Chapter 9

Food Forensics

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Chapter Outline

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1. INTRODUCTION

The term "food forensics" involves the possibility of using powerful scientific methods for the authentication and traceability of foodstuffs, in a way similar to popular TV series such as *CSI* in which scientific methods are used to solve forensic problems. Food forensics must be considered a discipline of primary importance. The global food import bills have been estimated at USD 1,29 trillion by Food and Agriculture Organization of the United Nations [1]; it is the fifth year in succession that the world bill has surpassed USD 1 trillion. Considering the high numbers expressed, it must not be surprising how high the fraud rate is. In 2007, John Spink, Director of the Packaging for Food and Product Protection Initiative at Michigan State University (USA) estimated the total value of food fraud $49 billion, while according to the UK Food Standards Agency, the level of fraud accounted for 10% of food market, i.e., around $7 billion. Examples are innumerable; to name a few among the most recent cases, the 2013 meat adulteration scandal, also known as *Horsegate*, with concern to foods advertised as beef that actually contained undeclared horse meat [2]; the latest case of wine fraud in Italy [3] in which 30,000 bottles were sold labeled as *Brunello di Montalcino*, *Chianti*, and other valuable wines, but indeed they contained false or low quality wines; finally, the so-called *Honey Laundering Conspiracy* [4] that has been dubbed as the "largest food fraud in the USA history," where honey produced in China has been introduced in the USA market using a network of Asian countries to "wash" Chinese origin product with new packaging and false documents.

Italy is with no doubt among the countries most damaged by food frauds. The list of frauds perpetrated to the detriment of Italian food brands is endless:

- cow buffalo *mozzarella* made with freeze-dried cow milk, with milk from Southern America or with curd from Eastern Europe;
- wine made synthetically with water, sugar, and tartaric acid;
- rapeseed oil or olive pomace oil from Mediterranean countries colored with chlorophylls and artificially flavored, sold as olive oil;
- Chinese eels and moribund mussels from Turkey revived with local seawater;
- *pummarola*, i.e., tomato sauce, produced in China then diluted and reworked in Italy;

- capers from Northern Africa sold as *Pantelleria capers*;
- *Aceto balsamico tradizionale di Modena* produced in Germany.

According to a 2007 report by Coldiretti [5], the Italian organization of agricultural entrepreneurs, in foreign food export one product in four is fake; the global amount of food fraud to the detriment of Italian export can be estimated in 60 billions of Euros [6]. In some countries, i.e., USA, only 2% of cheese labeled as Italian is based on original products. It must be noted that if a *made in Italy* product can be sometimes recognized (e.g., wines, cheeses, salami, etc.), much more complex is recognizing the culinary product, once that foodstuffs have been worked and transformed into recipes (*cannoli siciliani*, *pasta e fagioli*, etc.).

These are with no doubt impressive figures and high costs to both producers and consumers. In addition, a lot of technical resources must be spent in the inspection; at present, in fact, only a small percentage of food supply can be controlled. US Food and Drug Administration reported in its 2013 annual report on food facilities and food imports [7] that a mere 14% of domestic food facilities were inspected and an even lower percentage of foreign food facilities.

Indeed, fraud accompanied commercial transactions since ancient times possibly due to a reflection of human nature. Crooked traders always were all the rage, maximizing incomes by diluting their products with cheaper raw materials. In biblical times, rules and suitability standards were issued for inspection of meat, which can be found in the *Book of Leviticus*, possibly the most ancient health codex ever written. Galen, considered among the fathers of modern medicine, warned against adulteration of herbs and spices. In ancient Rome and Athens, there were laws concerning the adulteration of wines with flavors and colors [8]. In the first century AD, Pliny the Elder, in his *Naturalis Historia* [9], Book XII, Chapter XIV, tells that "…*piper lungum facillime adulteratur Alexandrino sinapi*…" (long pepper is very easily adulterated with Alexandrian mustard) and also that "…*adulteratur iunipiri bacis*…" (pepper is adulterated with juniper berries). In the nineteenth-century text, *A treatise on adulterations of food and culinary poisons* by German chemist Frederick Accum [10], possibly the first written account of food fraud, the author exposed culinary sharp practice in London, detailing how bakers cut their flour with alum and chalk to make loaves whiter, tipped in plaster and sawdust to make them heavier; how brewers added substances like strychnine to beer to make it taste bitter and save money on hops; and, perhaps worst of all, how lead, copper, or mercury salts were used to make brightly colored sweets and jellies that would be attractive to children.

In those times only simple, empirical methods were available to inspectors in order to recognize adulterations, so that the most clamorous frauds could be committed. Nowadays, both sides have increased their talents: impostors have developed more subtle ways to bypass regulations and inspectors have at their disposal more powerful analytical methods to investigate.

A great difference among ancient and modern times is also the huge amount of information available at present. Moore et al. [11] reviewed the information concerning food frauds issued on scholarly journals and general media and developed a database published in the US Pharmacopeial Convention's Food Chemicals Codex [12], labeled USP Food Fraud Database; this resource is also freely accessible at the Web site http://www.foodfraud.org.

Food fraud can be resumed in a simple concept: the will of selling a cheaper product at the price of a more valuable one. Three main strategies can be singled out: *adulteration*, i.e., the illicit variation in composition of a food product by means of addition or, most commonly, subtraction of some of its components; *sophistication*, i.e., the illicit variation in the natural or legal composition of a food product adding an external, unauthorized compound; *counterfeiting*, i.e., substitution of a food product with a similar but cheaper one. Inside these strategies, different types of frauds can be described:

- *partial or complete substitution of a product with similar but cheaper alternatives*: this kind of fraud is relatively easy to be identified because adulterants or sophisticants may contain substances acting as natural markers;
  - sea trout sold as salmon;
  - orange juice sophisticated with apple juice;
  - olive oil blended with other vegetable oils;
  - pork salami blended with donkey or horse meat;
- *false geographic provenance of the product*: it is well known that foodstuffs coming from certain regions may result more attractive to consumers with respect to equivalent products coming from less renowned regions: this kind of counterfeit can be discovered only if markers of the respective regions are identified;
  - truffles coming from Piedmont (Italy) versus truffles coming from other countries;
  - saffron coming from Tuscany or Abruzzi (Italy) versus saffron coming from other countries;
- *false declaration of process*: several foodstuffs have an added quality value when produced with specific processes that are usually time and resources consuming; fraud is carried out when a quality brand is used for a food obtained with cheaper production methods;
  - *extra virgin olive oil* is a valuable brand that can be applied only to a product obtained by means of physical or mechanical methods, while chemical extraction with solvents is not allowed;
  - food labeled as *organic* but produced with conventional methods;
- *processes not allowed*: several kinds of fraud concern with illicit practices carried out in the view of improving the quality features of foodstuffs;
  - addition of undeclared sugars to fruit juices in order to increase their taste;
  - addition of glycerine to wine to improve its body;

  - addition of natural but not allowed dyes (e.g., flavonoids from berries other than grapes) to wine to improve its hue;
- *sale of spoiled products*: this fraud can easily be identified.

Authentication of foodstuffs is strictly bound to labeling. For example, a product labeled "vegetable oil" will be any edible oil of vegetal origin, whereas a product labeled "olive oil" must be only the one obtained from olives. Labels imply rules imposing specific features from the technical point of view.

Problems arise frequently whereas rules are different from country to country. Some countries pursue more strict rules in the commercialization of foodstuffs, other are less strict; this may request observing more or less restrictive analytical parameters. One example is the addition of sugar to must in winemaking: in most jurisdictions (e.g., Italy) this practice is forbidden, while in others (i.e., Germany) its use in chaptalization is regulated but permissible in lower quality wines only and in France it is permitted, though under strict regulation.

1.1 Definitions

Food forensics implies the possibility to verify whether a foodstuff be authentic or not. It is useful at this stage to define some terms which will be used in the following. In particular, the difference among *authentication* and *traceability* must be pointed out [13]. *Authentication* is a procedure useful to verify the features declared by a product label and to reveal if a product has been adulterated or counterfeit (Figure 1). *Traceability* is a procedure useful to verify the link among a foodstuff and the raw materials with which it has been produced (Figure 2). Authentication studies look for chemical parameters useful to discriminate authentic products from nonauthentic products, using one or more groups of variables whose distribution must be evaluated with reference to geographic provenance, botanic or animal variety, and production technology of samples of a particular food. Instead, traceability studies look for chemical parameters useful to find tracks of the different stages inside a production chain. If a food product can be traced—linked to its raw materials—it can be certainly authenticated, but if a food product can be authenticated (i.e., has all the features declared in its label) not necessarily can be traced. Authentication and traceability are not, therefore, synonyms, but are concepts pointing in the same direction, i.e., working at the consumers' advantage by guaranteeing the quality of foodstuffs. For the sake of simplicity, in the following text we will use the term *classification* referring to the whole of authentication and traceability, while we will use either *authentication* or *traceability* when the specific meaning will be implied.

Considering the scientific literature in the field of food forensics, most classification studies are focused on food authentication. This is due to the fact that by selecting the proper variables, almost every food can be authenticated,

FIGURE 1 Food authentication.

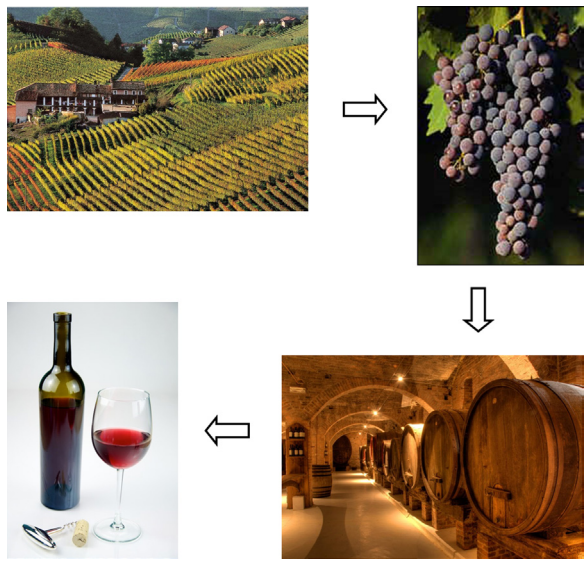
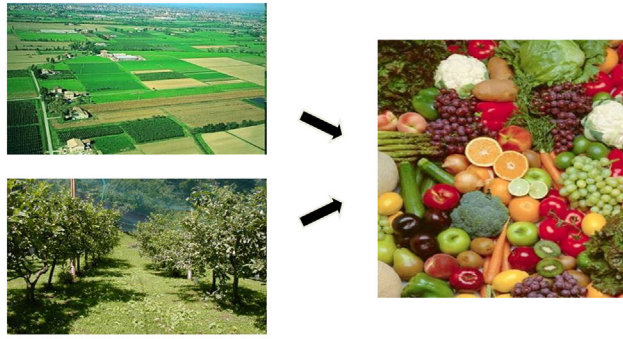


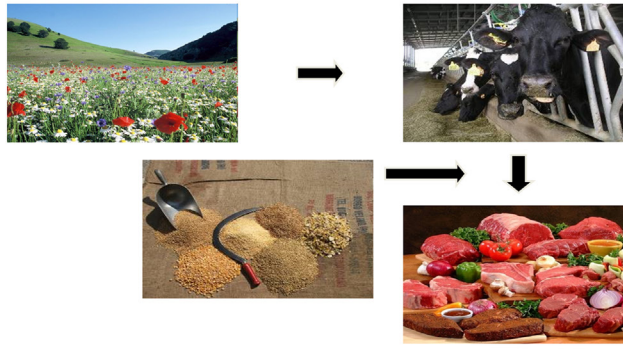
FIGURE 2 The concept of food traceability.

i.e., discriminated by its substitutes. Traceability has more strict rules and only a selection of foods can be actually traced. The following cases can be singled out:

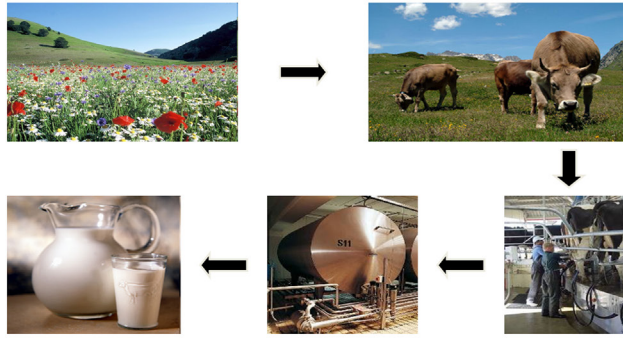
- *short and very short production chains*: foodstuffs which withstand very few or no chemical treatments in the passage from the raw materials to the table (Figure 3, top):
  - very good possibilities of authenticating;
  - good possibilities of tracing;
    - fruit and vegetables;



Fruits and vegetables: short production chain



Meat and sausages: long production chain



Milk: average production chain

FIGURE 3 Examples of food production chains.

