The geographical origin of fresh horticultural products: analytical methods to prevent food frauds

Agnese Aguzzoni* e Scandellari Francesca

Facoltà di Scienze e Tecnologie, Libera Università di Bolzano-Bozen

Ricezione: 08 settembre 2017; Accettazione: 27 ottobre 2017

L'origine geografica dei prodotti ortofrutticoli freschi: metodi analitici per la prevenzione delle frodi alimentari

Riassunto. Negli ultimi anni si è sviluppata una grande attenzione del consumatore verso la provenienza degli alimenti, con un conseguente aumento dei prodotti riportanti l'indicazione geografica. A causa di un sistema di tracciabilità insufficiente, soprattutto a livello internazionale, si sono diffuse frodi alimentari connesse alla non corretta dicitura d'origine. Diversi metodi analitici sono stati sviluppati per contrastare questa frode e distinguere i prodotti in funzione della provenienza. Grazie al perfezionamento strumentale e metodologico, tecniche come l'analisi multielemento e la determinazione del rapporto isotopico unitamente all'analisi chemometrica mostrano ottimi risultati di discriminazione tra prodotti ortofrutticoli freschi o parzialmente lavorati di origine differente.

Parole chiave: tracciabilità, frodi alimentari, composizione multielemento, rapporto isotopico.

Introduction

For thousands of years, food has been largely cultivated or bought locally, with little or no transformation and processing. This implied a short production chain. Urban and social transformations through the centuries, especially in the developed countries, weakened the link between food and territory (Luykx and van Ruth, 2008; Drivelos and Georgiou, 2012). More recently, new radical changes in consumers' habits have led to an all year round demand of a great variety of fresh products. Additionally, the request for non-local food is raised, eased by improvements in storage and transportation technologies. Therefore, the market largely shifted from local to global (Perez *et al.*, 2006; Brereton, 2013).

In the last decades, consumers have shown a new attention towards the origin of produces and their production process. In fact, as attested by a survey conducted on behalf of the Directorate-General in Agriculture and Rural Development of the European Union in March 2012 in 27 member states of the EU (fig. 1), about 71% of EU citizens recognize the importance of food origin in determining their buying habits (TNS Opinion & Social, 2012). Moreover, EU27 consumers assigned a great value to quality and price, respectively important for 96% and 91% of the interviewees, while brand is considered a marginal factor, declared not important by half of the survey participants (fig. 1). Many reasons can be ascribed to this attitude: patriotism, intrinsic features associated with regional food, higher quality or safety associated to specific production areas and local products, concerns about production methods in other countries, worries about food miles and environmental impact and need to support local economy (Kelly et al., 2005; Bingen et al., 2010; Drivelos and Georgiou, 2012).

Due to the complexity of the global food network and the difficulty to trace back the origin of goods without reliable and exhaustive records, false declaration about food provenance, classified as food fraud, may easily spread. For this reason, there has been an increasing attention of scientists and other stakehold-



Fig. 1 - Fattori che influenzano l'acquisto di beni alimentari (TNS Opinion & Social, 2012).

^{*} agnese.aguzzoni@natec.unibz.it

Fig. 1 - Consumers priorities when buying food (TNS Opinion & Social, 2012).

ers on this topic. This has been followed by an increase in the number of scientific publications and research projects with the main purpose of developing analytical methods, legally admissible, able to detect this type of fraud (Rossmann, 2001; Ehleringer and Matheson Jr., 2010; Camin *et al.*, 2017). Particularly, developments of the present methods to provide robust and reliable results are required to support legal cases. Existence of databanks based on data and metadata of authentic material, a suitable sampling design, method validation and laboratory accreditation, measurement of the uncertainty budget are some examples of requirements needed to support the validity of the analysis performed in front of a court (Camin *et al.*, 2017).

The aim of this review is to:

• define the phenomenon of fraudulent activities in

the food sector and its consequences, focusing on frauds related to food provenance and traceability;

- describe the underlying principles and the advantages and disadvantages of the analytical techniques applied to authenticate agrifood based on its provenance especially focusing on multielement composition and isotope ratio measurement;
- report a few representative case studies published in literature comparing the different analytical and chemometric approaches applied by authors to improve sample discrimination.

We have reviewed the most relevant papers found in literature dealing with the discrimination of horticultural products, solely based on their geographical origin (tab. 1). We decided to focus only on fresh or just slightly transformed (polished rice) horticultural products leaving therefore behind all transformed products

Tab. 1 - Summary of the most relevant literature related to the use of multi-element and multi-isotope analysis of fresh horticultural products to determine their geographical origin.

Food	Food origin	Analysis	Instrument	Ν	Data treatment	Reference
Apple	4 Italian provinces	δ ¹³ C, δ ¹⁵ N	IRMS	128	ANOVA, PCA, LDA	Mimmo <i>et al.</i> , 2015
Blackcurrant	4 Chinese production areas	$ \begin{array}{c} \delta^2 H, \delta^{13} C, \delta^{15} N, \\ \delta^{18} O \end{array} $	IRMS	-	ANOVA, DA	Li et al., 2013
Cabbage	Korea, China	ME, ⁸⁷ Sr/ ⁸⁶ Sr	ICP-AES, ICP-MS, MC-ICP-MS	363	DA	Bong et al., 2013
Clementine	PGI clementine vs non-PGI clementine	ME	DRC ICP-MS	88	PCA, LDA, SIMCA, PLS-DA	Benabdelkamel <i>et</i> <i>al.</i> , 2012
Green coffee bean	5 Hawaiian Islands	ME, δ^{13} C, δ^{15} N, δ^{18} O, δ^{34} S, 87 Sr/ 86 Sr	IRMS, ICP-MS, MC-ICP-MS	47	ANOVA, CDA	Rodrigues <i>et al.</i> , 2011
Green coffee bean	South and Central America, Africa, Asia	$\begin{array}{c} \text{ME, } \delta^2\text{H, } \delta^{13}\text{C,} \\ \delta^{15}\text{N, } \delta^{18}\text{O} \end{array}$	ICP-MS, IRMS	62	ANOVA, CDA	Santato <i>et al.</i> , 2012
Green coffee bean	Africa, Asia, Oceania, Central and South America	ME	ICP-MS, ICP-AES	51	PCA, LDA	Valentin and Watling, 2013
Fava	Greece, India, Iran, Australia, Canada, USA	ME	ICP-MS	39	PCA, PLS-DA	Drivelos <i>et al.</i> , 2014
Grape	Italy, Spain	$ \begin{array}{c} \delta^2 H, \delta^{13} C, \delta^{15} N, \\ \delta^{18} O \end{array} $	IRMS	146	PCA, DA	Longobardi <i>et al.</i> , 2016
Hazelnut	Italy, Turkey	ME	ICP-MS	-	PCA	Oddone <i>et al.</i> , 2009
Onion	Japan, China, USA, New Zealand, Thailand, Australia, Chile	ME	ICP-AES, ICP-MS	309	LDA	Ariyama <i>et al.</i> , 2007
Onion	Japan, China, USA, New Zealand, Australia, Thailand	Sr and ⁸⁷ Sr/ ⁸⁶ Sr	ICP-MS, MC-ICP- MS	139	LDA	Hiraoka <i>et al.</i> , 2016

Tab. 1 - Riassunto delle pubblicazioni più rilevanti che riportano l'applicazione dell'analisi multielemento e del rapporto isotopico di diversi elementi per determinare l'origine geografica dei prodotti ortofrutticoli freschi.

segue	tab	1
-------	-----	---

Food	Food origin	Analysis	Instrument	N	Data treatment	Reference
Paprika	Hungary, China, France, Germany, Italy, Romania, Senegal, Spain	ME, ⁸⁷ Sr/ ⁸⁶ Sr	HR-ICP-MS, MC- ICP-MS	64	PCA, CDA	Brunner <i>et al.</i> , 2010
Pistachio	Turkey, Iran, California (USA)	ME, $\delta^{13}C$, $\delta^{15}N$, C/N	ICP-AES, IRMS	372	PCA, CDA, LDA, ANN	Anderson e Smith, 2005
Potato	Six Italian regions	ME	ICP-MS	60	LDA	Di Giacomo <i>et al.</i> , 2007
Rice (polished)	Japan, USA, Australia	$\begin{array}{c} C,N,\delta^{13}C,\delta^{15}N,\\ \delta^{18}O \end{array}$	IRMS	14	-	Suzuki <i>et al.</i> , 2008
Rice	Spain , Japan, Brazil, India	ME	ICP-AES	153	LDA	Gonzálvez <i>et al.</i> , 2011
Rice (polished and brown)	Japan, USA, China, Thailand	ME, ⁸⁷ Sr/ ⁸⁶ Sr, PbIR	HR-ICP-MS	350	ANOVA, PCA, LDA, SIMCA, KNN	Ariyama <i>et al.</i> , 2012
Rice	4 Chinese provinces	ME	ICP-MS, FAAS	32	ANOVA, LDA, CA	Shen <i>et al.</i> , 2013
Rice (polished)	Thailand, France, India, Italy, Japan, Pakistan	ME	HR-ICP-MS	36	PCA, DA	Cheajesadagul <i>et</i> <i>al.</i> , 2013
Saffron (fresh steam)	3 Italian regions	ME	ICP-MS	27	LDA	D'Archivio <i>et al.</i> , 2014
Schisandra fruits	6 Chinese provinces	$\delta^{13}C$	IRMS	96	-	Li <i>et al</i> ., 2011
Tomato	Italy, China	⁸⁷ Sr/ ⁸⁶ Sr	TIMS	118	ANOVA, t-test	Trincherini <i>et al.</i> , 2014
Tropea red onion	PGI and non-PGI production area	ME	DRC ICP-MS	200	LDA, SIMCA, ANN	Furia <i>et al.</i> , 2011
Welsh onions	Japan, China	ME	FAAS, ICP-AES, ICP-MS	244	LDA, SIMCA	Ariyama <i>et al.</i> , 2004
Wheat	Australia, Turkey, Canada, Italy	δ^{13} C, δ^{15} N, δ^{18} O	IRMS	35	ANOVA	Brescia <i>et al.</i> , 2002
Wheat	4 Chinese production areas	ME	ICP-MS	240	ANOVA, LDA	Zhao et al., 2011
Wheat	3 Argentinean regions	ME, δ^{13} C, δ^{15} N, 87 Sr/ 86 Sr	ICP-MS, IRMS, TIMS	80	ANOVA, DA	Podio <i>et al.</i> , 2013
Wheat	Australia, USA, Canada, China	$\delta^{13}C, \delta^{15}N$	IRMS	35	ANOVA	Luo et al., 2015
Wheat	3 Chinese regions	δ^{2} H, δ^{13} C, δ^{15} N, 87 Sr/ 86 Sr	IRMS, TIMS	54	ANOVA, DA	Liu et al., 2016
Wheat	Six Indian states	$\delta^{13}C, \delta^{15}N$	IRMS	20	ANOVA	Rashmi et al., 2017
White asparagus	Austria, Germany, Slovakia, Hungary, Netherlands, Perù	Sr and ⁸⁷ Sr/ ⁸⁶ Sr	ICP-MS, MC-ICP- MS	155	-	Swoboda <i>et al.</i> , 2008
Burdock, Ginger, Taro, Garlic, Pea	Japan , China	Sr and ⁸⁷ Sr/ ⁸⁶ Sr	ICP-MS, MC-ICP- MS	403	LDA	Aoyama <i>et al.</i> , 2017
Strawberry	Oregon (USA) vs Mexico	ME,	ICP-AES,	80	ANOVA, t-test, CDA, LDA, QDA, PCA	Perez <i>et al.</i> , 2006
Blueberry	Oregon (USA) vs Chile	δ^{13} C, δ^{15} N,	IRMS	74	ANOVA, t-test, CDA, LDA, QDA, PCA	Perez <i>et al.</i> , 2006
Pear	Oregon (USA) vs Argentina	C/N		80	ANOVA, t-test, CDA, LDA, QDA, PCA	Perez <i>et al.</i> , 2006

