Trace-element composition and stable-isotope ratio for discrimination of foods with Protected Designation of Origin

A. Gonzalvez, S. Armenta, M. de la Guardia

We review the literature on authentication of foods with Protected Designation of Origin (PDO) from their trace-element composition or stable-isotope ratios in order to evaluate the state of the art of this field and to identify the main parameters of analytical techniques and chemometric-data treatments that permit accurate discrimination of samples of different geographical origins and with different characteristics.

Keywords: Analytical technique; Authentication; Chemometric-data treatment; Discrimination; Food; Geographical origin; Protected Designation of Origin; Sample; Stable-isotope ratio; Trace-element composition

A. Gonzalvez,
S. Armenta*,
M. de la Guardia
Department of Analytical Chemistry, Research Building, University of Valencia, 50th Dr. Moliner St., E-46100 Burjassot, Valencia, Spain

1. Introduction

Determination of food authenticity is an important issue in quality control and safety of food. The outbreak of diseases related to foodstuffs and scares around the world have raised consumer awareness about the quality and safety of food, so aspects of geographical origin and agricultural practices in food production have assumed great importance.

Authenticity is a quality criterion for food and food ingredients that enjoys increased emphasis within Europe as a result of legislative protection of regional foods. Authentication of food covers many different aspects, including characterization, mislabeling and misleading about origin, and adulteration, which is defined as a process by which the quality or the nature of a given substance is reduced by adding a foreign or an inferior substance and removing a vital element [1].

The European Union (EU) quality schemes identify products and foodstuffs farmed and produced to exacting specifications. A Protected Designation of Origin (PDO) of food covers agricultural products and foodstuffs which are produced, processed and prepared in a given geographical area using recognized know-how. Protected geographical indication therefore concerns agricultural products and foodstuffs closely linked to a geographical area. Typical foodstuffs with recognized PDO are wines, cheeses, oils, honey, beers, meats, pistachios and potatoes. However, this list will be expanded in the near future because it is of interest for producers to register their products in the European agricultural product quality policy as PDO [2].

The use of analytical techniques to determine the geographical origin of food products is the best way to preserve home agricultural production without adulteration. Strategies employed to detect adulterated products have relied on instrumental techniques mainly because food adulteration can be highly sophisticated. High-performance liquid chromatography (HPLC) [3], gas chromatography (GC) [4], UV-visible (UV-Vis) [5] and infrared (IR) spectroscopy [6], differential scanning calorimetry (DSC) [7] and nuclear magnetic resonance (NMR) spectroscopy [8] have been proposed for food authenticity in order to control the presence of the main components of the sample or some organic compounds that can be characteristic of a PDO.

However, the normal range of organic compounds in foods varies with fertilization, climatic conditions in the year of cultivation, history of fields and variety or

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*Corresponding author.
Tel.: +34 963544838;
Fax: +34 963544845;
E-mail: sergio.armenta@uv.es

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species as well as geographical location and soil characteristics, so it is sometimes difficult to be definitive about the authenticity of a material from the determination of organic components, so that there is continuing demand for effective techniques for authenticity control in food.

But it is well known that the content of selected minerals and trace elements in foods clearly reflects the soil type and the environmental growing conditions. Because of that, evaluation of trace-element content has been proposed to assure the geographical origin of food samples. Thus, mono-elemental techniques have been successfully employed in food authentication [e.g., flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS)], as have multi-elemental techniques [e.g., inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS)].

In addition, the content of hydrogen and oxygen are reliable indicators of climatic characteristics, as are the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ ratios, which depend on local agricultural practices and animal diets [9]. Thus, stable-isotope ratio (SIR) has been demonstrated to be a good descriptor for different food products, providing unique and representative fingerprints that make it possible to differentiate between food samples of different PDOs.

As can be seen in Fig. 1, the use of trace-element composition for characterizing the PDO of food samples has grown significantly (e.g., to 5.2 papers per year on trace-element composition published since 2000). This increasing activity is probably due to legal interest in protecting indigenous products and to tremendous improvement in available instrumentation.

However, the papers concerning SIR seem to have reached a steady state in recent years.

The aim of this review is to provide an overview of published reports on use of trace-element composition and SIR as analytical tools for discrimination of PDO in food products, highlighting the strengths and the weaknesses of these methodologies.

2. Analytical methods employed for sample characterization

2.1. Trace-element analysis

In order to guarantee product authenticity, based on its trace-element profile, different analytical techniques have been proposed (see Fig. 2).

The techniques of choice to obtain the elemental fingerprint of food are those with multi-element detection capability {e.g., ICP-based techniques (ICP-OES and ICP-MS) [10,11]}. ICP-MS typically provides limits of detection (LODs) for 70 elements in the range of ppb and ppt. Unfortunately, for a handful of elements (e.g., As, Se, Cr, Fe, Mn and Ca), conventional ICP-MS cannot provide the best LODs because the most abundant isotopes are overlapped by polyatomic interferences. In order to eliminate these interferences, it is possible to use a quadrupole analyzer equipped with dynamic reaction cell (DRC) or a sector-field instrument that greatly improves the selectivity and the sensitivity, reaching LODs of ng/g.

ICP-OES is a fast multi-element technique with an extended dynamic linear range and moderate-low LODs (~0.2–100 ppb). The instrument uses a plasma source to dissociate the sample into constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength. Up to 60 elements can be screened per sample run in less than 1 min and trace-element composition can be determined in a variety of aqueous or organic matrices. The possibility of working with axial and radial view provides high sensitivity, with low background avoiding interferences and involving minimal ionization effects. ICP-OES also allows the possibility of monitoring wavelengths down to 165 nm that provide high sensitivity for phosphorous and sulfur determinations.

However, the main drawbacks of ICP-MS and ICP-OES are their expense and the requirement for trained operators.

As can be see in Fig. 2A, AAS is also a technique of choice for determining the geographical origin of food [12,13]. AAS is a sensitive and highly selective spectrometric tool suitable for the determination of many elements at trace and ultra-trace levels. The main advantages of FAAS with atomization in a common air-acetylene flame are low operational costs and good analytical performance. The limitations of mono-elemental detection and the narrow range of linear response can be regarded as disadvantages of this analytical method. The use of FAAS for food-sample analysis is usually done to avoid possible spectral or polyatomic interferences, which can appear in plasma techniques. Furthermore, FAAS is commonly used to determine alkaline and alkaline-earth elements (K, Ca, Na and Mg) that are generally minor components of food samples, avoiding high dilution to match the dynamic ranges of calibration curves.

The direct analysis of solid samples with a reduced pretreatment is possible using the ETAAS technique that offers high sensitivity and selectivity at a reasonable cost with the possibility of determining low levels of non-metals (e.g., Cl, F, P or S), which are not so accessible in plasma instrumentation due to different interferences.

The most important drawback of AAS techniques is the lack of multi-elemental analysis. Nevertheless, it can be also considered an advantage due to less spectral and non-spectral interference that can be easily minimized using Zeeman-effect or continuum-source-based background corrections.