- *average production chains*: foodstuffs which withstand some recognizable chemical treatments in the passage from the raw materials to the table (Figure 3, bottom):
  - good possibilities of authenticating;
  - traceability to be verified;
    - vegetable oils;
    - wines;
    - milk;
    - honey;
    - products from cereals;
- *long and complex production chains*: foodstuffs which withstand many or unchecked chemical treatments in the passage from the raw materials to the table (Figure 3, middle):
  - fairly good possibilities of authenticating;
  - scarce possibilities of tracing;
    -dairy products;
    -meat and sausages.

1.2 The Role of Chemometrics in Food Forensics

Also, it is important to point out the relevant role of *chemometrics* in food classification. It is virtually impossible to define a food in terms of a single scientific description: very few products are made of pure substances (e.g., salt, sucrose) while the most are mixtures containing some main well-defined compounds and minor ingredients less known but maybe decisive for organoleptic features. The same product will show slight but significant differences depending on the provenance of raw materials, the way they were processed, and the animal/botanical species of origin. In order to be defined as authentic, a foodstuff must be characterized taking into account the possible variations along different directions. In many cases, therefore, classifying foodstuffs implies determination of several variables, e.g., trace elements or molecular ionic fragments. Since in very few cases a single parameter is sufficient, determining a large number of variables plays a key role in the possibility of authenticating or tracing a product. The variables determined can be used to individuate groups of samples, or *classes*, with homogeneous chemical features, with particular concern to *authentic* and *nonauthentic* samples, and to assign membership to unknown samples. In this instance, equal importance must be given in the chemical characterization of both authentic and nonauthentic samples, because only when the difference is clear the authenticity of unknown samples can be recognized. This implies, though, the need of managing large sets of data. This procedure can be carried out with *pattern recognition* (or *classification*) multivariate mathematical methods, using well-known techniques such as principal components analysis (PCA), cluster analysis (CA), discriminant analysis (DA), or soft independent modeling of class analogy (SIMCA). Pattern recognition methods have been applied to food forensics since at least 1975 and in the following decades, the number of applications has grown considerably [14,15]. The applications of chemometrics in food

forensics have been reviewed in several instances [16–18], putting particular focus on unsupervised [19] or supervised [20] methods of pattern recognition.

1.3 The Principal Foods Subjected to Fraud

In the development of methods for food classification, there is a strong difference among authentication and traceability. In order to trace a food product, a perfect knowledge of the whole production chain, from raw materials to the final product, is mandatory because every single passage can influence the possibility to follow the chain by means of analytical measurements. This feature is less essential in authentication, where it can be sufficient distinguishing the authentic finished product from the nonauthentic one, irrespective of the production chain. In this case also, however, the knowledge of the various passages inside the production chain allows individuating the suitable analytical tests in a more efficient way. For this reason, it is well timed to illustrate shortly the production chains of the most important foodstuffs and to understand, for each category, what the more common frauds are.

1.3.1 Wine, Fermented Drinks, and Other Beverages

Wine is with no doubt one among the foodstuffs mostly subjected to frauds. High-quality wines or particular vintages may reach high prices, becoming ideal objectives for illicit commerce. Although regulations on wines are among the most complete, the extent of frauds is so high that could hardly be quantified.

The role of analytical chemistry in wine classification is definitely strategic. In the past, the only way to verify the authenticity of a wine was the tasting by experts, but today powerful instrumental methods are available. Not all frauds, though, can be revealed.

The production chain of wine is complex and many passages occur among grapes and bottled wine. Trace elements and stable isotope ratios have been suggested as traceability markers, as it will be detailed further on. In the case of authentication, several classes of organic compounds, typical of specific passages in the production chain, can be used as markers.

Saurina [21] and Versari et al. [22] recently reviewed classification methods of wine with different analytical techniques.

The most common frauds in the wine and spirits market are the following:

- adulteration:
  - addition of water;
- sophistication:
  - use of sugars or alcohols from other plants different from grapes;
  - use of additives, flavors, and dyes not allowed;
  - use of vinous products made with table grapes;
- counterfeiting:
  - wines obtained totally with musts and/or with table grapes marketed as products derived from wine grapes;

- wines marketed under registered names, i.e. Italian *Denominazione di Origine Controllata* (DOC) and/or *Denominazione di Origine Controllata e Garantita* (DOCG), without having the prescribed chemical, physical, organoleptic, and documental requisites;
- Single malt whisky replaced by blended one.

The previous considerations have valid for all other fermented drinks, among which:

- spirits from grapes (e.g., cognac);
- spirits from other vegetable species (e.g., rhum, grappas, whisky, tequila);
- beer (from barley);
- cider (from apples);
- sakè (from rice).

In all these cases, raw materials undergo at least one chemical conversion due to alcoholic fermentation. Moreover, production and conservation can include other specific treatments. In addition, in some cases more than a single raw material is used: beer, as an example, is made from both barley and hop, which makes it more difficult to go back to their origin.

A particular fermented drink is *Aceto balsamico di Modena*, which stands out for quality and commercial value. It is a product obtained from cooked grapes must, fined in barrels for at least 12 years; along this period it is subjected to progressive concentration in a series of casks of different woods and sizes, called *acetaia*, until it becomes a dense juice, rich in flavors. The chemistry underlying the aging of *Aceto balsamico* is still partially unknown, but it is certain that all passages involved in the production (alcoholic and acetic fermentations, conservation in six different types of barrels) heavily modify the raw matters. A traceability study can hardly be figured, while authentication could be based on the development of typical flavoring compounds.

Besides alcoholic drinks, another drink of high consumption is of course mineral water. The production chain of mineral water is for sure the simplest. To be marketed as mineral, water must not withdraw any treatment from source to bottle, which is a striking difference among mineral and tap water (i.e., delivered by domestic water systems). Water would then seem to be the ideal food for classification studies, being the chemical features untouched all along the production chain. Indeed, the commercial value of mineral water does not justify application of powerful but expensive analytical techniques such as mass spectrometry or nuclear magnetic resonance (NMR).

The most common frauds in the mineral water market are the following:

- adulteration:
  - dilution with tap water;
- sophistication:
  - use of purification agents;
- counterfeiting:
  - bottles labeled as mineral water but containing tap water.

1.3.2 Milk and Dairy Products

Inside dairy products, two groups are present:

- products obtained from mechanical and physical transformations (milk);
- products with more elaborate production chains, including chemical transformation passages (yoghurt, cheeses, butter).

It is obvious that the first group is more suitable to be studied for traceability. Milk traceability is relatively simple as its composition reflects instantaneously the conditions at which, the producing animal is exposed to. Transfer of nutrients and/or contaminants from grass to milk, passing through the animal stomach, is fast and it is then possible to use different vegetal biomarkers such as carotenoids, terpenes, and polyphenolic compounds to yield information on the animal's diet, while determination of stable isotopes ratio can yield information of the provenance of milk. As for water, though, the market value of the product can hardly justify traceability studies.

For what concerns authentication, it is possible to identify organic markers allowing discrimination of different productions. The chemical composition of dairy products reflects that of the milk they come from, but it also depends on other factors such as processing, aging, and quality of microbial flora. Moreover, most of them are alive products, hosting microbial species which breed on a substrate rich in nutrients and whose metabolism generates chemical compounds continuously evolving. It is apparent that traceability studies can be difficult while authentication schemes can be easily developed based on typical organic compounds.

Zachar et al. [23] recently reviewed classification methods of milk and dairy products with different analytical techniques.

The most common frauds in the dairy products market are the following:

- adulteration:
  - addition of water to milk;
- sophistication:
  - preparation of cheeses with fraudulent use of milk powder, casein or caseinates instead of natural liquid milk;
  - use of milk different from the one declared in the label (e.g., the cheaper cow's milk in place of buffalo, sheep, or goat's milk, all more expensive);
  - use of expired cheeses in the preparation of *pasta filata* fresh cheeses;
  - use of casein and butter in the production of *pasta filata* fresh cheeses;
- counterfeiting:
  - use of milk of animal origin and/or geographic source different from those prescribed in product specifications;
  - production of butter from buttermilk of buffalo, sheep, and goat's milk and its marketing as butter obtained from cream or from buttermilk of cow's milk;
  - use of not allowed additives and colorants;

- use of animal and/or vegetal fats and/or butter produced in EU in the production of fresh butter:
- false declaration of cheese made from heat-treated milk instead of raw milk.

1.3.3 Vegetable Oils

Extra virgin olive oils are among the highest quality products in Europe, which attract counterfeit. Adulterated olive oil is possibly the biggest agricultural fraud in the EU. In the production of vegetable oils, and in particular of olive oil, there is difference among authentication and traceability. In fact, it is relatively easy, on the basis of several organic compounds, distinguishing oils from different botanical sources (e.g., olive, hazelnut, sunflower, etc.) and therefore identifying fraudulent additions to higher quality oils; on the other hand, it is more difficult in tracing the production chain as the passages from olives to the final product can be many, with both physical and chemical transformations, even if the higher quality products (i.e., extra virgin olive oils) must be produced with physical methods only. It must be considered, moreover, that olive oil in particular is a complex system bound to several variables such as olive cultivars, climatic features, modality of handling the raw matter and the final product, etc.

Ben-Ayed et al. [24] recently reviewed classification methods of oils with different analytical techniques.

The most common frauds in the vegetable oils market are the following:

- adulteration:
  - olive oil illicitly subjected to deodorization to obtain products deprived of organoleptic defects, passed off as extra virgin oil;
  - olive oil illicitly subjected to disacidification to obtain products with low acidity, passed off as extra virgin oil;
- sophistication:
  - blending of olive oil with seed oil unaltered or previously subjected to specific treatments (e.g., desterolization) in order of hiding specific compounds that could reveal its addition under an analytical check;
  - oil declared as extra virgin olive oil illicitly obtained by mixing refined oil with virgin oil;
- counterfeiting:
  - seed oil colored with chlorophyll, marketed as virgin olive oil;
  - virgin and extra virgin oil made in foreign countries sold as local product;
  - virgin oil introduced in one country with merceological denomination of seed oil or foreign olive oil, temporarily imported to be refined or packaged and then given back to the original country, which instead, by means of triangulation transactions, is input on the national market at low price thanks to fiscal advantages.

1.3.4 Meats

Meat has obviously a central role in the diet of most regions, with particular concern to Western countries. At the same time, in recent years, there have been several issues of security concern in the meat market, e.g., bovine spongiform encephalopathy (BSE), human variant Creutzfeldt–Jakob disease (CJD), and more recently the use of equine meat in products labeled as beef meat. Therefore, classification of meat products has potentially a strategic importance, even considering that most consumers address their choice of purchase according to the geographic provenance of animals. Yet, the whole traceability system, which should guarantee origin and so quality of meat, is actually based on brands, tattoos, and animal passports, that is ultimately on paper documentation, not on chemical analysis.

On the other hand, in order to develop a classification scheme, the complexity of the livestock system is from the traceability point of view must be considered. Several variables, such as environment, race, diet, drinking water features, conjugal conditions, etc., can influence. Moreover, analytical strategies are necessarily different for global or microregional scales. The feed used to feed livestock can come from different sources, the chemical features (e.g., isotopic ratios, trace metals, etc.) of which will be mixed while fixing into beasts' muscle fibers, a process that in addition occurs for long periods, so that the original fingerprints of diet foods are lost. It is also possible that animals had been bred in different farms along their lives, maybe with different feeding methods. Finally, the biological and physical factors influencing the isotopic composition of animal tissues are not entirely clarified, unlike the case of wine in which stable isotope analysis is by now a powerful, straightforward method of authentication.