Analysis: ME multielement fingerprint; δ^2 H hydrogen isotope ratio; δ^{13} C carbon isotope ratio; δ^{15} N nitrogen isotope ratio; δ^{18} O oxygen isotope ratio; 87 Sr/ 86 Sr strontium isotope ratio; PbIR lead isotope ratio. **Instrument**: IRMS isotope ratio mass spectrometer; FAAS flame atomic absorption spectrometer; ICP-AES inductively coupled plasma atomic emission spectrometry; ICP-MS inductively coupled plasma mass spectrometer; DRC ICP-MS dynamic reaction cell ICP-MS; HR-ICP-MS high resolution ICP-MS; MC-ICP-MS multicollector ICP-MS; TIMS thermal ionization mass spectrometer. **Data treatment**: ANN artificial neural network; ANOVA analysis of variance; CA cluster analysis; CDA canonical discriminant analysis; PCA principal component analysis; PIS-A partial least square discriminant analysis; SIMCA soft independent

pal component analysis; PLS-DA partial least square discriminant analysis; QDA quadratic discriminant analysis; SIMCA soft independent modelling of class analogy.

such as fruit juices, wine, canned vegetables, etc. For each of these produces, a dedicated review would be desirable, since several authors showed that the processing itself might introduce further modifications independent from geographical origin (Almeida and Vasconcelos, 2003; Hopfer *et al.*, 2015). Only studies in which multielement fingerprint and/or isotope ratio analysis are applied were included. Studies combining these techniques with other methods were excluded and papers published starting from year 2000 were chosen. Following these criteria, papers were selected from the two databases Scopus and Web of Science.

Fraudulent activities in the food sector

A food fraud mainly consists on the adulteration or misrepresentation of foods or food ingredients. Origin masking is recognized as one of the existing food frauds (Johnson, 2014). The National Centre for Food Protection and Defence (NCFPD) at the University of Minnesota compiled a registry analysing food frauds occurred worldwide since 1980. According to this database, food frauds included are either economically motivated (EMAs) or intentionally harmful, such as those related to agro-terrorism. Figure 2 summarizes the distribution of incidents according to the NCFPD EMA Incident Database sorted by type of adulteration (Johnson, 2014). Aside the economic damage, the direct consequence of adulterations is "a change of the identity and/or purity of the original and purported ingredient by substituting, diluting, or modifying it by physical or chemical means" (Moore et al., 2012). Unfortunately, often the fraudster has scarce awareness of the safety risks related to such adulteration with dramatic consequences, as happened for the 2008



Fig. 2 - Leading EMA Incidents by type of adulteration (Johnson, 2014).

Chinese milk scandal. Melamine, a nitrogen-based organic compound, was used to mask the dilution with water of milk, increasing the overall nitrogen content directly associated to food protein. The tainted milk was sold on the market for different purposes, including infant formula production. The melamine toxicity, that a few years earlier had already been associated to several cases of pet death in the USA (Ingelfinger, 2008; Pei et al., 2011), caused more than 52000 hospitalization of children due to renal and kidney failure, and the death of six infants in China. Another remarkable example is given by the horsemeat scandal in 2013, in which beef-products or beef-ingredients were found positive to the presence of undeclared horsemeat (Food Safety Authority of Ireland, http://www.fsai.ie). As consequence of this scandal, Irish consumers changed their purchasing behaviour and ca. 40-50% of the habitual consumers of processed food containing meat declared to have reduced their purchase because of that (FSAI 2013). Many other frauds do not evolve to the status of scandal but are well documented and affect consumers' confidence in buying food, leading to diffidence in paying a higher price for goods that easily may be not integer. Indeed, often, the fraud consists in replacing entirely or to a certain extent an expensive ingredient/product with a cheaper one: regular olive oil for extra virgin olive oil, bovine milk for sheep/goat milk, different types of syrup for honey, farmed for wild salmon, conventional for organic food. Several chemicals are used for blending spices (saffron, pepper, paprika) or natural compounds are substituted with synthetic ones (vanilla) especially for saving money on expensive raw material or enhancing its colour and taste in case of poor quality. False declaration of origin is committed either for increasing the appeal of a product (e.g. PGI and PDO labelled products) or for escaping paying taxes and tariffs in certain countries (Johnson, 2014). Even if origin mislabelling can be considered a marginal fraud, it should not be underestimated as it deeply affects subtle factors such as the reliability and intrinsic quality of an item that can be severely damaged by misidentification scandals (Anderson and Smith, 2002).

Food provenance and traceability

The geographical indication (GI) can confer a higher value to food, and many products are named or identified with their place of origin (Parmigiano-Reggiano, Champagne, Scotch whisky). To protect these goods and their unique characteristics, since 1992 with the European Union Protected Food Names Scheme the EU has introduced legal certification marks, such as PDO (Protected Designation of Origin), PGI (Protected Geographical Indication), and TSG (Traditional Specialties Guarantee). In this way, the EU officially recognized the importance of the place of origin. In Europe, more than 700 agricultural produces and processed foods received the PGI label. Almost half of these comes from France, Italy and Spain. As shown in figure 3, the largest class of products that received the geographical indications consists of agrifood (fruit, vegetables and cereals, fresh or processed) according to the database of origin and registration (DOOR) of the European Union (https://ec.europa.eu/agriculture/quality_en).

Protected food requires higher production costs that are reflected on the final price charged to consumers (Heaton et al., 2008). The possibility of profit attracts fraudsters who sell cheaper goods as typical products (Zhao et al., 2014), taking advantage of price variability of raw material from place to place (Ariyama et al., 2007). An explicative example is given by the case of PGI Tropea Red Onion: despite a production capacity of about 20000 tons the PGI labelled onions on market are more than 100000 tons (Furia et al., 2011). This causes a significant economic damage for honest producers of labelled goods; on top of that, once the fraud is discovered, it might adversely affect the GI-product reputation. Unfortunately, this is not an isolate case. A monthly report delivered by the European Commission summarizes the main investigations conducted to prevent and fight EMAs, highlighting that the agrifood sector is equally affected by the problem as others (wine production, meat industry, fishery) (JRC European Commission). Beside producers' protection, also consumers' tutelage must be ensured. The free and deliberate choice of buying based on food origin should be guaranteed. Therefore, the good practice of keeping



Fig. 3 - Classificazione dei prodotti IGP per categoria secondo il database DOOR (https://ec.europa.eu/agriculture/quality_en). Fig. 3 - Classification of PGI products per class according to DOOR database (https://ec.europa.eu/agriculture/quality_en).

record of the history of food must be implemented.

Traceability is defined as "the ability to follow the movement of a food through specified stages of production, processing, and distribution" (Codex Alimentarius, 2006). Nowadays, it is largely based on paper-records, easily falsifiable or insufficient to meet specific requirements (Germain, 2003). Recently, new instruments (labelling, bar-cording, radio frequency identification RFID) have been introduced to increase the reliability and accessibility of records (Regattieri et al., 2007; Charlebois et al., 2014). Traceability is even more difficult in international trading and commerce, since different countries developed different regulatory systems (Charlebois et al., 2014). It should be highlighted that several benefits should encourage companies to implement a traceability process:

- simplifying management procedure in case of risks or safety issues (e.g. products recall);
- ensuring product authenticity and quality;
- providing credible information to consumers or authorities;
- improving identification of non-compliance in the production process;
- increasing the production-chain efficiency (Germain, 2003; Alfaro and Rábade, 2009).

In this context, the need for analytical tools able to recognize and attest the food provenance has become a priority (Fortunato *et al.*, 2004; Kelly *et al.*, 2005; Perez *et al.*, 2006).

Analytical tools

Different techniques have been tested for food authentication and traceability through the years. Near infrared spectroscopy (NIR), mass spectrometry, chromatography, nuclear magnetic resonance (NMR) and DNA profiling have been largely employed (Kelly et al., 2005; Luykx and van Ruth, 2008). Many studies were based on the analysis of classes of organic compounds (fatty acids, volatile compounds, polyphenols) as non-targeting analysis. However organic compounds are susceptible to degradation processes (Anderson and Smith, 2002) and can be affected by several factors in addition to provenance, a fact that causes a low discrimination power (Anderson and Smith, 2005; Gonzalvez et al., 2009). Consequently, techniques independent from organic compounds, such as those based on the content of mineral elements and on the ratio of stable isotopes of light and heavy elements, have been improved for application in the field of geographical traceability. Many of these methods are also successfully applied

to discover other types of frauds, as in the case of the analysis of isotope ratio of light elements.

