property of the product, e.g. shikimic acid in wine or hydroxymethylfurfural in honey. The comparison of an actual measurement value with a control limit, which is in authenticity testing often a so-called experience value for a certain parameter, is a common approach of the control process. This part of the assessment is always based on whether the analytical parameter determined, considering also the measurement uncertainty, is violating the established limit or if it is still in compliance with it. Therefore, state-of-the-art of the official control practice is characterized by its possibly forensic utilization. Due to its high demand for reliability e.g. in case of an official objection — standing "beyond reasonable doubt", high efforts are put on the validation of the analytical method to ensure accuracy of the analytical determination. Moreover conservative data assessment and evaluation is done in practice.

Food Fingerprinting, the non-targeted chemical analysis of food with subsequent multivariate data analysis is based on the principle of the so-called *metabolomics*. This term has been established in the late 1990s, more specifically, Oliver et al. used the expression *metabolome* in the year 1998 for the first time (Oliver, Winson, Kell, & Baganz, 1998). By definition, *metabolomics* describes the scientific study of small molecules, the metabolites, of a biological system based on comprehensive chemical analysis (*omics* technologies) with the aim to detect as many substances as possible (Roessner, Nahid, Chapman, Hunter, & Bellgrad, 2011). Since both, origin and current focus of metabolomics are in the field of pharmacy and toxicology, the analysis of food using these techniques becomes more and more important e.g. in food and feed science. In this field, a distinction was made between the concepts of food fingerprinting and food profiling in accordance to

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the corresponding definitions in metabolomics (Table 1, Koek, Jellema, van der Greef, Tas, & Hankemeier, 2011). Food profiling focuses on the analysis of a group of metabolic products in combination with a certain metabolic pathway or a class of compounds (multi-component analysis). This strategy is based on the prior knowledge of the analyst concerning the respective present biological system and, hence, is rather performed by targeted analysis and optional subsequent multivariate data analysis. In contrast, food fingerprinting techniques do not deal with the identification of all metabolites, but on the recognition of patterns, the so-called *fingerprints* of the matrix (Antignac et al., 2011). The genetic background of agricultural commodities and various environmental or other external influences affect the fingerprint of food matrices dramatically. For example, wine of the same variety was certainly subject to different growing and production conditions depending on the vineyard location, the climate and the applied oenological practices, which to the end also affect the respective fingerprints. Those manifold influences on the food fingerprint make a proof of product identity challenging. The origin and certain oenological practices could cause specifically different food fingerprints, which might then result in decision-relevant differences after mathematical analysis. It is therefore important to analyze the acquired data sets carefully and perform statistics considering the available meta-data.

Food fingerprinting approaches are typically based on a high-throughput screening of samples (if necessary after a (simple) sample preparation) with the purpose of a differentiation or classification of samples. After identification and mapping of the patterns to individual food matrices, the aim is to differentiate various food fingerprints in terms of e.g. their botanical or geographical origin on the one hand or for instance with respect to possible adulterations on the other hand. The potential investigation of multiple objectives with only one analytical method is thereby a clear advantage of the non-targeted food fingerprinting over the classical targeted approaches.

The application of non-targeted food analysis in combination with the subsequent use of statistical methods to test for identity and authenticity is a growing field of food science. Lai et al. was among the first in 1994 who carried out investigations in the field of food fingerprinting (Lai, Kemsley, & Wilson, 1994). In this study the researchers tested edible oils for authenticity using a Fourier transform infrared spectrometer (FT-IR) in conjunction with two multivariate statistical methods, principal component analysis (PCA) and the discriminant analysis (DA). The authors used the spectral data to successfully differentiate several edible oils according to their plant species (e.g. grape seed, groundnut, corn, rapeseed or walnut) and in the case of olive oils their manufacturing process (cold pressed or refined). Since that time, the number of institutions dealing with food fingerprinting and the number of related publications are growing exponentially.

Besides fingerprinting and profiling, further terminologies are mentioned in literature referring to the field of food authentication. The most relevant definitions and principles are described in Table 1. Recently, *foodomics* has been adopted for the methodology, which studies the food and nutrition domains through the applications of advanced *omics* technologies (Cifuentes, 2009; Herrero, García-Cañas, Simo, & Cifuentes, 2010). Hence, food fingerprinting as well as food profiling might be considered as part of foodomics. So far, the term foodomics has not yet been used widely in science. *Food forensics* represents a term, not clearly defined in literature. This approach comprises all techniques to authenticate food (e.g. by stable isotope ratio analysis or methods based on DNA analysis, proteomics, metabolomics) and might therefore be used as a synonym for food authentication (Primrose, Woolfe, & Rollinson, 2010; Teletchea, Maudet, & Hänni, 2005; Woolfe & Primrose, 2004). However, besides the use by various companies providing services in authentication or the specific identification of exogenous particles in food, this term is not established in the scientific community.

The most commonly used methods in the field of food fingerprinting are based on spectroscopic data, for example, generated by using nuclear magnetic resonance (NMR)-, near-infrared (NIR)- or FT-IR spectroscopy. These techniques offer the possibility to analyze relatively small amounts

Table 1
Key terms and description of food characterization techniques adapted for authentication issues.

Authentication approach	Principle	Aim and advantage/disadvantage	Source
Classic targeted approaches	— "Bottom-up"-approach — Selective sample preparation — Targeted analysis of single compounds or group of compounds — Qualitative and/or quantitative — Univariate data analysis	Aim: e.g. authentication/characterization of food Advantage/Disadvantage — High sensitivity, high selectivity — "Simple" data evaluation — Time consuming (extensive sample preparation, multiple analysis) — Only known compounds detectable	(Fauhl, 2006; Koek et al., 2011)
Food profiling	— "Top-down"-approach — Selective or unselective sample preparation — Targeted analysis of a group of compounds or — Non-targeted analysis and subsequent identification of compounds — Qualitative and/or quantitative — Multivariate data analysis	Aim: e.g. authentication/characterization of food Advantage/disadvantage — High sensitivity, high selectivity — Extensive sample preparation — Need of compound data bases for identification (spectra comparison) — Need of sample databases for authentication (multivariate modeling)	(Antignac et al., 2011; Cevallos-Cevallos et al., 2009; Koek et al., 2011)
Food fingerprinting	— "Top-down"-approach — Unselective sample preparation — Non-targeted analysis of a spectral fingerprint — Qualitative and/or semi-quantitative — Multivariate data analysis	Aim: e.g. comprehensive authentication/ characterization of food Advantage/disadvantage — High-throughput approach — Simple or no sample preparation — Detection of unexpected additives/deviations possible — Investigation of multiple objectives possible — Need of sample databases for authentication (multivariate modeling)	(Antignac et al., 2011; Cevallos-Cevallos et al., 2009; Koek et al., 2011)
Foodomics	— Using omics techniques e.g. genomics, transcriptomics, proteomics, and/or metabolomics	Aim: investigation of food and nutrition for e.g. compound profiling, authenticity and/or biomarker detection	(Cifuentes, 2009; García-Canas, Simó, Herrero, Ibánez, & Cifuentes, 2012; Herrero, Simó, García-Canas, Ibánez, & Cifuentes, 2012)