Information that can be easily yielded from chemical analysis is the type of livestock feeding, which is reflected on the isotope fingerprint of slaughtered meat. Extensive systems of production, such as organic farming, are strongly related to the local environment. This livestock is let to spend free outdoors, sometimes even during winter. Feeding needs few supplements from sources external to farms as prescribed by EEC Regulation 2092/91 (and further amending acts) for organic farming [25]. As a consequence, animals could incorporate mineral substances and isotope profiles typical of a local, restricted area. For livestock subjected to intensive systems, the situation is more complicate: feeding systems can change from free grazing and assumption of local feeds to whole indoors housing with assumption of feeds produced externally, possibly from different sources. In particular, soy-based protein supplements are marketed all over the world. In meats slaughtered from animals fed with these systems, the assumed mineral substances reflect a mixture of provenances, which is not an ideal situation for classification and specifically for traceability. Particularly complex is the case of poultry, where animals are hardly bred with extensive systems so that their meats have weak links with the territory.

In the case of sausages, the possibility of traceability is even worst, due to the fact that their preparation, by definition, calls for addition of different substances to favor conservation: salt, spices, additives, and sometimes selected

microorganisms, all instances heavily influencing the original chemical features in terms of trace elements or isotope ratios. Authentication could nevertheless be possible thanks to identification of specific organic compounds; this is particularly important when high-quality handcrafted productions are involved, i.e., *Pata Negra raw ham*, *culatello di Zibello*, etc., which have relevant commercial values.

The analytical methods for meat classification have been recently reviewed by Vlachos et al. [26] and by Sentandreu and Sentandreu [27].

The most common frauds in the meat market are the following:

- adulteration:
  - addition of water in order to increase meat weight;
  - addition of disproportionately high amounts of extenders and fillers of non-meat origin;
- sophistication:
  - undeclared addition of offal;
  - undeclared addition of mechanically separated meat (MSM);
- counterfeiting:
  - meat produced in foreign countries sold as local meat;
  - meat of lower quality animals passed off as meat of higher quality animals (i.e., horse meat passed off as beef meat);
  - meat from animals stolen and/or illegally slaughtered;
  - meat from poached wild animals;
  - previously frozen meat labeled as fresh.

1.3.5 Fish

The term *fish* is collective term encompassing all water-dwelling animals of interest for human consumption; in the market sense, it comprises any fish, mollusc, or crustacean species, which is harvested, either from sea or from internal water sources. Fish is the most traded food commodity in the world; this means it is an ideal subject for falsification. Frauds in the fish market are very common: a recent survey [28] carried out in 21 states in the USA estimated that one-third of the analyzed fish samples were mislabeled, according to USA Food and Drug Administration (FDA) guidelines, with rates hitting as high as 52% in Southern California. This is not surprising if we consider that, once a fish is filleted and skinned, can be difficult to determine what species it actually is. From the analytical point of view, fish is not so different from meat: classification studies must start from diet of individuals destined to consumption, and this is valid only for what concerns bred individuals, while it is meaningless for what concerns caught individuals, whose diets cannot be controlled. Indeed, analytical controls on fishes are limited to sanitary check or to the possibility of distinguishing fresh items from preserved items. Processed fish products (i.e., canned products, pastes, etc.) pose additional difficulties as some chemical markers can be easily degraded.

The analytical methods for fish classification have been recently reviewed by Lavilla et al. [29]; a comprehensive list of methods is also reported in food and agriculture organization (FAO) Fisheries Technical Paper n.455 [30].

The most common frauds in the fish market are the following:

- adulteration:
  - addition of water in order to increase weight;
  - overglazing, i.e., use of excess ice in preservation;
  - soaking, i.e., use of excess additives in preservation;
- counterfeiting:
  - fish caught or farmed in foreign countries sold as local product;
  - fish of lower quality passed off as of higher quality (i.e., wild salmon passed off as farmed salmon);
  - meat from fish stolen and/or illegally caught;
  - transshipping, i.e., fish exported through different countries to avoid duties and tariffs;
  - previously frozen fish labeled as fresh.

1.3.6 Fruits and Vegetables

Fruits and vegetables are the ideal subjects for classification studies. The link between soil and the marketed product is almost free of intermediate passages that could alter chemical and physical features, in particular for what concerns inorganic parameters. Treatments with agrochemicals can introduce some organic and/or inorganic compounds; nevertheless it is not difficult to find chemical markers behaving as tracers. In most raw products, it could be possible to find the elemental of isotopic profile of the soil on which the plants grew. Basically, however, the geographical origin of most fruit and vegetable products does not appear as a real commercial argument and few labels mention their origin. As a result, classification studies on these matrices are scarce and limited to items of notable value. Particular productions, located in small areas and strictly regulated, could be easily subjected to counterfeit. In Italy, this can be the case of typical productions such as the *cardo gobbo of Nizza Monferrato* (near Asti, Piedmont), the *cherry tomato of Pachino* (near Siracusa, Sicily), or the *pistachio nut of Bronte* (near Catania, Sicily). A relevant product is the hazelnut, mostly employed in the confectionary industry; the most prized variety, the renowned *Tonda Gentile delle Langhe*, is easily counterfeit by substituting it with cheaper varieties.

The considerations made above are valid for the most common products. Some specific categories of fruit and vegetable products can draw particular attention for their commercial value. Truffle is the natural foodstuff *par excellence*, so that it is hard to obtain high-quality products by cultivation. It is possibly the foodstuff most suitable for classification studies: (1) its price is quite high (the variety *Tuber Magnatum pico*, the highly renowned white truffle from Alba costs 1500–2500 €/Kg), with prices strongly varying according to geographic provenance and variety; (2) in the passage from soil to table there is no transformation, so that its composition is only bound to soil and plant metabolism; (3) it has a complex composition, which is an advantage in order to develop classification schemes; (4) it has a fairly high content in metals,

which is an advantage for traceability studies based on the distribution of trace elements. Despite all these features, for market reasons very few classification studies have been carried out since now with concern to truffles. Similar considerations can be drawn on mushrooms: even these natural products are suitable subjects for classification studies, with a considerably lower commercial value.

Another class of relevant vegetable items include spices and herbs. Traditionally used worldwide, these items cover a large part of the food market. Saffron is unquestionably the world's most expensive spice [31] and definitely the foodstuff most suitable for classification studies. The real product, prepared with traditional, manual methods from stigmas of *Crocus sativus* can be sold at 15.000–20.000 €/Kg (gold costs 30.000 €/Kg!). This outstanding quotation is justified by the fact that for 1 g of saffron it takes 150 fresh blossoms, each giving three stigmas. Second in price comes vanilla, which is commonly counterfeit by introducing synthetic vanillin into less quality products, while authentic vanilla contains mostly 4-hydroxybelzaldehyde.

From the perspective of classification studies, tea and coffee also can be considered fruit and vegetable foodstuffs, ranking very high for what concerns the impact on the market. Their production is however more complex, as the final products intended for use withstand some manipulations (e.g., toasting of coffee) that can alter the original composition of raw matter.

Arvanitoyannis and Vaitsi [32] have reviewed the application of analytical and chemometrics methods for the classification of vegetables, with particular concern to tomato.

The most common frauds in the market of fresh fruits and vegetables are the following:

- adulteration:
  - addition of water or low value materials to increase weight of products;
- sophistication:
  - addition of substitutes such as maltodextrins in coffee;
- counterfeiting:
  - products marketed under registered names (i.e. (PDO) or protected designation of origin) without having the prescribed chemical, physical, organoleptic, and documental requisites;
  - incorrect botanical declaration.

Far more complex, from the classification point of view, is the matter of fruit and vegetable juices and conserves. Inside the food market these products have a highly relevant importance, due to the fact that transformation of fresh products into conserved products is particularly interesting to food industry: in this way less perishable products (juices or conserves) are generated instead of others (fresh fruits or vegetables) whose organoleptic features are more difficult to preserve. Of course, the physicochemical operations (pressing, clarification, addition of preservatives, etc.) involved render hard traceability, leaving some possibilities for authentication based on identification of chemical markers of the original fruit or vegetable raw matters.

The most common frauds in the juices and conserves market are the following:

- sophistication:
  - addition of glucose and complex sugars for lowering acidity index;
  - addition of thickening agents (e.g., gelatin, agar–agar, fecula, etc.) for improving stability and consistency of products and for hiding the effect of the use of defective raw matters or of undesired or noncompliant production techniques;
  - addition of natural and synthetic dyes to not-fully ripe raw matter;
  - addition of antiseptic substances in order to guarantee conservation of products of unsuitable matter;
  - extreme squeezing of fruits;
  - preparation of synthetic juices;
  - addition of fruit and vegetable products different from those declared;
- counterfeiting:
  - declaration in labeling unequal to what is inspected inside confections, in terms of net weight, drained weight, residues, nutritional values, ingredients, etc.;
  - reuse of expired products, changing expiry date.

1.3.7 Animal Products

Several foodstuffs are produced by animals but consumed by man. Among these, particularly relevant are *eggs* and *honey*.

The composition of eggs should strongly reflect chicken's diet, since there is no chemical transformation in the passage from collection to marketing (at least for correctly preserved eggs). It is therefore a case similar to meat, for what concerns classification studies. A different matter is, on the contrary, for egg-based foodstuffs, whose production can involve addition of several compounds. The commercial value of eggs and egg-based products cannot justify the need of traceability.

The most common frauds in the market of eggs and egg-based products are the following:

- counterfeiting:
  - sale of broken eggs delivered to food industry;
  - marketing of broken eggs;
  - marketing of loose eggs lacking the prescribed labeling systems;
  - apposition of wrappers on packages in the days following the day of classification and selection of egg or the day of recommended sale, which corresponds to 21 days after picking up;
  - marketing of eggs belonging to weight categories different to the one declared;
  - marketing of eggs reporting a deposition date successive to the real one;
  - labeling indicating a chicken breeding system different from the one adopted in the farm from which eggs come (e.g., battery farming in place of free range).

Honey is a highly concentrated solution of carbohydrates in water. It is with no doubt a product strongly linked to the territory, being its composition and organoleptic features deriving mostly from the type of flora gathered by bees; EU regulations, moreover, specify that no additive can be added to the product. In addition to botanic variations, other relevant parameters linked to territory are the type of soil and the human activities that can have consequences on the quality.

Considering honey, the geographical parameter does not allow establishing absolute rankings, but it is well known the fact that some origins are more recognizable in terms of composition and quality. For example, honeys from Ethiopia and Italy are renowned for being among the best in the world.

At present, the most suitable method for obtaining the botanical and geographical origin of honey is melissopalynology, which is the identification of honey pollens. Also promising are techniques that allow determining the distribution of sugars and other organic compounds. For what concerns traceability, the production chain is simple, as from the collection of bees' secretion to the packaging, no chemical process are included. Therefore, the composition of packed honey reflects the inorganic parameters of the area of origin, but it must be considered that it is frequently hard to establish the territory on which bees stand on. The matter is even more complicate for *thousand flower-type* honeys, i.e., honey produced from a variety of flowers.

Arvanitoyannis et al. [33] and Camina et al. [34] have recently reviewed the application of analytical and chemometrics methods for the classification of honey.

The most common frauds in the honey market are the following:

- adulteration:
  - honey produced with illicit addition of water;
- sophistication:
  - honey produced with illicit addition of sugars (mostly glucose) or molasses;
- counterfeiting:
  - honey labeled as unifloral (e.g., *Acacia honey*) which is actually *thousand flower honey*, i.e., with botanical origin different from the one declared;
  - honey made in foreign countries sold as local product.

1.3.8 Products from Cereals

Cereals have been used since antiquity for both human and animal nutrition. The most common cereals are corn, wheat, rice, barley, rye, and oats. From milling of some cereals, flours are obtained which are the bases for production of several common derivatives, such as bread, pasta, and bakery products. The industrial processing of cereals comes through milling and other mechanical procedures, which make flours and other intermediate products easily traceable. The same holds for cereals, which are consumed after collection and refining, as in the case of rice. In the case of bread and bakery products, instead, additional substances are involved such as yeasts, fats, salt, eggs, etc., which complicate the possibility of tracing.