Multielement fingerprint

Basic concept. Each plant produce is characterized by a unique profile of inorganic elements, which are absorbed by plants and distributed in the biomass. Hydrogen (H), carbon (C) and oxygen (O) are essential non-mineral elements that are absorbed from air and water and are the main constituents of organic molecules in plants. Mineral elements are absorbed mainly through the soil solution and are classified according to their nutritional value as primary macronutrients (N, P, K), secondary macronutrients (Ca, S, Mg) and micronutrients (B, Cl, Mn, Fe, Cu, Zn, Mo). In addition, the soil contains many other elements, such as strontium (Sr), rubidium (Rb), barium (Ba), etc., that can be absorbed by the plant even if they do not have any biological role. While the uptake of elements with high nutritional value is mainly controlled by plant needs, the uptake of non-nutritional elements is mostly related to their concentration and bioavailability in the soil. This, in turn, mainly depends on chemical-physical processes such as soil pH, moisture, mineral weathering, organic matter decomposition (Perez et al., 2006; Drivelos and Georgiou, 2012) or on external factors such as anthropogenic pollution, atmospheric depositions, agricultural practices and the use of fertilizers or soil improvers (Perez et al., 2006). Therefore, the multielement composition of a produce is generally highly correlated to the soil and environmental conditions of the growing area (Gonzalvez et al., 2009), and much information can be inferred from its analysis, which is often restricted to specific groups of elements that are considered soil markers. For instance, many authors showed that a good separation between areas of origin can be achieved focusing on elements present at trace and ultra-trace levels, such as those belonging to the group of rare earth elements composed by scandium, yttrium and the fifteen lanthanides (Oddone et al., 2009; Joebstl et al., 2010; Gonzálvez et al., 2011; Aceto et al., 2013; Ma et al., 2016).

Advantages and disadvantages of multielement analysis. Elemental analysis has been widely applied to traceability studies due to the strong influence of the environment on the multielement composition of crops. Therefore, one of the advantages of this technique is that well described analytical methods and pre-treatment procedures for several matrices are already available in literature.

The disadvantages are mainly related to the behaviour of elements in the soil and in the plant. Indeed, dissimilarities in cation uptake through the root system exist due to differences in species and variety even when plants grown in the same environment are investigated (Almeida and Vasconcelos, 2003; Chietera and Chardon, 2014). In addition, the transfer from the soil to the plant of mineral elements with no or little nutritional importance can be controlled not only by their concentration in the soil, but also by mechanisms intrinsic to plants (Hopfer et al., 2015). For instance, biopurification processes imply the preferential absorption of nutrients and consequently the exclusion of non-nutrient substances within a nutrient cycle. Considering the elements of the second group of the periodic table (alkaline earth metals), this phenomenon explains why moving from the soil to the plant there is a decrease of the Sr/Ca and Ba/Ca ratio (Elias et al., 1982; Blum et al., 2000). Consequently, the mineral profile of vegetable material can be partially or completely not directly comparable to that of the soil and the final relationship between the two matrices can be weak (Tyler, 2004; Shen et al., 2013). Nevertheless, characteristic trends and patterns for specific areas can still be present in vegetable material ensuring provenance discrimination (Oddone et al., 2009; Furia et al., 2011; Benabdelkamel et al., 2012; Zhao et al., 2013; D'Archivio et al., 2014; Drivelos et al., 2014).

Another disadvantage is that the multielement profile of a produce can be severely altered by its transformation process, as it happens in the wine production chain (Almeida and Vasconcelos, 2003; Hopfer *et al.*, 2015; Kaya *et al.*, 2017). Consequently, all these factors must be considered when approaching to traceability using multielement fingerprints.

Available instruments. The main analytical techniques used for the multielement detections are inductively coupled plasma (ICP) techniques where a stable plasma source ionizes the elements. Since most of the analytical methods for ICP techniques works with liquid samples, pre-treatment procedure is required. For instance, organic samples are usually acid digested at high temperature to dissolve the organic material and release analytes into solution. The ICP-based techniques differ consistently for the separation module that can be either an atomic emission spectrometer (AES) (figure 4), also called optical emission spectrometer (OES), or a mass spectrometer (MS) (figure 5). Other techniques employed for multielement analysis are based on atomic absorption spectrometry (AAS). Even if mass spectrometry techniques are highly performant and can reach very low detection limits (typically 1-10 ppt), the choice of the instrument is not univocal and depends on many factors (Thermo Elemental, 2001). The type of application



Fig. 4 - ICP-OES (Thermo Fisher Scientific) disponibile presso Eco-research srl. Fig. 4 - ICP-OES (Thermo Fisher Scientific) instrument available at Eco-research srl.

and the nature of the element of interest should be considered. ICP-MS should be preferred to detect trace metals, whereas ICP-AES or HR-ICP-MS is required to detect sulphur. The relatively low temperatures reachable by FAAS instruments (2600 °C) limit the detection capability only to certain elements in the sub-ppm range, slightly improved by GFAAS (subppb range). However, flame AAS systems are easy to set up and use, precise and their costs are moderate. The number of elements to detect is a considerable



Fig. 5 - ICP-MS (Thermo Fisher Scientific) disponibile presso Eco-research srl. Fig. 5 - ICP-MS (Thermo Fisher Scientific) instrument available at Eco-research srl.

factor of choice: FAAS works quickly for less than five elements, but moving up to 15 or more elements the total analysis time is reduced with simultaneous ICP-AES and ICP-MS. Finally, each technique suffers for several types of interferences (spectral, background, matrix) that must be considered to avoid serious problems affecting the measurement. Table 2 summarizes the main features per technique.

Stable isotope ratio

Basic concept. Among the natural elements, more than 50 have two or more stable isotopes. For specific

	Flame AAS	GFAAS	ICP-AES	ICP-MS
Detection limits	sub-ppm range	sub-ppb range	1-10 ppb	1-10 ppt
Linear dynamic range	103	102	$10^{5} - 10^{8}$	10^{4} - 10^{8}
Precision				
Short term	0.1-1%	0.5-5%	0.3-2%	1-3%
Long term	-	tube lifetime	< 5%	< 5%
Interferences:				
spectral	almost none	few	common	few
chemical (matrix)	many	many	almost none	moderate
ionization	some	minimal	minimal	minimal
isotopes	no	no	no	yes
Applicability (<i>n</i> elements)	>68	>50	>73	>75
Samples usage	high	low	high	low
Throughput per sample	10-15 s per el.	< 3 min per el.	1-60 el. per min	all el. in $< 1 \min$
Ease of use	easy	moderately easy	easy	moderately easy
Method development	easy	difficult	moderately easy	difficult
Capital costs	low	medium-high	high	very high
Running costs	low	medium	high	high

Tab. 2 - Confronto tra diversi strumenti per l'analisi multielemento (Tyler, 1994; Thermo Elemental, 2001). Tab. 2 - Comparison between multielement analysis instruments (Tyler, 1994; Thermo Elemental, 2001).

elements, the ratio between some of their isotopes can provide valuable information and many applications in several fields have been developed through the years. Since these ratios can show local variability (depletion or enrichment), their application as provenance tracers has been highlighted. The most used isotope ratios for this purpose are those of the light elements hydrogen (H), carbon (C), nitrogen (N) and oxygen (O). In the last decade, also the number of papers regarding the isotope ratio of heavy elements such as strontium (Sr) and lead (Pb) has increased.

Light elements are characterized by very small differences in absolute abundance of their stable isotopes. Therefore, by convention, their isotope ratio is compared to that of a standard material and expressed in delta notation:

$$\partial^{n} E = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1 \times 1000$$

where E is the element of interest (e.g. O), *n* represents the atomic mass of the heavier isotope (e.g. 18), R is the absolute ratio of the two isotopes considered (e.g. ¹⁸O/¹⁶O). A multiplication factor of 1000 is included to facilitate data handle. A positive δ value means that the sample is enriched in the heavier isotope compared to the standard while a negative δ value corresponds to a sample depleted of the heavier isotope compared to the standard (Dawson and Siegwolf, 2007). For the isotopes of light elements, the difference of mass between isotopes is relevant respect to their atomic masses (for example, ¹³C is 8% heavier than ¹²C); therefore, several common biochemical, chemical and physical processes can result in isotope separation based on their mass. This phenomenon is called isotope fractionation.

• Carbon isotope ratio $({}^{13}C/{}^{12}C)$ - The main process affecting carbon fractionation in plants is photosynthesis. The first fractionating step occurs when ¹²CO₂ preferentially passes through plant stomata from the atmosphere. Then, different photosynthetic pathways (C3, C4 or crassulacean acid metabolism CAM) contribute to enhance more or less the fractionation: in C3 plants (e.g. wheat, rye, oats and most trees), the depletion of ${}^{13}C$ is higher compared to C4 plants (e.g. maize, sugar cane) so that δ^{13} C of C4 and C3 plants is around -10‰ and -28‰, respectively. CAM plants (e.g. pineapple) cover the entire δ^{13} C range between C3 and C4 plants. Finally, terrestrial plants are usually characterized by a higher fractionation than marine and aquatic plants, where also dissolved carbon dioxide is available (Dawson and Siegwolf, 2007). Additionally, also the growing environment plays a role in determining carbon isotope composition in plants, since climatic factors affect the exchange mechanism of several compounds among which CO_2 in the plant-atmosphere system (Brescia *et al.*, 2002)

- Nitrogen isotope ratio (¹⁵N/¹⁴N) The nitrogen isotope composition is severely altered by anthropogenic sources and large shifts can be measured in different ecosystems. N isotopic fractionation in plant-soil system is still not fully understood due to the complexity of the N cycle. However, several biogeochemical processes are considered responsible for nitrogen fractionation: biological fixation, mineralization, nitrification or denitrification, ammonium and nitrate ion exchange, volatilization, N reallocation and assimilation, foliar uptake (Dawson and Siegwolf, 2007). Plants growing near the costs, in saline environment or, to a lesser extent, in hot and dry ecosystems are generally characterized by higher $\delta^{15}N$ (Heaton, 1987). In cultivated areas, agricultural practices deeply affect the δ^{15} N: the application of animal manure is reflected by an enrichment of ¹⁵N in the plants, compared to chemical fertilizers or unfertilized plants, considering equal N-availability (Szpak, 2014). δ¹⁵N values of plant materials range between -10% and +20% (Dawson and Siegwolf, 2007).
- Hydrogen $({}^{2}\text{H}/{}^{1}\text{H})$ and oxygen $({}^{18}\text{O}/{}^{16}\text{O})$ isotope ratio – Hydrogen and oxygen fractionation is mainly related to the water cycle. Seasonality, latitude, altitude and "continentality" (the distance covered by an air mass rich of water from the cost to the point where the meteoric event takes place) impact on the water isotope ratio of precipitations (Dawson and Siegwolf, 2007). Plant water derives principally from the soil solution, whose isotopic profile reflects to some extent that of precipitations (Roden and Ehleringer, 1999; De Rijke et al., 2016). Water absorption in root and transport is little or no affected by fractionation and isotopic signal is retained in structural organic compounds in plants (Deniro and Epstein, 1979; Cernusak et al., 2016). Therefore, it is possible to link food to specific geographical areas analysing its H and O isotope ratio. Referring to agrifood in particular, the use of irrigation water should be taken into account, since it can affect significantly the final isotope ratio (Gómez-Alonso and García-Romero, 2010). δ^2 H ranges between -350‰ and +50‰ in plant water, while δ^{16} O ranges between -35‰ and +5‰ in plant water and between 0‰ and +40‰ in plant organic matter(Dawson and Siegwolf, 2007).