It must be considered that the commercial value of cereals and bakery products can hardly justify classification studies; nevertheless, valuable niche productions,

such as the *pane nero di Castelvetrano* (Sicily) or some rice varieties (Indian–Pakistani basmati rice), could take advantage from authentication studies.

Vlachos and Arvanitoyannis recently reviewed the methods for classification of rice [35] and maize [36].

The most common frauds in the cereals market are the following:

- sophistication:
  - production of pasta labeled *durum wheat semolina*, made from durum wheat *semolato*;
  - production of pasta labeled *durum wheat semolina*, made from soft wheat flour;
- counterfeiting:
  - partial or total substitution of higher quality products, i.e., *basmati* rice with lesser value rice cultivars;
  - products of similar cultivars sold as original productions, i.e., *basmati* rice brand assigned to rice produced from countries other than Himalayan foothill regions of India and Pakistan.

1.3.9 Organic Food

The term *organic food* is limited to foodstuffs and agricultural productions obtained in the respect of biological equilibria, of human and animal health, and in the safeguard of environmental resources. This statement includes use of natural technical means, exclusion of chemical products and excessive exploitation of natural resources. Organic farming systems involve using organic fertilizers, such as animal manure and extensive cultivation of nitrogen-fixing plants. Conventional farming systems, on the contrary, allow to use agrochemicals and synthetic fertilizers.

From the classification point of view, the sector of organic foodstuffs is delicated. In this case, more than individuating the link between soil and product, it is important to verify analytically whether an organic product can be distinguished from a conventional or industrially made one. Differences in farming systems should be reflected in the chemical composition of plants growing on different crops, but it is difficult to evidence chemical markers able to trace or even authenticate really organic products. Several analytical tests exist based on the presence/absence of prohibited compounds (e.g., agrochemicals, pesticides, heavy metals, etc.). The content of pesticide residues is systematically lower in organic plant products than in conventional products; the same holds with concern to drugs in organic meat versus conventional meat. However, the number of undesired compounds is too large to be wholly checked. At present, the discrimination among organic and conventional products is troublesome on an analytical base. Better chemical markers are needed.

The analytical methods for classification of organic foodstuffs have been recently reviewed by Capuano et al. [37].

The most common frauds in the organic food market are the following:

- sophistication:
  - foodstuffs produced with illicit addition of various compounds;

- counterfeiting:
  - production of foodstuffs using technical means not allowed (fertilizers, pesticides, etc.);
  - marketing of agricultural products declared as obtained from organic farming, with a label quoting certification, while they come from conventional farming;
  - importing, packaging, or marketing of products labeled as organic, lacking the mandatory certificate;
  - production and manipulation of products labeled as organic without the producer had submitted to the requested control system;
  - improper use of captions such as *natural*, *bio-*, *eco-*, incorrectly recalling an organic method for conventional products;
  - undeclared use of genetically modified food.

2. MASS SPECTROMETRIC ANALYSIS FOR FOOD FORENSICS

2.1 Analytical Methods in Food Forensics

In the last 15–20 years, a large number of highly sophisticated techniques, not specifically developed for food classification, have been found to be suitable in food forensics. Spectroscopic techniques such as nuclear magnetic resonance (NMR) and infrared spectrophotometry (FT-IR) have been used in several applications on all kinds of foodstuffs [38,39]. Other techniques, usually developed for determination of compounds of biological interest, resulted to be useful; this is the case of chromatographic, electrophoretic, and enzymatic analysis. More recently, DNA analysis has proven to be one of the most powerful techniques in food forensics [40] as it is in all sectors of forensic analysis. It is no doubt, however, that the lion's share in food forensic is played by mass spectrometric (MS) techniques. The key role of MS in individuating elemental and molecular parameters that can be used as markers in the classification of foodstuffs cannot definitely be underestimated. Due to the great diagnostic potential in classification of foodstuffs, the application of MS techniques in food forensics has received much attention in the scientific literature; the subject has been recently reviewed by Aiello et al. [41] and by Drivelos and Georgiou [42] with concern to the geographical origin of foods in the European Union. Further references to applications of MS can be found in more general discussions on the subject of food forensics [40,43–48].

MS techniques can be used in food forensics with concern to three main classes of chemical markers (Figure 4):

- *isotope ratios*: the most powerful markers for food classification, a fact certified by several hundred of scientific publications;
- *trace elements*: mass spectrometry coupled with plasma techniques can determine elements at trace and ultratrace level, which are known to act as geochemical markers;
- *molecular ions of ionic fragments*: whole molecular ions or low molecular weight ions can be used to identify typical patterns.

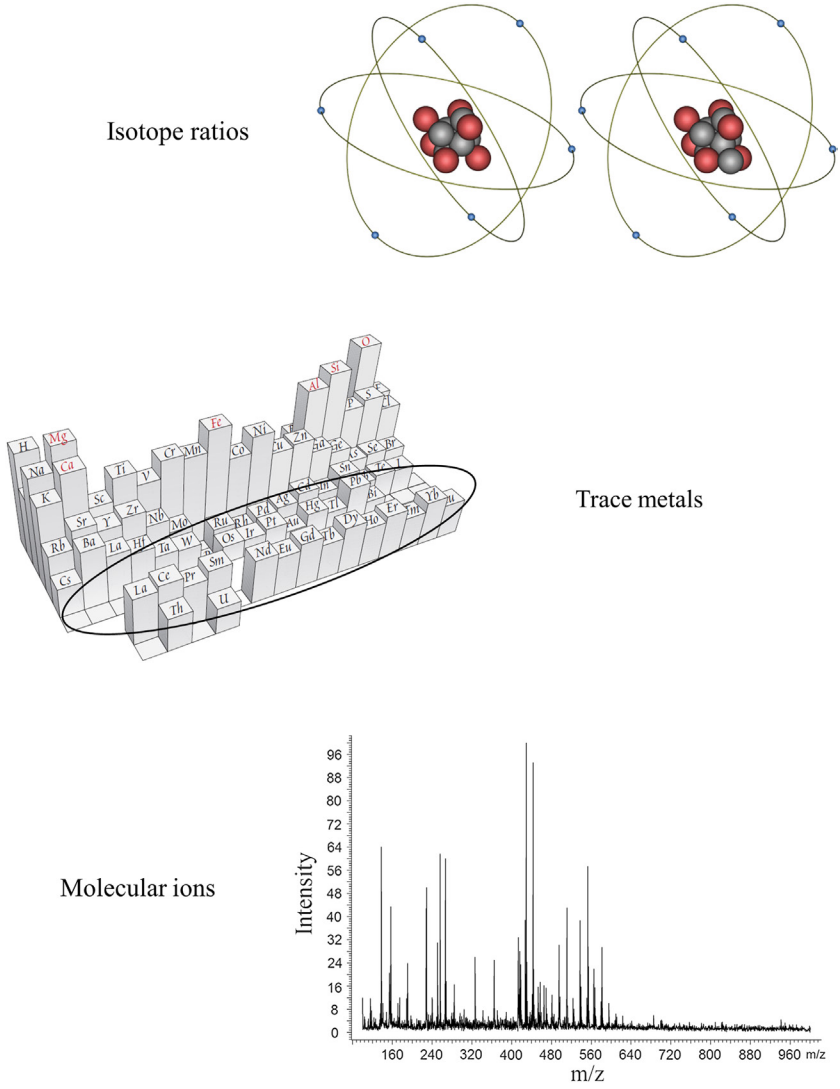


FIGURE 4 Chemical markers useful in food classification.

2.2 Isotope Ratios as Chemical Markers

The role of isotope ratio analysis is well known and consolidated in scientific field, in particular with concern to stable isotopes analysis (SIA). Its potential has been soon recognized in the field of food forensics, thanks to the comprehension of the mechanisms ruling isotopic fractionation of light elements, i.e., the elements constituting living matter. On the basis of ultraslight variations in isotope ratios, SIA allows identifying molecules in foodstuffs with similar chemical structure but coming from different raw materials or

produced with different processes, e.g., for biological versus industrial synthesis. With concern to determination of hydrogen isotope ratio, the most powerful SIA method is site-specific natural isotope fractionation–nuclear magnetic resonance (SNIF-NMR), developed by Martin and Martin [49] at the beginning of 1980s; further on, Caer et al. showed the potential of SNIF-NMR for determination of $^{13}C/^{12}C$ ratio also [50]. The use of mass spectrometry to perform isotope ratio measurements is much older, as it has been initiated in the field of geosciences in the 1940s and 1950s. This soon has led to the development of the powerful technique known as isotope ratio mass spectrometry (IRMS). Technical details on SIA and IRMS can be found in several publications [51–53].

The high diagnostic power of IRMS has been recognized at legislative level by indication of its use, together with SNIF-NMR, inside national and international laws ruling food analysis. In the European Union legislation, EC Regulation No 2676/90 [54] and successive amendment in EC Regulation No 822/97 [55], ruling Community methods for the analysis of wines, indicated IRMS for determination of $^{18}O/^{16}O$ isotopic ratio of water content in wines, useful for identifying fraudulent addition of water. A further amendment in EC Regulation No 440/2003 [56] indicated IRMS also for determination of $^{13}C/^{12}C$ isotopic ratio in wine alcohol in order to identify fraudulent addition of sugar from cane or beet. Similar solutions have been adopted by organisation international de la vigne et du vin (OIV) in Resolution OENO 17/2001 [57] concerning IRMS determination of $^{13}C/^{12}C$ ratio on wine ethanol, Resolution OENO 7/2005 [58] concerning IRMS determination of $^{13}C/^{12}C$ ratio on CO_2 in sparkling wines, and Resolution OENO 353/2009 [59] concerning IRMS determination of $^{18}O/^{16}O$ ratio on water in wine and must. In the UK, the application of SIA techniques for food forensics has been strongly supported by the British Food Standards Agency (FSA) since the mid-1990s. In a similar way, the European Office for Wine, Alcohol and Spirit Drinks (BEVABS), established by EU in 1993, recommended the use of SIA to combat major fraud in the beverage sector since 1997. In the USA, the Association of Official Analytical Chemists indicated IRMS as method of choice for determination of $^{13}C/^{12}C$ isotopic ratio in honey [60] and fruit juices and maple syrups [61].

IRMS applied to whole samples is usually known as *bulk SIA*. Since the middle of 1980s, a new type of instrument, resulting from the interface of IRMS to a gas chromatographic system, became available. This hyphenated system allowed performing what is commonly known as *compound-specific isotope analysis* (CSIA), i.e., determination of isotope signatures at the molecular level. Despite the main applications of CSIA are in environmental studies, this technique has also proved to be a powerful method for food forensics. CSIA can be also carried out by extraction of single compounds from the sample.

IRMS has been used for classification of several different types of foodstuffs. Once again, it is necessary to distinguish between authentication and traceability. Isotope ratios of light elements, such as hydrogen, boron, carbon,

nitrogen, oxygen, and sulfur, are strongly influenced by chemical, physical, and biological phenomena. Instead of using the simple ratio, it is more common to compare δ value that is the ratio of isotopes in the sample to the ratio in a standard. δD values in plant products originate from the water taken up by the roots and are higher in regions with relatively low humidity. $\delta^{13}C$ values are more bound to the metabolism of plants, with particular concern to the pathway followed in fixation of CO_2: the main discrimination is between C3 (the first product of photosynthesis is 3-phosphoglycerate) and C4 (the first product of photosynthesis is a C4 unit) plants [62]. C3 plants account for 95% of edible species, among which sugar beet, potato, rice, barley, wheat, soy, sunflower, olive, rye, apricot, orange, grapes, and peanut. C4 plants are 1%, examples are sugarcane, sorghum, maize, and millet. A minor category, to which pineapple, vanilla, agave, and cactus belong, is the one associated with Crassulacean acid metabolism (CAM). $\delta^{18}O$ values originate from CO_2, H_2O, and O_2 and correlate with water, reflecting the isotopic composition of groundwater and the average precipitations in the region (related to latitude, distance from the sea and altitude) and the extent of evapotranspiration, mainly influenced by humidity and temperature [63]. The geographical signature from water is transferred into plant and animal products [64]. $\delta^{15}N$ values have relatively shorter ranges but vary according to different factors: the nitrogen cycle (fixation, uptake, mineralization, nitrification, and denitrification), trophic ecology (an increase in trophic level correlates with an increase in $\delta^{15}N$ value), and anthropogenic activity [65]. Finally, $\delta^{34}S$ values are bound to sulfur sources such as bedrock weathering, atmospheric deposition, and microbiological activity. When plants are converted into food for man or animals, geographic provenance, animal/botanic species, or way of processing are all factors that can cause strong fractionation in the ratios of light elements in products, providing therefore the basis of authentication schemes. At the same time, high rates of fractionation are a negative feature if traceability, where constant parameters are sought for, is the objective; therefore, light elements isotope ratios usually are not efficient tracers. On the contrary, isotope ratios of heavy elements, such as strontium or lead, are not influenced by biological phenomena, since the corresponding elements are usually kept off from biological cycles; therefore, once established into rocks, they are potentially maintained unaltered in the passage from soil to food. Isotope ratios of Sr and Pb change strongly from rock to rock. In the case of strontium, ^{87}Sr is a radiogenic nuclide generated by the radioactive decay of ^{87}Rb, so its content in rocks (and consequently in soils derived from them) increases with age; $^{87}Sr/^{86}Sr$ values are therefore lower in younger rocks such as carbonaceous, volcanic, and basaltic rocks and higher in older rocks such as magmatic and metamorphic rocks. The case of lead is more variegated: this element has three radiogenic nuclides, ^{206}Pb, ^{207}Pb, and ^{208}Pb, plus one nonradiogenic, ^{204}Pb. Different ratios are possible with a strong link to the age of rocks. The role of the isotopic signatures of strontium and lead as suitable markers for geologic and therefore geographic provenance of foodstuffs has been generally

discussed in many studies [42,66–68]. Of particular interest is a recent, fundamental study by Voerkelius et al. [69] in which authors showed that an $^{87}Sr/^{86}Sr$ database of surface waters could be used to predict the geographic origin of some types of food, such as honey and wheat.

To resume, isotope ratios of light elements are more useful to study authentication of foodstuffs, while isotope ratios of heavy elements are more useful to study traceability (and therefore authentication also). The main information yielding by means of IRMS analysis is listed in Table 1.

A fascinating application of IRMS analysis in food forensics is the characterization of *palaeodiets* in order to obtain information concerning diets of ancient people and cultures. Carbon and nitrogen isotopic signatures can help in identifying the types and amounts of proteins and plant matter consumed by individuals [70] following the fractionation mechanisms in edible matter described before. $\delta^{13}C$ values measured in bone collagen mainly indicate the protein component of the diet [71] while in bone apatite they provide a picture of dietary energy, including carbohydrates and lipids [70]. Accordingly to what it was cited before, $\delta^{13}C$ values can help in distinguishing a diet based on C3 plants (i.e., temperate grasses such as wheat and barley) from C4 plants (i.e., millet and sorghum). $\delta^{13}C$ values from bone collagen and apatite provides additional information concerning the individual's dietary energy source (C3, C4, or mixed) and protein source (C3, C4, or marine) [72]. Stable isotopes of nitrogen discriminate more efficiently between aquatic and terrestrial protein [70]; moreover, $\delta^{15}N$ values are correlated with the trophic position of the edible organism in the food chain: body tissues

TABLE 1 List of Main Isotope Ratios of Interest in Food Forensics

Isotope Ratio	Fractionation	Information
$^{2}D/^{1}H$[a]	Origin of water, biochemical	Geographical, botanical, natural versus synthetic
$^{13}C/^{12}C$[a]	Fixation of CO_2 (C3 vs C4 plants)	Botanic origin, diet
$^{15}N/^{14}N$	Trophic level, marine and terrestrial plants	Diet, agricultural practices
$^{18}O/^{16}O$	Origin of water	Geographical
$^{34}S/^{32}S$	Atmospheric deposition, biochemical	Diet, geographical
$^{87}Sr/^{86}Sr$	Underlying geology	Geographical
^{208}Pb, ^{207}Pb, ^{206}Pb, ^{204}Pb	Underlying geology	Geographical

[a]*It can also be determined by means of SNIF-NMR.*

are generally 3–4‰ higher than the $\delta^{15}N$ of the diet [73]. Examples of recent palaeodietary studies were those by Killgrove and Tycot [74] who investigated human skeletons found in two cemeteries in Rome dating to the Imperial period (first–third centuries AD) and by Gregoricka and Sheridan [75] who analyze skeletons from an early medieval Byzantine monastery in Jerusalem.

In the following paragraphs, examples of applications of IRMS analysis to food forensics are cited with concern to different food categories. This matter has been reviewed by Rossmann [66].

2.2.1 Wine, Fermented Drinks, and Other Beverages

A major part of IRMS applications in food forensics is devoted to wine. Three main objectives are sought for: (1) identification of addition of water; (2) identification of addition of sugars coming from plants other than grapes; (3) recognition of the geographic provenance.

The first objective can be obtained from the determination of $^{18}O/^{16}O$ isotopic ratio of water [76]. A close correlation between the oxygen isotope signature of must and the related wine water must be found in genuine wines. Actually, there is a very low chance that water illicitly added to wine had the same isotopic signature of the original water, which confirms the potentiality of the method in recognizing this kind of fraud.

Addition of sugars obtained from plants other than grapes needs a two-step approach. The discriminating factor is the metabolic pathway followed by plants to fix CO_2: C3 plants have $^{13}C/^{12}C$ isotopic ratio values more negative in terms of $\delta^{13}C$ [77]. Sugars from cane or maize can be easily detected, being them C4 plants while grape is a C3 plant. Addition of sugar from beet needs a further step, being beet a C3 plant as well; in this case determination of D/H ratio by means of SNIF-NMR helps in further discrimination between grapes and beet, being δD values higher in sugars from grapes.

Also of interest in enological field is the identification of addition of synthetic ingredients in winemaking. Moreno Rojas et al. [78] investigated the possibility of frauds committed using natural external L-tartaric acid in wines by means of IRMS. Particular focus was given to L-tartaric acid extracted from tamarind in place of the natural compound present in grapes, which is the only source allowed for acidification treatments according to both EU and OIV regulations. Samples of L-tartaric extracted from musts in Romania were compared with samples extracted from commercial tamarind pulp of four different origins (India, Mexico, Colombia, and Thailand). The different botanical sources (grapes vs tamarind) were discriminated on the basis of δD, $\delta^{13}C$, and $\delta^{18}O$ values. Combining hydrogen, carbon, and oxygen isotopic signatures, it was also possible to distinguish between natural L-tartaric acid and synthetic L-tartaric acid (petroleum by-products).

For what concerns the determination of the geographic provenance, the situation is more complicate. EU regulation 2676/90 [54], apart from establishing rules for identification of fraudulent water addition to wine, set the rules for

creation of a database of isotopic ratio values in wines in order to allow the possibility of recognizing the geographic provenance of a wine. Wines from the main European wine-producing countries and also from some foreign countries have been analyzed since then, collecting every year hundreds of samples and determining D/H values of ethanol by ^{2}H-NMR, δ^{13}C values of ethanol, and δ^{18}O values of wine water. Conventional wine analysis data are included. Due to the different possibilities of adulteration and to the relevant seasonal and regional variability, though, it is hard to obtain a reliable assessment of geographic provenance [66]. This is a consequence of the intrinsic variability of light elements isotopic signature.

On the contrary, the isotopic signatures of heavy elements are more constant, because they are not subject to relevant seasonal variability and to biological cycles. Several studies showed that strontium and lead isotope ratios are powerful markers of geographic provenance. Horn et al. [79] were among the first suggesting that the isotopic signature of strontium could be a tracer for the geographic provenance of wine. Almeida and Vasconcelos [80] demonstrated that, while total Sr concentration changes dramatically along the passage from soil to bottled wine, ^{87}Sr/^{86}Sr ratio keeps identical, providing a tool for the identification of the geographic provenance of a wine. This result is justified by the fact that the isotopic signature of strontium, once set into rocks, has not influenced biological or chemical phenomena so that it can be considered a powerful geographic marker. Several studies thereafter have confirmed these results [81–83]. Similar but not identical considerations can be drawn on the use of lead isotope ratios. Contrarily to strontium, which is almost totally an element of natural origin, lead in wine has two major sources [84]: the primary source is linked to soil, as for strontium, while the secondary source is anthropogenic and it involves fertilizers, pesticides, road traffic (the introduction of leaded gasoline in 1939 by Ford has caused an increasing lead pollution in the environment, reversed in the 1970s due to the introduction of unleaded fuel), and the equipment used during vinification. Therefore, the isotopic signature of anthropogenic lead can overlap to the geochemical one. Despite this, several studies have investigated the possibility of determining the geographical origin of wine samples on the basis of lead isotopic signature [85,86]. An additional feature is that in the case of lead, more than one isotope ratio can be exploited. The key factor in the determination of lead isotope ratio is the precision of the instruments used. Conventional quadrupole inductively coupled plasma–mass spectrometry (ICP-MS) has a limited potential for distinguishing very small differences between isotope ratios, while higher precision of measurement is yielded by ICP-Time of Flight-MS, thermal ionization mass spectrometry, and multicollector sector-field-ICP-MS.

Recently, the use of boron as ^{11}B/^{10}B isotope ratio has been suggested as additional means for wine traceability; the results obtained by Vorster et al. [87] in discrimination of wines from South Africa seems promising, but at present this element has not found many applications in food forensics, though its natural isotopic variation could go as wide as 90‰ [88].

In food forensics, a relatively lower amount of research has been devoted to spirits. In this field also, however, do exist authenticity issues such as deliberate and illegal substitution of a prised brand with a cheaper one. Simpkins and Rigby [89] were among the first to apply IRMS for identification of counterfeit spirits. Among hard liquors, whisky is a traditional drink with a strong commercial value, which production is defined by both EU and local regulations. Prices for whisky bottles can vary dramatically according to purity (*single malt* vs *blended*), vintage, geographic provenance (Scotland vs Ireland vs Northern American countries), and raw matters (barley vs corn/wheat). For this reason, several studies have tried to develop methods for whisky classification according to the variables cited. Using compound-specific isotope analysis of hydrogen in ethanol, Hilkert et al. [90] discriminated *single malt* whiskies made from barley (a C3 plant) from *blended* whiskies made from barley and corn (a C4 plant) and from whiskies made from corn alone. This classification was made possible due to the high rate of variation of δD among C3 and C4 plants. Parker et al. [91] used compound-specific isotope analysis of carbon in volatile congeners, classifying whiskies of different brands. More recently, Meier-Augenstein et al. [92] found a good correlation among δD and $\delta^{18}O$ values for waters used in the production of Scottish whiskies and the corresponding bottled whiskies, allowing to develop a method for geographic classification and for identification of counterfeit products. Again, with application of compound-specific isotope analysis of carbon, Rhodes et al. [93] developed a method for identification of illicit addition of neutral alcohol to whisky, based on internal isotopic correlations for ethanol and the congeners from the same sample.

Bottled water accounts for a relevant segment of the food market, with particular concern to the Italian market. Frauds are always possible in terms of product misrepresentation. As an example, carbonated water can contain natural CO_2 coming from sources or industrial CO_2 artificially added. IRMS can be applied to the classification of mineral waters, investigating the correlation among the isotopic signature of hydrogen and oxygen in bottled water with estimated mean annual precipitation isotope ratios for source or bottling locations. Carbon isotopic signature in the dissolved inorganic carbon of carbonated bottled water can yield information on the origin of CO_2; extreme negative values of $\delta^{13}C$ in bottled waters can be due to exogenous (industrial) CO_2 sources. Raco et al. [94] investigated samples of bottled water from Italy, among which some sparkling waters (i.e., naturally carbonated). $\delta^{2}D$ and $\delta^{18}O$ values of samples were found to vary within the reported natural variations for Italian waters as samples lied along the global and Italian meteoric water line. According to the authors' opinion, these values might reflect relatively unaltered source water signatures. Voerkelius et al. [69] carried out a large-scale investigation of strontium isotope ratios on 650 different European natural mineral waters as part of the food traceability project ''TRACE" funded by the EU. Isotopic data were combined with a GIS-based geological map of Europe in order to elaborate a

novel spatial prediction for strontium isotopic composition of groundwater and thus the composition of bioavailable strontium, which is available for uptake by plants and subsequently transferred into the food chain.