Contrarily to light elements, heavy elements such as strontium (Sr) and lead (Pb) are hardly fractionated during biogeochemical cycles due to the low relative mass difference between isotopes (Drivelos and Georgiou, 2012). In this case, the variability of the isotope ratio is given by the peculiar nature of these elements. Both Sr and Pb have primordial and radiogenic isotopes. Primordial isotopes exist in nature since the Earth formed, while radiogenic isotopes derive from the radioactive decay of other isotopes with specific half-life time. The combination of time and parent/daughter ratio brought to nowadays values of isotope ratios. Even if they tend to increase with time, they can be assumed as constant within a time scale $< 10^4$ years (Nakano, 2016). For these elements, the isotope ratio is expressed by the absolute ratio, that is the ratio between the heavy and the light isotope (e.g. 87 Sr/ 86 Sr), without δ notation.

- Strontium isotope ratio (⁸⁷Sr/⁸⁶Sr) The ⁸⁷Sr/⁸⁶Sr of plants reflects that of the soil in which they are grown, since strontium is principally absorbed through root uptake from the soil solution with calcium. Indeed, both the metals belong to the group of the alkaline earth elements and share common chemical features. Due to their similar ionic radius, roots do not significantly discriminate between the two. Local geological features give the variability of the ⁸⁷Sr/⁸⁶Sr in the soil. In fact, Sr is released by rocks into the soil through physico-chemical processes such as weathering, and here its soluble fraction becomes bioavailable for plants. Many authors showed that Sr does not fractionate during root uptake and translocation to the different plant organs (Blum et al., 2000; Flockhart et al., 2015) independently from species or cultivars. (Aoyama et al., 2017). Consequently, the isotope ratio is kept unaltered from the soil to the plant allowing its use to detect food origin.
- Lead isotope ratios Lead has many relevant isotopes, namely ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, and their ratio have been used for fraud detection. From a plant perspective, soil represents the main reservoir from which Pb is absorbed. Pb presence and isotopic composition in soil is related to soil formation and weathering, but it is also contaminated by atmospheric deposition due to the substantial Pb pollution (Reimann *et al.*, 2012). As reported in literature, Pb isotope ratio (PbIR) measured in aerosols all over the world varies significantly especially due to anthropogenic sources whose contribution to Pb emission in the atmosphere is at least two order of magnitude higher than that from natural sources (Bollhöfer and Rosman, 2000,

2001; Komárek *et al.*, 2008). The use of alkyllead compounds in leaded petrol from 1940s until its ban starting from the end of the 80s, dramatically increased global Pb pollution, while nowadays-industrial activities represent the major source. Consequently, Pb isotope composition in food may reflect both geogenic and anthropogenic sources, a fact that allows its application to determine food origin as effective geographical tracer (Ariyama *et al.*, 2011; Evans *et al.*, 2015).

Advantages and disadvantages. Thanks to the improvements of isotopic mass spectrometer (IRMS) instruments at the beginning of the 90s, isotope ratio analysis of light elements applied to food studies gained much interest. There are several advantages in applying this technique in the food sector. Isotope ratio analysis of light elements can reveal not only food geographical origin but provides valuable information about other frauds. Relevant applications in the second case are exhaustively described in literature (Rossmann, 2001; Camin et al., 2017). Several analytical procedures already exist as routine methods for detecting specific frauds. Some examples are the detection of dilution with water measuring δ^{18} O or the addition of organic compounds (e.g. sugars) measuring δ^2 H and/or δ^{13} C for goods such as fruit juice, honey, vinegar, wine and spirits (Rossmann, 2001). Moreover, official methods to distinguish between synthetic and natural vanillin are based on the analysis of δ^2 H (AOAC, 2006). More recently, efforts to detect the production process of horticultural products through the analysis of $\delta^{15}N$ have been published. N-fertilizers are among the main sources of N for plants, and synthetic N-fertilizers are characterized by a lower isotope ratio compared to manure and organic fertilizers. Consequently, many authors showed the feasibility of this approach for distinguishing between conventional and organic crops (Bateman et al., 2005; Camin et al., 2011; Chung et al., 2017b), even if further studies are required. Another advantage related to the analysis of the isotope ratio of light elements in food is that usually the sample pre-treatment is very limited, including only few steps such as drying and powdering. Regarding food traceability, an important limitation is related to varietal-dependent fractionation that has to be accounted when different cultivars are included in the study. Isotopes of light elements are differently fractionated by diverse plant cultivars and species causing a significant intra-region data variability that can reduce the discrimination power of the parameters (Di Giacomo et al., 2007; Mimmo et al., 2015; Chung et al., 2016, 2017a).

The advantage of using the isotopes of heavy elements is that their fractionation is negligible and that they are directly linked with geolithological features. Their analysis is linked to many applications, such as geochronological, environmental and archaeological studies, for dating evidences and establishing products authenticity or sources of pollution (Komárek et al., 2008; Yip et al., 2008; Irrgeher and Prohaska, 2015; Nakano, 2016). In particular, in the last decades, the number of papers dedicated to ⁸⁷Sr/⁸⁶Sr for traceability purposes increased also thanks to instrumental improvements. However, there are some limits to its applicability: crops cultivated in districts with similar geological features are not easily distinguishable (Mercurio et al., 2014), and intensive agricultural practices or anthropogenic sources may significantly alter the ⁸⁷Sr/⁸⁶Sr of the soil solution compromising the origin identification (Techer et al., 2017). The main disadvantage of using lead for food traceability is that it is present at low concentration in food sample and there is a high risk of contamination during the analytical steps. Hence, publications related to PbIR for traceability studies are still uncommon. In addition, from a methodological viewpoint, the analysis of the isotope ratio of heavy elements is more time-consuming since separation steps for isolating the element of interest are required and dedicated laboratory facilities are necessary.

Available instruments. Light element isotope ratio is generally measured through IRMS instruments (fig. 6) after conversion into gas that are ionized and separated for their mass-to-charge ratio (m/z) in the mass spectrometer before reaching the detector. Several peripherals for sample gasification can be coupled to the IRMS according to the type of material and isotope to be analysed. Solid and liquid samples for the analysis of C and N isotopes are burned at 950 °C into CO₂ and N₂ in an elemental analyser (EA). Solid and liquid samples for the analysis of O and H isotopes are burned at 1350-1450 °C into CO and H₂ in a temperature conversion elemental analyser (TC/EA). EA is a bulk measurement technique and the measured isotope ratio is the average of the whole sample. If specific compounds need to be analysed, for example sugars or amino acids, gas or liquid chromatography (GC or LC) separation can be performed before gaseous transformation. TC/EA and EA-IRMS require no or very few preparative steps, while in general GC- and LC-IRMS require extensive extraction steps before the sample is clean enough from contaminants to be injected. LC-IRMS is still at an early stage of applications and analytical problems are not fully solved yet (Muccio and Jackson, 2009).



Fig. 6 - IRMS (Thermo Fisher Scientific) disponibile presso la Libera Università di Bolzano-Bozen.
Fig. 6 - IRMS (Thermo Fisher Scientific) instrument available at the Free University of Bozen-Bolzano.

In recent years, an optical spectrometer called cavity ring down spectrometer (CRDS) has been developed (fig. 7), which, in different configurations, can analyse the isotopes of C, N, O and H. Compared to traditional IRMS instruments, CRDS is cheaper, com-



Fig. 7 - CRDS (Picarro Inc) disponibile presso la Libera Università di Bolzano-Bozen.
Fig. 7 - CRDS (Picarro Inc) instrument available at the Free University of Bozen-Bolzano.

pact and easily moveable for in-situ measurements. For these reasons, this new technology is becoming particularly popular for food traceability (Chesson *et al.*, 2010) and adulteration detection (Meier-Augenstein *et al.*, 2012; Beer *et al.*, 2015).

Isotopic composition of H and/or C can also be detected using the site-specific natural isotope fractionation studied by nuclear magnetic resonance (SNIF-NMR). In this case, only pure or purified molecules are analysed and a larger amount of sample is required.

The isotope ratio of heavy elements can be determined using two types of instruments: thermal ionization mass spectrometer (TIMS) or multi-collector ICP-MS (MC-ICP-MS) (fig. 8). Until recently, the TIMS was the instrument of choice, while nowadays the MC-ICP-MS is getting more popularity after improving its precision, sensitivity and accuracy. In both cases, before injecting the sample into the instrument, the element for which the isotope ratio has to be measured must be separated from the other elements on a selective resin to prevent interferences. Comparing the two instruments, TIMS is less affected than MC-ICP-MS by the isotope fractionation effects that can occur during the analysis. In both cases, the instrumental bias must be corrected. Therefore, the results must be adjusted using a correction factor inferred measuring reference material isotope ratio, calculating the ratio between the certified and the measured value. Moreover, quality control protocols are still not established for MC-ICP-MS (Walczyk, 2004). Nevertheless, MC-ICP-MS is less time consuming, has a greater ionization potential and comparable costs to TIMS (Walczyk, 2004; Yang, 2009).



Fig. 8 - MC-ICP-MS (Thermo Fisher Scientific) disponibile presso Eco-research srl.
Fig. 8 - MC-ICP-MS (Thermo Fisher Scientific) instrument available at Eco-research srl.

Data treatment

Since usually the number of variables considered in traceability/authentication studies is large, chemometric tools are essential for a better comprehension of the data. Multivariate data analysis helps maximizing the information that can be extracted from data. The first papers applying chemometrics to food fraud studies were published in 1988 (Moore et al., 2012). Since then, there has been a great expansion in chemometrics use and in the reviewed literature (tab. 1) most of the authors applied multivariate data analysis. Chemometric tools are divided in unsupervised and supervised methods. All the a priori knowledge of the sample is excluded performing unsupervised methods. These methods are used for exploratory data analysis since they permit to separate samples based on common patterns (Berrueta et al., 2007; Cocchi et al., 2017). Examples of unsupervised methods are principal component analysis (PCA) and cluster analysis (CA). Supervised methods are applied in authentication studies, in which an unknown sample has to be compared with authentic material predicting similarity among samples. A priori knowledge is required to build the proper model on a training set. The prediction ability is then evaluated on a test set. They are divided into two categories: classification and modelling methods. In classification, the focus is on the differences between classes while in modelling on the similarities among samples of the same class. Practically, the major difference resulting from the two categories is that classification always assigns an unknown sample to one class while in modelling the sample can be assigned to one, more than one or no class (Berrueta et al., 2007; Cocchi et al., 2017). Examples of supervised methods are K-nearest neighbours (KNN), discriminant analysis (DA), partial least squares discriminant analysis (PLS-DA), soft independent modelling of class analogy (SIMCA), artificial neural networks (ANN).

Case studies on food provenance

The reviewed literature, chosen accordingly to the parameters previously discussed, is representative of different analytical techniques, combination of variables (for example only multielement, which may include different combinations of elements; only stable isotopes of light and/or heavy elements; or a combination of multielement and stable isotope analysis) and data treatments. Results refer to a great variety of fresh agrifood, comprising fruit and vegetables, tubers, spices, and cereals.

All but two of the included papers combined at least two variables or used a technique that includes multiple variables (multielement profile) to discriminate sample geographical origin. Indeed, a multi-technique or multi-variable approach strengthen the power of the separation since more information about sample is available. For instance, the separation of Schisandra fruits based uniquely on δ^{13} C was not fully effective as several Chinese production areas included in the comparison overlapped, unless macroregions were considered (Li et al., 2011). This is an example of the limited capacity of a single parameter to assess food origin, particularly if not linked to specific territorial features such as δ^{13} C. Although still using only one parameter, better results were obtained by Trincherini et al. (2014) who applied the measurement of the ⁸⁷Sr/⁸⁶Sr to tomato authentication. The comparison was between samples coming from distant production areas, Italian and Chinese, and the corresponding samples showed distinct ranges: 0.70810 ± 0.00036 and 0.71051 ± 0.00033 , respectively. Despite the use of a single variable, Trincherini et al. (2014) proved the discrimination potential of the ⁸⁷Sr/⁸⁶Sr due to its strong link with the geo-lithological features of the investigated growing area. To improve sample discrimination, the obvious way to go is increasing the number of analysed variables to two or more (Swoboda et al., 2008; Luo et al., 2015; Hiraoka et al., 2016; Aoyama et al., 2017; Rashmi et al., 2017). An alternative, if other parameters cannot be added to the study, information extrapolated from samples can be increased considering not only the bulk sample but also its sub-fractions. An example is given by Mimmo et al. (2015) who significantly increased the accuracy of the method analysing δ^{13} C and δ^{15} N in different apple parts (peel, pulp, seeds) in addition to the whole fruit.

The great advantage given by multielement fingerprint is that dealing with a high number of variables is intrinsic within the method and therefore multivariate data analysis is always applicable for data treatment. Indeed, with ME analysis there are enough variables to run the method and highlight useful patterns otherwise not evident. The number of elements analysed varies a lot, from a minimum of 8, but combined with other parameters by Ariyama et al. (2011), to a maximum of 59, used without additional variables (Valentin and Watling, 2013). Not all the elements, though, are always suitable to be included in the data treatment. When elements at trace and ultra-trace levels are measured, instrumental analytical limits have to be considered. Certain authors reported that despite the initial large number of elements analysed they had to discharge part of them, reducing the number of variables, because present in samples at concentration lower than the instrumental detection limit (Gonzálvez *et al.*, 2011; Benabdelkamel *et al.*, 2012; Bong *et al.*, 2013; Podio *et al.*, 2013).

The degree of discrimination power associated to each variable varies largely, and different studies can reach different conclusions. For instance, several authors worked on the geographical origin of wheat, applying different analytical tools or combination of variables. Two works report data of $\delta^{13}C$ and $\delta^{15}N$ visualized on a two-dimensional scatter plot (Luo et al., 2015; Rashmi et al., 2017). In these papers, a good separation was obtained, even if overlapping areas of samples with different provenance were still present. Another work including $\delta^{18}O$ in addition to δ^{13} C and δ^{15} N also obtained significantly different values for each variable using the analysis of variance (ANOVA) (Brescia et al., 2002). However, the authors chose to show the data on two-dimensional scatter plots, combining each time two variables, despite of having three. In this case, using two-dimensional plots clearly hid the differences among wheat origins, since the overall dataset was split in different plots and data visualization was more difficult. Again for wheat, Liu et al. (2016) demonstrated that the correct classification rate obtained by discriminant analysis could be considerably improved, from 77.8% to 98.1%, including the ⁸⁷Sr/86Sr measurement in addition to light element isotope ratio (δ^2 H, δ^{13} C, δ^{15} N). A different approach was used by Zhao et al. (2011), who compared wheat from four Chinese provinces sampled in two years based on the concentration of 15 elements obtaining an overall classification rate in cross-validation of 79.4%. The results obtained from two provinces were particularly overlapped and misclassification was high between the two probably due to soil type and agricultural practices as well as annual and cultivar variability. However, the best result was obtained by Podio et al. (2013) whose approach included the determination of the multielement fingerprint together with light and heavy element isotope ratio. They identified through discriminant analysis the 11 variables giving 100% accuracy. Among the isotope ratio measured, 87 Sr/ 86 Sr and ${\delta}^{13}$ C gave the greatest contribution to samples separation. Interestingly, they extended the number of variables of the multielement profile including ratio among element concentration with remarkable results. For instance, they found out that K/Rb and Ca/Sr have a great discrimination power, contrarily to the corresponding single elements that do not appear among the 11 discriminating variables.

Not only the method of analysis of the samples, but also the chemometric tools used for data analysis are of great importance, especially when supervised methods for sample classification are run. Since each method is based on a different statistical model, the ability of correctly recognize and assign samples to a specific group varies from one method to another. Many authors compared several methods to test the accuracy in classification, showing how misclassification can be reduced choosing the proper method (Anderson and Smith, 2005; Perez et al., 2006; Furia et al., 2011; Benabdelkamel et al., 2012; Ariyama et al., 2012). Furia et al. (2011) evaluated the possibilities of discriminating Tropea red onion production from non-Tropea red onions comparing the prediction ability of LDA, SIMCA, ANN. They obtained satisfying results for all the three methods (> 90%) with LDA giving the highest classification rate (94%). Different models are also able to separate different countries as proved by Ariyama et al. (2012). These authors compared the discrimination power of three supervised methods (KNN, LDA and SIMCA) to separate rice production countries (Japan, USA, China, Thailand) based on the results of multielement fingerprint and Sr and Pb isotope ratio. Considered singularly the performance of these chemometric methods was not satisfying, while their combination proved to be effective with a considerable reduction of sample misclassification and 97% accuracy. Another strategy to improve sample classification is to group together several countries/regions according to common features. This is particularly useful when products labelled according to their geographical indication are compared to focus the attention on the GI-product (Swoboda et al., 2008; Furia et al., 2011; Benabdelkamel et al., 2012). For instance, Benabdelkamel et al. (2012) included in their study clementine samples coming from Calabria (Italy), Algeria, Spain, Tunisia. Since clementine from Calabria are awarded with the PGI label, they decided to group together all the samples from abroad the borders of the "Clementine of Calabria" production area, specifically Algeria, Spain, Tunisia, creating the non-PGI clementine group. With this approach, they obtained excellent results in distinguishing between PGI and non-PGI produce.

Another factor that is crucial for the success of origin discrimination is an appropriate sampling step, both for sample size and distribution (Benedetti *et al.*, 2015). Particularly, a great variability in sample size per country or area considered in the published literature was observed. For instance, Bong *et al.* (2013) included more than 360 samples comparing cabbages from Korea (N=219) and China (N=144) while Cheajesadagul et al. (2013) indicated to have collected only 31 samples of Thai rice to be compared with 5 samples from 5 countries abroad (one per country). Choosing the number of samples is highly related to economic and logistic constrains, especially when foreign countries are included in the study. Moreover, there are no specific guidelines indicating sample numerosity for traceability studies. Sample size depends closely, among others, on the research purpose and it is a function of the target population size. Even if there are statistical tests that can be applied, sample size is often a choice of the analyst. An excess of samples requires a large amount of resources along the analytical pathway, while a defect leads to statistically inaccurate results (Benedetti et al., 2015). Therefore, it is important to underline that representative and generalized information can only be obtained if the dataset is properly constructed.

Conclusions

Multielement profile together with multi-isotope ratios are widely used in traceability works to authenticate the origin of agricultural produce. Many successful studies are reported in literature showing through classifying and modelling that high discrimination power is associated to these variables, especially if used in a combined approach. Several instruments dedicated to these analyses are available nowadays, characterized by different performances and features. The choice of the analytical apparatus depends on several factors and is highly related to the research purpose. Elemental composition is characterized by a large number of variables that can be successfully treated through chemometric tools. Specific ratio among element concentration can provide additional useful information. C and N isotope ratios have been often measured, but results show a low connection with geographical features. The analysis of the isotope ratio of heavy elements such as Sr and Pb is a recent technique, however, due to their link with the geo-lithological features of the growing area they show a great potential as geographical tracers. Further studies are needed for better investigating and comprehending the limits and potential of the described techniques, specifically when applied to detect origin misdeclaration. These methods are promising to hinder food frauds, however in order to be used in official controls or for supporting legal cases, they need to be standardized and officially recognized by certification bodies through a procedure of inter-laboratory validation. Moreover, known samples can be used to define the analytical features of authentic goods. These data can be included in reliable and exhaustive databanks that can be used to compare unknown samples or as support for data interpretation.