2.2.2 Milk and Dairy Products

The classification of milk and some dairy products can be obtained by IRMS analysis. Scampicchio et al. [95] analyzed raw, pasteurized (HTST), and ultrapasteurized (UHT) milk from different Italian origins by determining $\delta^{13}C$ and $\delta^{15}N$ for milk and milk fractions (fat, casein, and whey). Significant changes in $\delta^{13}C$ and $\delta^{15}N$ were observed as a function of heat processing, which allowed identifying markers useful for pattern recognition methods. It was possible to discriminate simultaneously the geographical origin and type of processing of milk samples.

Of particular concern is the possibility of verifying the provenance of cheeses, which in several cases are high-quality products. Intermediate processes in the production chain play, of course, a relevant role in fixing the isotopic signatures of light elements. $^{13}C/^{12}C$ ratio in milk fat and in cheese protein reflects the type of forage fed to the cows mainly constituted of C3 plants. Also $^{15}N/^{14}N$ ratio results from forage, but the use of organic fertilizers and intensive farming methods can increase this value; other influent factors are climate and soil conditions. Finally, nitrogen-fixing plants, such as leguminosae, have lower $\delta^{15}N$ than nonnitrogen-fixing plants and can be administered in the cows' fodder. $^{18}O/^{16}O$ ratio of milk depends on the water ingested and the proportion of fresh versus dry fodder; ultimately, climatic features play a primary role.

Mozzarella cheese is a highly renowned Italian product made from buffalo milk, characterized by a protected designation of origin (PDO). Brescia et al. [96] analyzed buffalo milk and mozzarella cheese from two sites in Southern Italy; authors found that milk could be distinguished on the basis of $^{13}C/^{12}C$ versus $^{15}N/^{14}N$ ratios, probably due to a difference in the diets of buffalos in the two locations, while in order to distinguish mozzarella samples, D/H data determined by means of SNIF-NMR must be included. Pillonel et al. [97] distinguished Emmental cheeses produced in six European regions: Allgau (Germany), Bretagne and Savoie (France), Finland, Switzerland and Vorarlberg (Austria). Different variables were used in the study: stable isotope ratios of light elements ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, and D/H) and of $^{87}Sr/^{86}Sr$ and concentrations of major (Ca, Mg, Na, K), trace (Cu, Mn, Mo, I), and radioactive elements (^{90}Sr, ^{234}U, ^{238}U) elements. A complete discrimination was obtained only by using all the variables determined, since isotope ratios yielded a partial classification.

2.2.3 Vegetable Oils

Olive oil is a noble product with a very long tradition, with particular concern to the Mediterranean area (olive tree was already cultivated in Syria at least 6000 years ago). It is commonly recognized that the highest quality oils are produced in Italy and Spain. Frauds in the olive oil market are frequent since

it is not easy to identify products with features different from those declared in labels, at least for what concern the geographic provenance of the raw matter. For this reason, several studies have investigated the possibility to classify samples. Most of the studies concern *extra virgin* olive oils, the products with highest quality. Camin et al. [98] carried out a thorough analytical study within the framework of the food traceability project "TRACE" funded by EU, in which authors analyzed 267 olive oils coming from eight European sites. Both isotopic (H, C, and O stable isotope ratios) and elemental concentrations were determined. In addition, the same parameters were measured in 314 fresh surface waters from the same sites. The main scope of the project was verifying whether olive oils could be discriminated according to the climatic and geological characteristics of the sites on which they were produced, and finding a possible relation with the corresponding surface waters. δD and $\delta^{18}O$ values in oils resulted to be correlated to each other and to corresponding waters. $\delta^{13}C$ and $\delta^{18}O$ showed significant correlation with geographical parameters, such as latitude and distance from the coast, and climatic parameters, such as temperature, relative humidity, and amount of precipitation; δD correlated with latitude, distance from the coast, altitude, and temperature. Pattern recognition carried out with canonical discriminant analysis (CDA) allowed a good classification on a geographic scale; this result was improved adding elemental data as variables in the classification.

Also, it is possible to verify the addition of lesser quality oils to olive oil with compound-specific IRMS (even if this issue can be addressed much more easily by GC-MS). Blending of olive oil with edible oils with slightly different fatty acid composition (olive pomace, sunflower, hazelnut) might be detected by using $\delta^{13}C_{16:0}$ versus $\delta^{13}C_{18:1}$ covariations combined with molecular information and carbon isotopic composition of the bulk oil [99].

2.2.4 Meats

It is not surprising, due to the importance of meat in the diet of Western countries, that stable isotopes, together with trace element distribution, had been frequently used for meat classification. As discussed before, the production chain of meat is complex due to several confounding factors such as the variegated diet of livestock, the movement of animals among different farms (or even farming systems) before slaughtering, and the metabolic turnover times of animal tissues [100]. Studies have been carried out on beef [101–105], lamb [106,107], and pork meat [108]. More recently, Heaton et al. [109] carried out an extensive study in which they analyzed beef samples from the major cattle producing regions of the world (Europe, USA, South America, Australia, and New Zealand) with both IRMS and ICP-MS. The results were promising for what concerns the geographic classification. Measurements carried out on defatted dry mass (DDM) showed that $\delta^{13}C$ values were clearly lower in beef samples from England, Ireland, and Scotland than in American samples (Brazil and USA); similar results have been reported by Schmidt et al. [105]. It is well

known that differences in $\delta^{13}C$ values are bound to the proportion of C3 and C4 plant materials in the diet of livestock. Extensive C3 pasture feeding is the prevailing system in Northern Europe, while feeding with maize or grain (C4) is more common in American countries, which accounts for the less negative values. Beef samples from Central and Southern Europe show an intermediate behavior, indicating possibly prolonged periods of maize feeding. $\delta^{15}N$ values have smaller variations, but higher values may indicate the use of marine products (fishmeal, seaweed) in the cattle feed [110] or feeding with other animal products: it is known that increases in the trophic level can raise $\delta^{15}N$ values of around 3‰; this practice, however, is forbidden in Europe because of the risks of BSE infection [111]. Low values of $\delta^{15}N$ may be due to the use of synthetic nitrogen-based fertilizers, whose isotopic signature can pass through crops, cereals, and eventually cattle diet, or to foraging of leguminous clover or concentrates. Of particular interest is the isotopic signature described by $^{18}O/^{16}O$. This parameter was measured on beef lipid in place of beef DDM due to instrumental problems. It was found that a significant correlation existed among $\delta^{18}O$ values and latitude of the production region. Data from $^{2}D/^{1}H$ analysis gave similar responses and a plot of $\delta^{2}D$ versus $\delta^{18}O$ mean values in beef lipid showed even better this feature, with samples from higher latitudes (Scotland, New Zealand, Shetland, England, etc.) ranging at lower values and samples from warmer climates and lower latitudes (Southern Africa, Australia, Brazil, and Uruguay) ranging at the opposite side. A supervised pattern recognition analysis with CDA, applied to isotopic and elemental data, allowed classifying samples into three broad groups, i.e., European, South American, and Australasian. Finally, Guo et al. [112] showed that information on the dietary intake of livestock and geographical origin could be obtained with isotopic analysis of C and N from defatted beef as well as from crude fat and tail hair.

The classification of meat and meat products with isotopic analysis has been reviewed by Montowska and Pospiech [113] and by Zhao et al. [114].

2.2.5 Fish

In the classification of fish using isotopic (as well as elemental) parameters, it is usual analyzing otoliths and/or scales, while soft tissues and bones are less useful. Otoliths have metabolic inertness and their composition can reflect the environmental history of organisms. Determination of isotopic signature can help establishing fish origin. $^{18}O/^{16}O$ and $^{2}D/^{1}H$ ratios are strongly latitude dependent, while $^{13}C/^{12}C$ ratio is bound to metabolism and diet [115]. $^{87}Sr/^{86}Sr$ has great potential in determining the geographic origin [116].

Salmon is a fish typically subjected to frauds, with particular concern to the actual geographical provenance and whether the fish is caught or farmed. Wild or line-caught salmon can cost three times farmed salmon. A comprehensive study on salmon classification was carried out by Thomas et al. [117], who analyzed a large number of samples of wild and farmed Atlantic salmon from 32 origins within Europe, North America, and Tasmania. Hydrogen, carbon,

oxygen, and nitrogen isotope ratios were determined in different parts of animals (muscle, oil, and body water) and in different molecular fractions extracted (glycerol, fatty acids, lipids). It can be assumed that the isotopic signatures in salmon reflected both the environment in which it is grown and the composition of the diet consumed. Results of IRMS analysis evidenced that $\delta^{15}N$ values measured on choline and $\delta^{18}O$ values measured on total oil were the best variable for discrimination between wild and farmed fish, while it was more difficult to discriminate between different geographical origins. These results were confirmed by Anderson et al. [118] who analyzed for its elemental and isotopical composition of a large number of salmon muscle tissues from the Pacific Ocean.

Isotopic methods of classification of fish have been recently reviewed by Lavilla et al. [29].

2.2.6 Fruits and Vegetables

This category comprised fruits, vegetables, spices, flavors, herbs, tea, and coffee. A large part of food forensics studies involving IRMS are devoted to classification of these products, due to low complexity of their production chains. Zhao et al. [114] recently reviewed the applications of IRMS in classification of agroproducts from plant sources. Bontempo et al. [63] carried out a vast research on characterization of tomato and its derivatives, using isotopic ($\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{34}S$, δD), elemental (trace elements), and anionic parameters (major anions), verifying how these variables change along the production chain and evaluating their usefulness as geographical origin markers. Tomato samples were from three Italian regions: Piedmont, Emilia-Romagna, and Apulia. Juice, *passata*, and paste were analyzed in all cases. Analysis of variance evidenced the statistically significant variables in the discrimination: for what concerns the differently processed tomato products δD, $\delta^{18}O_{bulk}$, $\delta^{18}O_{water}$, B, Cr, Sr, Ba, phosphate, sulfate, and chloride were highlighted, while for the different geographical origin $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O_{bulk}$, $\delta^{34}S$, $\delta^{18}O_{water}$, Li, Mg, P, K, Cr, Fe, Co, Ni, Ga, As, Se, Mo, Cd, Sn, Sb, Ba, La, Eu, Gd, Tm, Tl, Pb, and U were found. Classification with linear discriminant analysis (LDA) allowed a good discrimination on the basis of geographic provenance, with selection of 10 variables: Gd, La, Tl, Eu, Cs, Ni, Cr, Co, $\delta^{34}S$, and $\delta^{15}N$.

Spices can be considered quality foods in cases in which they express traditional values and are obtained with highly selected raw matters and difficult processes. Among spices, the most valuable is saffron, obtained from stigmas of *C. sativus*. Saffron of the highest quality can be sold at 15.000–20.000 €/Kg, which renders a good idea of the importance of classification. Martin et al. [119] used the carbon isotopic signature to distinguish between safranal extracted from authentic saffron versus that produced by chemical synthesis, but $\delta^{13}C$ values were not so different; application of SNIF-NMR for determination of $^{2}D/^{1}H$ ratio was more successful. More recently, Maggi et al. [120] analyzed 28 saffron samples from leading producers (Greece, Iran, Italy, and Spain) and from the

same harvesting year (2006). Analyses were carried out on defatted dry matter. Using data from hydrogen, carbon, and nitrogen isotopic analysis treated with CDA, authors succeeded in discriminating samples with concern to geographical origin, with better results than using conventional chemical parameters. A further valuable example of this category is paprika (dried and powdered red pepper), a traditional spice in the Hungarian diet but a well-known and widely used product all over the world. In Hungary, the so-called *Szegedi Füszerpaprika* was acknowledged of PDO. Brunner et al. [121] investigated the production chain of *Szegedi Füszerpaprika* in order to verify whether processing could alter the isotopic signatures provided by soil. Results of both isotopic and elemental analysis (ICP-MS) showed that the production process has no significant influence on the Sr isotopic signature and on most of the investigated elements, with the exception of Al, Ti, Cr, and Fe, which were mainly introduced through the cutting process of the dried pods. A unique fingerprint for PDO *Szegedi Füszerpaprika* could be created in order to discriminate it from foreign paprika products.