Acknowledgements

This work is part of a PhD project focused on agrifood traceability in collaboration with Laimburg Research Centre and Eco-research srl. An overview of the overall project can be seen in a documentary that was shot for the local branch of the public television channel (https://www.youtube.com/watch?v=p8-A_OCkSEY). The Autonomous Province of Bolzano, Department of Innovation, Research and University (Decision n. 1472, 07.10.2013) is gratefully acknowledged for financial support.

Abstract

Modern food chain is highly complex and food is transported all around the world to satisfy consumers' demand. However, in the last years there has been an increased interest for local products and a major attention towards food provenance. Moreover, there are goods for which the geographical origin is recognized as an added value and is highlighted through specific indications or labels. It is known that fraudulent activities with the aim of a financial gain or illicit behaviours in trades related to origin misdeclaration are spreading and therefore tools for hindering this fraud are required. In the agrifood sector, traceability systems are largely based on paper-records, and despite recent implementations, they are still insufficient for following all the movement of food, especially in case of international trades. Consequently, in the last decades many efforts have been made to implement analytical methods able to discriminate samples based on their geographical origin. Very often different approaches are combined together to collect more information and increase the discrimination power. Particularly, in this review the application of multielement fingerprint and of the light and heavy elements stable isotope ratio analysis is examined, considering solely horticultural products, fresh or with slight transformation (polished rice). The main features of each technique together with an evaluation of the advantages/disadvantages and a brief description of the instruments available for these analysis are discussed. The most common multivariate approaches used for data interpretation are also reported. A critic overview of different approaches from papers published in literature since 2000 is provided, analysing specific aspects such as the chosen approach, the number and nature of the included variables, the chemometric tools applied, and the sample size. Many authors reached satisfying classification rates, showing that these techniques are very promising in the field of food authentication and traceability and that can become useful analytical tools to support legal cases.

Key words: traceability, food frauds, multielement composition, isotope ratio.

References

- ACETO M, ROBOTTI E, ODDONE M, BALDIZZONE M, BONIFACINO G, BEZZO G, DI STEFANO R, GOSETTI F, MAZZUCCO E, MANFREDI M, MARENGO E (2013) *A traceability study on the Moscato wine chain*. Food Chem 138:1914–1922. doi: 10.1016/j.foodchem.2012.11.019
- ALFARO JA, RABADE LA (2009) Traceability as a strategic tool to improve inventory management: A case study in the food industry. Int J Prod Econ 118:104–110. doi: 10.1016/j.ijpe.2008.08.030
- ALMEIDA CMR, VASCONCELOS MTSD (2003) Multi-element composition and ⁸⁷Sr/⁸⁶Sr of wines and their potentialities as fingerprints of wine provenance. J Agric Food Chem 51:4788–4798. doi: 10.1021/jf034145b
- ANDERSON KA, SMITH BW (2002) Chemical profiling to differentiate geographic growing origins of coffee. J Agric Food Chem 50:2068–2075. doi: 10.1021/jf011056v
- ANDERSON KA, SMITH BW (2005) Use of chemical profiling to differentiate geographic growing origin of raw pistachios. J Agric Food Chem 53:410–418. doi: 10.1021/jf048907u
- AOAC (2006) Site-specific deuterium/hydrogen (D/H) ratios. Available at: www.aoacofficialmethod.org
- AOYAMA K, NAKANO T, SHIN K-C, IZAWA Å, MORITA S (2017) Variation of strontium stable isotope ratios and origins of strontium in Japanese vegetables and comparison with Chinese vegetables. Food Chem 237:1186–1195. doi: 10.1016/j.foodchem.2017.06.027
- ARIYAMA K, AOYAMA Y, MOCHIZUKI A, HOMURA Y, KADOKURA M, YASUI A (2007) Determination of the geographic origin of onions between three main production areas in Japan and other countries by mineral composition. J Agric Food Chem 55:347–354. doi: 10.1021/jf062613m
- ARIYAMA K, HORITA H, YASUI A (2004) Application of inorganic element ratios to chemometrics for determination of the geographic origin of Welsh onions. J Agric Food Chem 52:5803–5809. doi: 10.1021/jf049333w
- ARIYAMA K, SHINOZAKI M, KAWASAKI A (2012) Determination of the Geographic Origin of Rice by Chemometrics with Strontium and Lead Isotope Ratios and Multielement Concentrations. J Agric Food Chem 60:1628–1634. doi: 10.1021/jf204296p
- ARIYAMA K, SHINOZAKI M, KAWASAKI A, ISHIDA Y (2011) Strontium and Lead Isotope Analyses for Determining the Geographic Origins of Grains. Anal Sci 27:709–709. doi: 10.2116/analsci.27.709
- BATEMAN AS, KELLY SD, JICKELLS TD (2005) Nitrogen isotope relationships between crops and fertilizer: Implications for using nitrogen isotope analysis as an indicator of agricultural regime. J Agric Food Chem 53:5760-5765. doi: 10.1021/jf050374h
- BEER C, FIEDLER T, HOFSOMMER M (2015) Using Cavity Ring-Down Spectroscopy for the Detection of Food Fraud.

Available at: https://public.od.cm4allbusiness.de/public/ BEODP0AVBDAE-0919f3a3d76e63acc6695b001 f8050860375/Poster Abstract RAFA2015.pdf?cdp=a

- BENABDELKAMEL H, DI DONNA L, MAZZOTTI F, NACCARATO A, SINDONA G, TAGARELLI A, TAVERNA D (2012) Authenticity of PGI "Clementine of Calabria" by multielement fingerprint. J Agric Food Chem 60:3717–26. doi: 10.1021/jf2050075
- BENEDETTI R, PIERSIMONI F, POSTIGLIONE P (2015) Sample size and sample allocation. In: Advances in Spatial Science. Springer, Berlin, Heidelberg, pp 197–217
- BERRUETA LA, ALONSO-SALCES RM, HÉBERGER K (2007) Supervised pattern recognition in food analysis. J Chromatogr A 1158:196–214. doi: 10.1016/j.chroma.2007.05.024
- BINGEN J;, SAGE J;, SIRIEIX L, BINGEN J, SAGE J, SIRIEIX L (2010) Consumer perceptions and coping strategies of consumers committed to eating local in Michigan (USA).
- BLUM JD, TALIAFERRO EH, WEISSE MT, HOLMES RT (2000) Changes in Sr/Ca, Ba/Ca and 87Sr/86Sr ratios between trophic levels in two forest ecosystems in the northeastern U.S.A. Biogeochemistry 49:87-101. doi: 10.1023/A:1006390707989
- BOLLHÖFER A, ROSMAN KJ. (2000) Isotopic source signatures for atmospheric lead: the Southern Hemisphere. Geochim Cosmochim Acta 64:3251-3262. doi: 10.1016/S0016-7037(00)00436-1
- BOLLHÖFER A, ROSMAN KJ. (2001) Isotopic source signatures for atmospheric lead: the Northern Hemisphere. Geochim Cosmochim Acta 65:1727–1740. doi: 10.1016/S0016-7037(00)00630-X
- BONG Y-S, SONG BY, GAUTAM MK, JANG CS, AN HJ, LEE KS (2013) Discrimination of the geographic origin of cabbages. Food Control 30:626–630. doi: 10.1016/j.foodcont.2012.09.008
- BRERETON P (2013) Verifying the origin of food: an introduction. In: New Analytical Approaches for Verifying the Origin of Food. Elsevier, pp 3–11
- BRESCIA MA, DI MARTINO G, GUILLOU C, RENIERO F, SACCO A, SERRA F (2002) Differentiation of the geographical origin of durum wheat semolina samples on the basis of isotopic composition. Rapid Commun Mass Spectrom 16:2286–2290. doi: 10.1002/rcm.860
- BRUNNER M, KATONA R, STEFÁNKA Z, PROHASKA T (2010) Determination of the geographical origin of processed spice using multielement and isotopic pattern on the example of Szegedi paprika. Eur Food Res Technol 231:623–634. doi: 10.1007/s00217-010-1314-7
- CAMIN F, BONER M, BONTEMPO L, FAUHL-HASSEK C, KELLY SD, RIEDL J, ROSSMANN A (2017) Stable isotope techniques for verifying the declared geographical origin of food in legal cases. Trends Food Sci Technol 61:176–187. doi: 10.1016/j.tifs.2016.12.007
- CAMIN F, PERINI M, BONTEMPO L, FABRONI S, FAEDI W, MAGNANI S, BARUZZI G, BONOLI M, TABILIO MR, MUSMECI S, ROSSMANN A, KELLY SD, RAPISARDA P (2011) Potential isotopic and chemical markers for characterising organic fruits. Food Chem 125:1072-1082. doi: 10.1016/j.foodchem.2010.09.081
- CERNUSAK LA, BARBOUR MM, ARNDT SK, CHEESMAN AW, ENGLISH NB, FEILD TS, HELLIKER BR, HOLLOWAY-PHILLIPS MM, HOLTUM JAM, KAHMEN A, MCINERNEY FA, MUNKSGAARD NC, SIMONIN KA, SONG X, STUART-WILLIAMS H, WEST JB, FARQUHAR GD (2016) Stable isotopes in leaf water of terrestrial plants. Plant, Cell Environ 39:1087–1102. doi: 10.1111/pce.12703
- CHARLEBOIS S, STERLING B, HARATIFAR S, NAING SK (2014) Comparison of global food traceability regulations and requirements. Compr Rev Food Sci Food Saf 13:1104–1123. doi: 10.1111/1541-4337.12101

CHEAJESADAGUL P, ARNAUDGUILHEM C, SHIOWATANA J,

SIRIPINYANOND A, SZPUNAR J (2013) Discrimination of geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry. Food Chem 141:3504–3509. doi: 10.1016/j.foodchem.2013.06.060

- CHESSON LA, BOWEN GJ, EHLERINGER JR (2010) Analysis of the hydrogen and oxygen stable isotope ratios of beverage waters without prior water extraction using isotope ratio infrared spectroscopy. Rapid Commun Mass Spectrom 24:3205–3213. doi: 10.1002/rcm.4759
- CHIETERA G, CHARDON F (2014) Natural variation as a tool to investigate nutrient use efficiency in plants. In: Nutrient Use Efficiency in Plants. Springer, Cham, pp 29–50
- CHUNG I-M, KIM J-K, JIN Y-I, OH Y-T, PRABAKARAN M, YOUN K-J, KIM S-H (2016) Discriminative study of a potato (Solanum tuberosum L.) cultivation region by measuring the stable isotope ratios of bio-elements. Food Chem 212:48–57. doi: 10.1016/j.foodchem.2016.05.161
- CHUNG I-M, KIM J-K, LEE J-H, AN M-J, LEE K-J, PARK S-K, KIM J-U, KIM M-J, KIM S-H (2017a) *C/N/O/S stable isotopic and chemometric analyses for determining the geographical origin of Panax ginseng cultivated in Korea.* J Ginseng Res 1–11. doi: 10.1016/j.jgr.2017.06.001
- CHUNG I-M, PARK S-K, LEE K-J, AN M-J, LEE J-H, OH Y-T, KIM S-H (2017b) Authenticity testing of environment-friendly Korean rice (Oryza sativa L.) using carbon and nitrogen stable isotope ratio analysis. Food Chem 234:425–430. doi: 10.1016/j.foodchem.2017.05.014
- COCCHI M, VIGNI ML, DURANTE C (2017) Chemometrics -Bioinformatics. In: Food Authentication: Management, Analysis and Regulation. John Wiley & Sons Ltd, Chichester, UK, pp 481–518
- CODEX ALIMENTARIUS (2006) Principles for traceability/product tracing as a tool within a food inspection and certification system.
- D'ARCHIVIO AA, GIANNITTO A, INCANI A, NISI S (2014) Analysis of the mineral composition of Italian saffron by ICP-MS and classification of geographical origin. Food Chem 157:485–489. doi: 10.1016/j.foodchem.2014.02.068
- DAWSON TE, SIEGWOLF RTW (2007) Using stable isotopes as indicators, tracers, and recorders of ecological change: some context and background. In: Stable isotopes as indicators of ecological change. Academic Press, pp 3–18
- DE RIJKE E, SCHOORL JC, CERLI C, VONHOF HB, VERDEGAAL SJA, VIVÓ-TRUYOLS G, LOPATKA M, DEKTER R, BAKKER D, SJERPS MJ, EBSKAMP M, DE KOSTER CG (2016) The use of $\delta^2 H$ and $\delta^{18}O$ isotopic analyses combined with chemometrics as a traceability tool for the geographical origin of bell peppers. Food Chem 204:122–128. doi: 10.1016/j.foodchem.2016.01.134
- DENIRO MJ, EPSTEIN S (1979) Relationship Between the Oxygen Isotope Ratios of Terrestrial Plant Cellulose, Carbon Dioxide, and Water. Science (80-) 204:51-53. doi: 10.1126/science.204.4388.51
- DI GIACOMO F, DEL SIGNORE A, GIACCIO M (2007) Determining the geographic origin of potatoes using mineral and trace element content. J Agric Food Chem 55:860–866. doi: 10.1021/jf062690h
- DOOR DATABASE. Available at: https://ec.europa.eu/agriculture/ quality_en.
- DRIVELOS SA, GEORGIOU CA (2012) Multi-element and multi-isotope-ratio analysis to determine the geographical origin of foods in the European Union. TrAC - Trends Anal Chem 40:38–51. doi: 10.1016/j.trac.2012.08.003
- DRIVELOS SA, HIGGINS K, KALIVAS JH, HAROUTOUNIAN SA, GEORGIOU CA (2014) Data fusion for food authentication. Combining rare earth elements and trace metals to discriminate "fava Santorinis" from other yellow split peas using chemometric tools. Food Chem 165:316-322. doi:

10.1016/j.foodchem.2014.03.083

- EHLERINGER JR, MATHESON JR. SM (2010) Stable isotopes and courts. Utah Law Rev 2010:385–442.
- ELIAS RW, HIRAO Y, PATTERSON CC (1982) The circumvention of the natural biopurification of calcium along nutrient pathways by atmospheric inputs of industrial lead. Geochim Cosmochim Acta 46:2561–2580. doi: 10.1016/0016-7037(82)90378-7
- EVANS JA, PASHLEY V, RICHARDS GJ, BRERETON N, KNOWLES TG (2015) Geogenic lead isotope signatures from meat products in Great Britain: Potential for use in food authentication and supply chain traceability. Sci Total Environ 537:447–452. doi: 10.1016/j.scitotenv.2015.07.133
- FLOCKHART DTTT, KYSER TK, CHIPLEY D, MILLER NG, NORRIS DR (2015) Experimental evidence shows no fractionation of strontium isotopes (⁸⁷Sr/⁸⁶Sr) among soil, plants, and herbivores: implications for tracking wildlife and forensic science. Isotopes Environ Health Stud 51:372–381. doi: 10.1080/10256016.2015.1021345
- FORTUNATO G, MUMIC K, WUNDERLI S, PILLONEL L, BOSSET JO, GREMAUD G (2004) Application of strontium isotope abundance ratios measured by MC-ICP-MS for food authentication. J Anal At Spectrom 19:227–234. doi: 10.1039/b307068a
- FSAI (2013) The aftermath of the horse meat incident. Available at: https://www.fsai.ie/publications/horse meat survey 2013/
- FURIA E, NACCARATO A, SINDONA G, STABILE G, TAGARELLI A (2011) Multielement fingerprinting as a tool in origin authentication of PGI food products: Tropea Red Onion. J Agric Food Chem 59:8450–8457. doi: 10.1021/jf201556e
- GERMAIN C (2003) Traceability implementation in developing countries, its possibilities and its constraints A few case studies. 1–159. Available at: ftp://ftp.fao.org/es/esn/food/traceability.pdf
- GÓMEZ-ALONSO S, GARCÍA-ROMERO E (2010) Effect of irrigation and variety on oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) stable isotope composition of grapes cultivated in a warm climate. Aust J Grape Wine Res 16:283–289. doi: 10.1111/j.1755-0238.2009.00089.x
- GONZALVEZ A, ARMENTA S, DE LA GUARDIA M (2009) Trace-element composition and stable-isotope ratio for discrimination of foods with Protected Designation of Origin. TrAC Trends Anal Chem 28:1295–1311. doi: 10.1016/j.trac.2009.08.001
- GONZÁLVEZ A, ARMENTA S, DE LA GUARDIA M (2011) Geographical traceability of "Arròs de Valencia" rice grain based on mineral element composition. Food Chem 126:1254–1260. doi: 10.1016/j.foodchem.2010.11.032
- HEATON K, KELLY SD, HOOGEWERFF J, WOOLFE M (2008) Verifying the geographical origin of beef: The application of multi-element isotope and trace element analysis. Food Chem 107:506–515. doi: 10.1016/j.foodchem.2007.08.010
- HEATON THE (1987) The ¹⁵N/¹⁴N ratios of plants in South Africa and Namibia: relationship to climate and coastal/saline environments. Oecologia 74:236–246. doi: 10.1007/BF00379365
- HIRAOKA H, MORITA S, IZAWA A, AOYAMA K, SHIN K-C, NAKANO T (2016) Tracing the geographical origin of onions by strontium isotope ratio and strontium content. Anal Sci 32:781–788. doi: 10.2116/analsci.32.781
- HOPFER H, NELSON J, COLLINS TS, HEYMANN H, EBELER SE (2015) *The combined impact of vineyard origin and processing winery on the elemental profile of red wines*. Food Chem 172:486–496. doi: 10.1016/j.foodchem.2014.09.113
- INGELFINGER JR (2008) Melamine and the global implications of food contamination. N Engl J Med 359:2745–2748. doi: 10.1056/NEJMp0808410
- IRRGEHER J, PROHASKA T (2015) Application of non-traditional stable isotopes in analytical ecogeochemistry assessed by MC ICP-MS - A critical review. Anal Bioanal Chem. doi: 10.1007/s00216-015-9025-3

JOEBSTL D, BANDONIENE D, MEISEL T, CHATZISTATHIS S (2010)

Identification of the geographical origin of pumpkin seed oil by the use of rare earth elements and discriminant analysis. Food Chem 123:1303–1309. doi: 10.1016/j.foodchem.2010.06.009