With concern to flavors, vanilla is one of the most important and widely used products in the food industry. Natural vanilla flavor, extracted from the pods of the tropic orchid *vanilla*, is much more expensive than synthetic vanillin: the difference is \$1200–\$4000/kg for the natural versus \$15/kg for its synthetic equivalent. A particular feature of the vanilla orchid is that it is a CAM-type plant, which is advantageous from the diagnostic point of view since its $\delta^{13}C$ values are in a characteristic range (around −21.0‰), so they are distinguishable from C3 and C4 plants. However, measurement of $\delta^{13}C$ values of bulk vanillin is no longer sufficient for classification purposes because it is possible to enrich synthetic vanillin in ^{13}C on both the methoxyl and aldehydic groups and thereby produce synthetic material with the same $\delta^{13}C$ value as that of natural vanillin. Greule et al. [122] determined carbon and hydrogen ratios of vanillin molecule and vanillin methoxyl groups of samples of different origins, including authentic, synthetic, and semisynthetic samples, the last ones obtained biosynthetically by wood lignin and eugenol. Results showed that the combined isotopic approach with ^{13}C and $\delta^{2}H$ values of both vanillin bulk and vanillin methoxyl groups allowed to fully differentiate between natural vanillin extracted from orchid, synthetic ex guaiacol, and semisynthetic ex lignin, providing a rapid and reliable authenticity assessment of vanillin.

Fruits juices were among the first foodstuffs to be subjected to SIA for identification of frauds. As for wine, measurement of $^{13}C/^{12}C$ ratio by means of IRMS soon proved to be useful to identify sugars produced from C4 plants, such as corn or cane, in C3 plant products, such as citrus, apple, or grape juices [123]. This measurement is also useful in order to identify fraudulent addition of L-ascorbic acid to juices [124]; most commercially available L-ascorbic acid is produced starting from C4 plant carbohydrates (e.g., maize starch) whereas authentic L-ascorbic acid comes, of course, from C3 fruits so that after isolation from sample juice exhibits $\delta^{13}C$ values of 10–14%, range from 19% to 23%.

Measurement of $^{18}O/^{16}O$ ratio is used in order to distinguish among directly pressed and rediluted single strength juices. Values of $\delta^{18}O$ are higher in authentic juices since tap water, used as diluent, is relatively depleted in heavy isotopes [125]. Guyon et al. [126] used an hyphenated system composed by HPLC linked to IRMS via an interface allowing the chemical oxidation of organic matter (HPLC-co-IRMS); in this way they were able to determine $\delta^{13}C$ values of organic acids, glucose, and fructose in lime and lemon juices from various geographical origins. These samples constituted a basis to define a confidence domain to which comparing commercial samples of uncertain origin. Among these samples, several of them presented $\delta^{13}C$ values outside the defined range revealing the unlabeled addition of C4-type organic acids or sugars (lemons are C3-type plants), in disagreement with EU regulation.

Tea and coffee are two products of vegetable origin consumed all over the world. For these items, the price is strongly determined by quality, flavor, and the reputation of the producing area; classification is therefore strategic for the market value. Pilgrim et al. [127] classified tea samples from different Asian and African countries by isotopic (δD, $\delta^{13}C$, and $\delta^{15}N$) and elemental (trace elements) data. Geographical classification with pattern recognition methods yielded good results, unaffected by tea type (black, green, or oolong), quality, or harvest year. For what concerns coffee, the isotopic composition of oxygen and strontium [128] and of boron and strontium [129] in samples from different countries were found to be useful in the geographic classification.

Rummel et al. [130] discriminated orange juice samples from different regions in North and SouthAmerica, Africa, and Europe. Isotopic signature of δD, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{87}Sr$ allowed a good classification of samples. In addition, authors showed the possibility of recognizing fraudulent addition of orange juice concentrate by comparing $^{87}Sr/^{86}Sr$ of soluble and insoluble components of the juices.

2.2.7 Animal Products

Studies on animal products are mainly focused on eggs and honey. Rogers [131] determined carbon and nitrogen isotope values in whole and delipidized yolk, albumen and egg membrane in eggs samples from 18 different brands of chicken eggs laid under caged, barn, free range, and organic farming regimes. It was possible to distinguish free range and organic egg from caged and barn laid eggs on the basis of higher $\delta^{15}N$ values, possibly due to a higher animal protein (trophic) contribution to the chicken's diet in contrast to pure plant-based foods, as suggested by De Niro and Epstein [132]. $\delta^{13}C$ values, instead, did not elucidate laying regimen. Rock [133] recently reviewed the applications of IRMS techniques for eggs classification.

An important study by Schellenberg et al. [134], within the framework of the food traceability project "TRACE" funded by EU, was focused on the possibility to classify honey samples produced in different European regions by the isotopic signatures of light elements. 516 authentic honeys from 20 European regions were

analyzed. Floral types of samples were acacia, brambles, buckthorn, chestnut, citrus, clover, dandelion, eucalyptus, heather lavender, rape, rosemary, sunflower, thyme, forest, and honeydew, plus mixed floral honeys and samples of unknown floral origin. On all samples the stable isotope ratios of hydrogen, carbon, nitrogen, and sulfur were determined. Analyses were made upon precipitation of honey proteins in order to increase the concentrations of nitrogen and sulfur. Results showed the high potential of SIA in honey geographic classification. A significant correlation was found between δD values in honey protein and climatic conditions in the production regions. $\delta^{13}C$ values also were found to be influenced by climate, with higher values in samples from warmer and drier regions; regional differences were more significant than botanical origin. Nitrogen isotopic composition was not clearly correlated with geographical or botanical features of the samples. Finally, $\delta^{34}S$ values were correlated with soil sulfur isotopic ratio and eventually with geographical locations of the plant's growing areas, with strong influence of sea spray for regions close to the sea. Chemometric analysis with LDA identified $^{13}C/^{12}C$ and $^{34}S/^{32}S$ as the most discriminant variables.

A further field of forensic investigation on honey is the identification of illicit use of sugar syrups either by addition to honey or by feeding the bee colonies. $\delta^{13}C$ values from honey protein, as indicated by the official White method [135], can reveal honey manipulation with C4 plant sugars such as high-fructose corn syrup (HFCS), which derives mainly from maize, while the main nectar-providing sources of the honeybees are C3 plants; the difference between $\delta^{13}C$ value of protein and whole honey should be lower than 1‰ [136]. The addition of sugars from C3 plants (beet, wheat), however, cannot be proved by this method. To overcome this drawback, Daniele et al. [137] proposed honey organic acids as internal standards in order to detect honey adulteration.

2.2.8 Products from Cereals

Cereals are a major part in the diet of most cultures all over the world. Among cereals, rice has attracted most of the attention in classification studies, due to the fact that in many countries the geographic provenance of this product is an important issue to consumers. Several studies indicated that SIA can help in distinguishing the provenance of rice samples [138,139]. Ariyama et al. [140] used isotope signatures of heavy elements, i.e., strontium and lead, to distinguish rice samples from Japan, China, Thailand, and USA. $\delta^{87}Sr$ was found to be more effective in the discrimination, also coupled to total Sr and Rb concentration, while lead isotope ratios were found to be more influenced by anthropogenic sources of pollution and therefore less useful in the classification.

2.2.9 Organic Food

The possibility of discriminating organic foodstuffs from the equivalent items obtained by means of conventional systems has been frequently discussed in the last two decades. Particular interest has been given to the application of $\delta^{15}N$ values, due to the fact that the isotopic signature of nitrogen is strongly

influenced by the type of fertilizers. Synthetic nitrogen fertilizers, commonly used in conventional agriculture, generate low $\delta^{15}N$ values (from −6‰ to 6‰) in crops while manures and fertilizers permitted in organic agriculture have much higher values (from 1‰ to 37‰). Camin et al. [141] in their recent study involving a large set of fruits grown in Italy, verified that $\delta^{15}N$ is the only isotopic parameter suitable for discrimination of organic fruits from conventional fruits, being less influenced by variables such as cultivar, year, and site of production. However, this isotopic parameter becomes unreliable in cases in which organic production is managed with crop rotation or derived from green manure based on leguminous (N-fixing) plants. Laursen et al. [142] investigated the possibility of distinguishing vegetables grown with organic agriculture from conventionally grown products, using the isotopic signatures of H, C, N, O, Mg, and S to analyzed winter wheat, spring barley, faba bean, and potato. Vegetables were obtained with organic (two different systems, using respectively animal and green manure) and conventional farming systems under similar controlled conditions in two different harvests, 2007 and 2008. Results from SIA analysis showed that none of the isotope ratios measured could allow discrimination of organic versus conventional samples for all the products studied. δD values discriminate organic versus conventional cereals, while $\delta^{15}N$ was useful to identify the use of animal manure in organic wheat, barley, and potato. On the contrary, compound-specific isotope analysis of nitrogen and oxygen isotopes in isolated nitrate allowed a good discrimination of organic and conventional plants [143]. These studies suggest that discrimination with $\delta^{15}N$ is not valid in all instances and nitrogen isotopic analysis should be combined with other analytical approaches (e.g., other stable isotope ratios or secondary metabolic profiling).

Schmidt et al. [105] investigated the isotopic signatures of carbon, nitrogen, and sulfur in samples of Irish beef coming from organic and conventional farming. Conventional beef samples showed slightly less negative and more variable $\delta^{13}C$ values, higher $\delta^{15}N$ and lower $\delta^{34}S$ values, as a result of different diet regimes of cattle. In the case of poultry meat, Rhodes et al. [144] developed a method based on determination of $\delta^{13}C$ to verify whether animals had been corn-fed, a label assigned by EU legislation to chicken fed with a diet containing at least 50% corn for the greater part of the fattening period. $\delta^{13}C$ value in protein resulted to be a reliable marker of the dietary status of the chicken, depending on the difference in the ratio of C3 versus C4 plants assumed.

Chung et al. [145] investigated the isotopic signatures of carbon and nitrogen in organic and conventional milk. Organic milk samples presented on average $\delta^{13}C$ values higher and $\delta^{15}N$ values lower than those of conventional milk samples, as expected considering dairy cow's diet and the use of natural versus synthetic fertilizers, but significant variations were found as a function of the collection date and the milk brand. Much better results were obtained by a combination of $\delta^{13}C$ and $\delta^{15}N$ values which was effective in the discrimination among organic and conventional milk.

2.3 Trace Elements as Chemical Markers

Geochemists used trace and ultratrace elements (called for simplicity *trace elements* further on) since long time ago for their role as markers of rock origin [146]. This is due to several reasons:

- variations of concentration in trace elements are wider than in major and minor elements;
- every system has many more trace elements than major and minor elements, which means a larger set of variables and therefore a potentially higher discrimination power;
- trace elements are collectively sensitive to processes to which major and minor elements are not.

These reasons are still valid when trace elements are used for food classification. In fact, these analytes are considered as suitable variables for geographic classification because they act as territory markers, providing information linked to the geochemical origin of the raw matters with which a food is produced. They can be called *primary geographic indicators*, differently from organic parameters (e.g., volatile compounds, polyphenols, etc.), which can be considered as *secondary geographic indicators* when they reflect technologies typical of regional or national traditions.

Of course, not all elements can play this role: chemical transformation of raw matters and addition of external substances all along the production chain can change the original distribution of some elements. From food to food, adequate elemental markers must be individuated.

Determination of trace elements can be performed with different elemental techniques, such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma–atomic emission spectrometry (ICP-AES), or anodic stripping voltammetry (ASV), but the performance features of the plasma–MS system cannot be matched. ICP-MS is at present the most suitable elemental technique in food forensics. This is due to its features of sensitivity, accuracy and precision, speed of analysis, and ability of determining a large amount of variables in short time. The last feature implies that large set of data can be produced and further on treated with pattern recognition methods for classification studies. Table 2 lists the main analytical features of elemental techniques.

The application of ICP-MS analysis to food forensics is relatively straightforward since at least 25 years. At the beginning of 1990s, the work by McCurdy et al. [147] on wine analysis was one of the first suggesting that trace element distribution could be utilized for traceability studies of foodstuffs. Since then, several publications have deepened this point.