- JOHNSON R (2014) Food fraud and "economically motivated adulteration" of food and food ingredients. Congr Res Serv Rep January:1–40. Available at: https://fas.org/sgp/crs/misc/R43358.pdf
- JRC EUROPEAN COMMISSION Available at: https://ec.europa.eu/jrc/en/research-topic/food-authentic.
- KAYA AD, BRUNO DE SOUSA R, CURVELO-GARCIA AS, RICARDO-DA-SILVA JM, CATARINO S (2017) Effect of wood aging on wine mineral composition and 87 Sr/ 86 Sr isotopic ratio. J Agric Food Chem 65:4766-4776. doi: 10.1021/acs.jafc.7b01510
- KELLY S, HEATON K, HOOGEWERFF J (2005) Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis. Trends Food Sci Technol 16:555–567. doi: 10.1016/j.tifs.2005.08.008
- KOMÁREK M, ETTLER V, CHRASTNÝ V, MIHALJEVIČ M (2008) Lead isotopes in environmental sciences: A review. Environ Int 34:562–577. doi: 10.1016/j.envint.2007.10.005
- LI GC, WU ZJ, WANG YH, DONG XC, LI B, HE WD, WANG SC, CUI JH (2011) Identification of geographical origins of Schisandra fruits in China based on stable carbon isotope ratio analysis. Eur Food Res Technol 232:797–802. doi: 10.1007/s00217-011-1445-5
- LI Q, CHEN L, DING Q, LIN G (2013) The stable isotope signatures of blackcurrant (Ribes nigrum L.) in main cultivation regions of China: Implications for tracing geographic origin. Eur Food Res Technol 237:109–116. doi: 10.1007/s00217-013-1967-0
- LIU H, WEI Y, LU H, WEI S, JIANG T, ZHANG Y, GUO B (2016) Combination of the ⁸⁷Sr/⁸⁶Sr ratio and light stable isotopic values (δ13C, δ15N and δd) for identifying the geographical origin of winter wheat in China. Food Chem 212:367–373. doi: 10.1016/j.foodchem.2016.06.002
- LONGOBARDI F, CASIELLO G, CENTONZE V, CATUCCI L, AGOSTIANO A (2017) Isotope ratio mass spectrometry in combination with chemometrics for characterization of geographical origin and agronomic practices of table grape. J Sci Food Agric 97:3173–3180. doi: 10.1002/jsfa.8161
- Luo D, Dong H, Luo H, XIAN Y, WAN J, Guo X, WU Y (2015) The application of stable isotope ratio analysis to determine the geographical origin of wheat. Food Chem 174:197–201. doi: 10.1016/j.foodchem.2014.11.006
- LUYKX DMAM, VAN RUTH SM (2008) An overview of analytical methods for determining the geographical origin of food products. Food Chem 107:897–911. doi: 10.1016/j.foodchem.2007.09.038
- MA G, ZHANG Y, ZHANG J, WANG G, CHEN L, ZHANG M, LIU T, LIU X, LU C (2016) Determining the geographical origin of Chinese green tea by linear discriminant analysis of trace metals and rare earth elements: Taking Dongting Biluochun as an example. Food Control 59:714–720. doi: 10.1016/j.foodcont.2015.06.037
- MEIER-AUGENSTEIN W, KEMP HF, HARDIE SML (2012) Detection of counterfeit scotch whisky by ²H and ¹⁸O stable isotope analysis. Food Chem 133:1070–1074. doi: 10.1016/j.foodchem.2012.01.084
- MERCURIO M, GRILLI E, ODIERNA P, MORRA V, PROHASKA T, COPPOLA E, GRIFA C, BUONDONNO A, LANGELLA A (2014) A "Geo-Pedo-Fingerprint" (GPF) as a tracer to detect univocal parent material-to-wine production chain in high quality vineyard districts, Campi Flegrei (Southern Italy). Geoderma 230–231:64–78. doi: 10.1016/j.geoderma.2014.04.006
- MIMMO T, CAMIN F, BONTEMPO L, CAPICI C, TAGLIAVINI M, CESCO S, SCAMPICCHIO M (2015) Traceability of different apple varieties by multivariate analysis of isotope ratio mass

spectrometry data. Rapid Commun Mass Spectrom 29:1984–1990. doi: 10.1002/rcm.7306

- MOORE JC, SPINK J, LIPP M (2012) Development and application of a database of food ingredient fraud and economically motivated adulteration from 1980 to 2010. J Food Sci 77:R118–R126. doi: 10.1111/j.1750-3841.2012.02657.x
- MUCCIO Z, JACKSON GP (2009) *Isotope ratio mass spectrometry*. Analyst 134:213–222. doi: 10.1039/B808232D
- NAKANO T (2016) Potential uses of stable isotope ratios of Sr, Nd, and Pb in geological materials for environmental studies. Proc Jpn Acad 92:167–184. doi: 10.2183/pjab.92.167
- ODDONE M, ACETO M, BALDIZZONE M, MUSSO D, OSELLA D (2009) Authentication and traceability study of hazelnuts from Piedmont, Italy. J Agric Food Chem 57:3404–3408. doi: 10.1021/jf900312p
- PEI X, TANDON A, ALLDRICK A, GIORGI L, HUANG W, YANG R (2011) The China melamine milk scandal and its implications for food safety regulation. Food Policy 36:412–420. doi: 10.1016/j.foodpol.2011.03.008
- PEREZ AL, SMITH BW, ANDERSON KA (2006) Stable isotope and trace element profiling combined with classification models to differentiate geographic growing origin for three fruits: Effects of subregion and variety. J Agric Food Chem 54:4506–4516. doi: 10.1021/jf0600455
- PODIO NS, BARONI M V., BADINI RG, INGA M, OSTERA HA, CAGNONI M, GAUTIER EA, GARCÍA PP, HOOGEWERFF J, WUNDERLIN DA (2013) Elemental and isotopic fingerprint of argentinean wheat. Matching soil, water, and crop composition to differentiate provenance. J Agric Food Chem 61:3763–3773. doi: 10.1021/jf305258r
- RASHMI D, SHREE P, SINGH DK (2017) Stable isotope ratio analysis in determining the geographical traceability of Indian wheat. Food Control 79:169–176. doi: 10.1016/j.foodcont.2017.03.025
- REGATTIERI A, GAMBERI M, MANZINI R (2007) Traceability of food products: General framework and experimental evidence. J Food Eng 81:347–356. doi: 10.1016/j.jfoodeng.2006.10.032
- REIMANN C, FLEM B, FABIAN K, BIRKE M, LADENBERGER A, NÉGREL P, DEMETRIADES A, HOOGEWERFF J, ALBANESE S, ANDERSSON M, ARNOLDUSSEN A, BARITZ R, BATISTA MJ, BEL-LAN A, CICCHELLA D, DINELLI E, DE VIVO B, ... ZOMENI Z (2012) Lead and lead isotopes in agricultural soils of Europe - The continental perspective. Appl Geochemistry 27:532–542. doi: 10.1016/j.apgeochem.2011.12.012
- RODEN JS, EHLERINGER JR (1999) Observations of hydrogen and oxygen isotopes in leaf water confirm the craig-gordon model under wide-ranging environmental conditions. Plant Physiol 120:1165–74.
- RODRIGUES C, BRUNNER M, STEIMAN S, BOWEN GJ, NOGUEIRA JMF, GAUTZ L, PROHASKA T, MÁGUAS C (2011) Isotopes as tracers of the Hawaiian coffee-producing regions. J Agric Food Chem 59:10239–10246. doi: 10.1021/jf200788p
- ROSSMANN A (2001) Determination of stable isotope ratios in food analysis. Food Rev Int 17:347–381. doi: 10.1081/FRI-100104704
- SANTATO A, BERTOLDI D, PERINI M, CAMIN F, LARCHER R (2012) Using elemental profiles and stable isotopes to trace the origin of green coffee beans on the global market. J Mass Spectrom 47:1132–1140. doi: 10.1002/jms.3018
- SHEN S, XIA L, XIONG N, LIU Z, SUN H (2013) Determination of the geographic origin of rice by element fingerprints and cor-

relation analyses with the soil of origin. Anal Methods 5:6177–6185. doi: 10.1039/c3ay40700d

- SUZUKI Y, CHIKARAISHI Y, OGAWA NO, OHKOUCHI N, KORENAGA T (2008) Geographical origin of polished rice based on multiple element and stable isotope analyses. Food Chem 109:470–475. doi: 10.1016/j.foodchem.2007.12.063
- SWOBODA S, BRUNNER M, BOULYGA SF, GALLER P, HORACEK M, PROHASKA T (2008) Identification of Marchfeld asparagus using Sr isotope ratio measurements by MC-ICP-MS. Anal Bioanal Chem 390:487–494. doi: 10.1007/s00216-007-1582-7
- SZPAK P (2014) Complexities of nitrogen isotope biogeochemistry in plant-soil systems: implications for the study of ancient agricultural and animal management practices. Front Plant Sci 5:1–19. doi: 10.3389/fpls.2014.00288
- TECHER I, MEDINI S, JANIN M, ARREGUI M (2017) Impact of agricultural practice on the Sr isotopic composition of food products: Application to discriminate the geographic origin of olives and olive oil. Appl Geochemistry 82:1–14. doi: 10.1016/j.apgeochem.2017.05.010
- THERMO ELEMENTAL (2001) AAS, GFAAS, ICP or ICP-MS? Which technique should I use? Available https://www.researchgate.net/file.PostFileLoader.html?id=53 6d29c3d3df3e447c8b45a2&assetKey=AS%3A273531932217 348%401442226502426
- TNS OPINION & SOCIAL (2012) Europeans' attitudes towards food security, food quality and the countryside - Report Special Eurobarometer 389 / Wave EB77.2. Available at: ec.europa.eu/commfrontoffice/publicopinion/archives/ebs/ebs 389 en.pdf
- TRINCHERINI PR, BAFFI C, BARBERO P, PIZZOGLIO E, SPALLA S (2014) Precise determination of strontium isotope ratios by *TIMS to authenticate tomato geographical origin*. Food Chem 145:349–355. doi: 10.1016/j.foodchem.2013.08.030
- TYLER G (1994) ICP-MS, or ICP-AES and AAS?— a comparison.
- Tyler G (2004) Rare earth elements in soil and plant systems A review. Plant Soil 267:191–206. doi: 10.1007/s11104-005-4888-2
- VALENTIN JL, WATLING RJ (2013) Provenance establishment of coffee using solution ICP-MS and ICP-AES. Food Chem 141:98–104. doi: 10.1016/j.foodchem.2013.02.101
- WALCZYK T (2004) *TIMS versus multicollector-ICP-MS: coexis*tence or struggle for survival?. Anal Bioanal Chem 378:229–231. doi: 10.1007/s00216-003-2053-4
- YANG L (2009) Accurate and precise determination of isotopic ratios by MC-ICP-MS: A review. Mass Spectrom Rev 28:990–1011. doi: 10.1002/mas.20251
- YIP Y, LAM JC, TONG W (2008) Applications of lead isotope ratio measurements. TrAC Trends Anal Chem 27:460–480. doi: 10.1016/j.trac.2008.02.011
- ZHAO H, GUO B, WEI Y, ZHANG B (2013) Multi-element composition of wheat grain and provenance soil and their potentialities as fingerprints of geographical origin. J Cereal Sci 57:391–397. doi: 10.1016/j.jcs.2013.01.008
- ZHAO H, GUO B, WEI Y, ZHANG B, SUN S, ZHANG L, YAN J (2011) Determining the geographic origin of wheat using multielement analysis and multivariate statistics. J Agric Food Chem 59:4397–4402. doi: 10.1021/jf200108d
- ZHAO Y, ZHANG B, CHEN G, CHEN A, YANG S, YE Z (2014) Recent developments in application of stable isotope analysis on agro-product authenticity and traceability. Food Chem 145:300–305. doi: 10.1016/j.foodchem.2013.08.062