As for isotope ratios determination, in the case of trace elements determination, the difference between authentication and traceability must be taken into account. In order to set up an authentication scheme for a particular food, a number of elements are determined, from major to trace and ultratrace. The

TABLE 2 Analytical Features of Elemental Techniques

	ICP-MS	ICP-AES	Flame AAS	GFAAS
Detection limits	Excellent for most elements	Very good for most elements	Very good for some elements	Excellent for some elements
Sample throughput	All elements/2–6 min/ sample	5–30 elements/ min/sample	15 s/ element/ sample	4 min/ element/ sample
Linear dynamic range	10^5 (10^8 with range extension)	10^5	10^3	10^2
Precision				
Short term	1–3%	0.3–2%	0.1–1%	1–5%
Long term (4 h)	<5%[a]	<5%[a]		
Interferences				
Spectral	Few	Common	Almost none	Few
Chemical (matrix)	Moderate	Almost none	Many	Many
Ionization	Minimal	Minimal	some	Minimal
Mass effects	High on low	NA	NA	NA
Isotopes	Yes	No	No	No
Dissolved solids				
(Maximum tolerable concentration)	0.1–0.4%	2–25%	0.5–3%	>20%
No. of elements	>75	>73	>68	>50
Sample usage	Low	High	Very high	Very low
Semiquantitative analysis	Yes	Yes	No	No
Isotope analysis	Yes	No	No	No
Routine operation	Easy	Easy	Easy	Easy
Method development	Skill required	Skill required	Easy	Skill required
Unattended operation	Yes	Yes	No	Yes

Continued

TABLE 2 Analytical Features of Elemental Techniques—cont'd

	ICP-MS	ICP-AES	Flame AAS	GFAAS
Combustible gases	No	No	Yes	No
Operating cost	High	High	Low	Medium
Capital cost	Very high	High	Low	Medium/ high

ICP-MS, inductively coupled plasma–mass spectrometry; ICP-AES, inductively coupled plasma–atomic emission spectrometry; AAS, atomic absorption spectrometry; GFAAS, graphite furnace atomic absorption spectrometry.
[a]*Precision improves with use of internal standards.*

distribution of elements is determined in groups or *classes* of food samples having particular features, according to differences in geographic provenance, animal/botanical species, processing method, or any other discriminating scheme. Using pattern recognition methods, a comparison is made between the different classes and the possibility of discrimination is evaluated. In this instance, the highest number of variables is obtained, the highest possibilities are of succeeding in discrimination among different classes, i.e., authentic versus nonauthentic. For this reason, all elements are potentially useful, regardless of their concentration, so that some authentication schemes could rely mostly on major and minor elements, some other could rely on trace and ultratrace elements. As a role of thumb, major and minor elements can be more useful when discrimination depends on animal/botanical species or process methods, which can cause larger variations in elemental compositions, while trace and ultratrace elements are more useful when geographic provenance is involved.

Traceability of foodstuffs based on element determination involves a different approach. It is not a matter of comparison between different classes of samples of the same type, but a comparison of different samples inside the same production chain. If in the case of isotopic analysis the feature to look for is the similarity of isotopic fingerprinting (mostly of heavy elements), in the case of elemental analysis the feature to look for is the similarity of elemental *distribution*. This can be done with simple statistic methods. Geochemists are used to evaluate relative data by dividing the concentration of each element by its concentration in a set of normalizing values, such as those found in chondritic meteorites [148,149]. This is particularly useful in order to eliminate the saw tooth pattern caused by the Oddo–Harkins rule, according to which even-numbered nuclides are more stable than odd-numbered nuclides. If the distribution of the elements considered is kept unaltered along the production chain, i.e., if there is no *fractionation*, then the whole chain is traceable.

Of particular interest in traceability of foods are considered the rare earth elements (REE). These elements are popular among geochemists as geological markers, because they can help identifying the origin of rocks. The potential of REE as markers is due to their similar chemical behavior. In biological systems, they do not seem to participate actively to plant metabolism: it is suggested that REE 3+ ions can compete with calcium in some instances but with no discrimination among different REE. Plants tend to assume REE ions from soil with little or no fractionation of the original distribution [150–152]. It has been proposed, therefore, that REE distribution in soil could be reflected on plants [13]. It can be hypothesized that only slight or no variations of the original distribution of REE occur when passing from soil to products, in foods with favorable production chains (see Section 1.1).

In the following paragraphs, examples of applications of ICP-MS analysis to food forensics are cited with concern to different food categories.

2.3.1 Wine, Fermented Drinks, and other Beverages

Authentication studies on wine using trace elements distribution are possibly among the first classification works on foodstuffs. Several works evidenced that elemental patterns can be used to classify wines because these patterns may reveal their geographic provenance [153–156]. Factors such as soil chemistry and regional geology influence the elemental composition of crops and can be exploited positively in the classification. On the contrary, anthropogenic factors such as viticultural practices and processing methods, which can have a strong effect, are more difficult to elucidate.

In 1994, Latorre et al. [157] differentiated the prised *Rias Baixas* Spanish wine from Galicia—Certified Brand of Origin—from its imitations. Pattern recognition analysis, performed on ICP-MS data, revealed that Li and Rb were the most discriminating variables. Similar studies were carried out by Baxter et al. [158] on wines from different regions of Spain and England. Marengo and Aceto [159] analyzed with ICP-MS samples of five different DOC and DOCG wines obtained from Nebbiolo variety: *Barolo*, *Barbaresco*, *Nebbiolo d'Alba*, *Roero*, and *Langhe Nebbiolo*. These wines are different with concern to aging (respectively 3 years, 2 years, 1 year, 6 months, and no aging) and partially to geographic provenance (different areas inside the province of Cuneo, Piedmont). It was possible to discriminate the five brands by means of pattern recognition methods. The variables with the most discriminating power resulted to be Si, Mg, Ti, Mn, and Mo, which could be related to the aging method more than to the geological features of soil, considering that samples come from a narrow area.

Relatively, fewer studies have been carried on the traceability of wines through determination of elements. Taylor et al. [160] studied soils and wines from the Okanagan Valley and the Niagara Peninsula, the Canada's two major wine-producing regions. They found that, among trace elements, strontium was able to differentiate both soils and wines from the two regions. Oddone et al.

[161] analyzed the samples of soil, grapes, must and wine in four enological production chains from Piedmont (Italy): Gavi, Barbera, Brachetto d'Acqui, and Freisa. Particular concern was given to the role of REE. Data obtained by ICP-MS showed that REE distribution was clearly maintained unaltered in the passage from soil to must; from must to wine some fractionation occurred on heavier analytes (Gd-Lu), possibly as a consequence of winemaking processes, while lighter analytes (La-Eu) seem to remain unaltered. Similar results were obtained by Aceto et al. [162] in a study on Moscato d'Asti white wine in which samples were analyzed at every step of the production chain. The fingerprint of REE was kept unaltered in the passage soil–grapes–must, while fractionation occurred in wine after the clarification with bentonites. In addition, analysis of Moscato musts from 102 samples showed that is possible to classify their geographic origin, building a basis for identification of possible addition of foreign musts.

Classification of wines by means of elements distribution has been recently reviewed by Gonzálvez and de la Guardia [163].

2.3.2 Milk and Dairy Products

The classification of milk samples by means of trace elements distribution must take into account two different sources: the metabolism of the animal species producing milk and the geographic location of farms, a factor bound to local geology and hydrology features. Benincasa et al. [164] studied the effect of animal species on milk composition. Milk samples were obtained from cows and water buffaloes fed in an Italian farm with identical forage and water, herded in the same field and managed with similar regimes of veterinary medicinal care. Sixteen elements were determined by ICP-MS. Treatment of data with PCA evidenced that cow and water buffalo milk samples could be clearly discriminated; in particular, Ca, P, Ga, Zn, Mn, Ba, and S were higher in the water buffalo milk samples while K and Rb were higher in cow milk samples. The final purpose was to identify "biomarker" elements that could be used to check fraudulent labeling of milk and associated by-products, e.g., *mozzarella* cheese.

In authentication of dairy products based on trace metals, it can be hypothesized that most of them, with few exceptions (e.g., Cu), are not influenced by milk transformation processes and therefore, they can reflect the geochemical features of soil-cows' milk chain. Pillonel et al. [97] in the already cited classification study on Emmental cheeses, determined trace elements with ICP-MS together with and radioactive elements activity. Interesting elements for discrimination were molybdenum and sodium.

2.3.3 Vegetable Oils

Classification studies on edible oils based on elemental analysis require the superior sensitivity of ICP-MS, since the lipophilic environment of oils keeps the metal content obviously at a minimum. In addition, the high carbon content is a drawback for most spectroscopic techniques and requires to be addressed with particular devices,

such as addition of oxygen to the plasma and low temperature inside the nebulization chamber. Nevertheless, using ICP-MS, several studies have been issued that allowed to classify oil samples coming from different countries. Trace metals in oil can originate from soil, environment, genotype of the plant, fertilizers and/or metal-containing pesticides, manipulation of olives during the manufacturing, or contamination from the metal-processing equipment. If suitable variables (i.e., elements of natural origin only) are selected, the trace elements distribution in oil samples should reflect the geographic provenance. Benincasa et al. [165] developed an ICP-MS method to determine 18 trace elements in organic extra virgin olive oils coming from the Italian regions Apulia, Calabria, Umbria, and Abruzzo. Oil samples were obtained from two different cultivars, *Carolea* and *Coratina*. A model with LDA was built that allowed optimal discrimination of geographic provenances. The most discriminating variables resulted to be Fe, Mg, Sr, Ca, and As. Llorent-Martínez et al. [166] focused their study on the possibility of distinguishing different types of oils produced in Spain. They determined 18 elements by ICP-MS in samples of virgin olive, olive, pomace olive, corn, sunflower, and soybean oils. Application of PCA allowed a good discrimination among the different categories, in particular olive oils from other lesser quality oils. Cr, Cu, Fe, and Mn resulted to be the most discriminating variables, with Cr and Fe mostly abundant in vegetable oils while Cu and Mn were higher in olive oils. In the already cited study by Camin et al. [98] in which authors analyzed several samples of European olive oils obtaining both isotopic and elemental data, the contribution of trace elements variables in the geographic classification was a relevant one. First at all, authors classified samples on a geological basis, i.e., dividing the whole samples set into three groups according to soil type: shale/clay, limestone, or acid magmatic. Analysis of variance (ANOVA) procedure highlighted statistically significant differences in the content of 16 elements (Mg, Al, K, Ca, V, Mn, Ni, Zn, Rb, Sr, Ce, Sm, Cs, La, Eu, U) among the olive oils produced in the three different geological zones; this classification was confirmed by means of CDA. Similar results were obtained by combining elemental and isotopic data in order to perform geographic classification.

2.3.4 Meats

Trace elements in meat and meat products may derive from different sources. The occurrence of minerals in soils is obviously a primary source, with particular concern to livestock herded on pasture lands; other relevant sources are feed supplements and environmental pollution. Franke et al. [104] reviewed the information concerning the sources of trace elements in meat. They concluded that selenium and rubidium could be interesting geochemical markers. According to some studies these elements, more than to mineral supplementation, i.e., feeding practices, could be related to geographic origin, reflecting the differences of these elements in soils [167]. Other studies [168], instead, suggest a more relevant role to feeding supplements. Pollution from industry, mining or occasional events such as disasters (i.e., Chernobyl) can contribute to soil composition and ultimately to meat. In some cases, it is possible to use

polluting elements as markers of geographic origin of meat. A study on tissues of livestock grazing nearby Kidston Gold Mine (North Queensland, Australia) showed that liver, muscle, and blood of animals were enriched in As and Zn [169]. In contrast, Chessa et al. [170] did not find statistically significant differences in Pb, Zn, and Cd between muscle tissues of sheep from a polluted area in Southwest Sardinia and sheep herded on unpolluted areas.

The already cited study by Heaton et al. [109] used trace element distribution in addition to isotopic data to classify beef samples from different countries. The most important elements in the classification were strontium, iron, rubidium, and selenium. The classification into three broad groups, i.e., European, South American, and Australasian was obtained with CDA.

2.3.5 Fish

In the classification of fish, several factors can influence the elemental distribution: metabolism of organisms, geomorphology, lithology, food availability, contamination from external sources, etc. An example of high-quality fish is the Galician mussel (*Mytilus galloprovincialis*), the first fish acknowledged by European PDO. Costas-Rodriguez et al. [171] established the geographical origin of mussels from different areas of Galician Rías (Vigo, Pontevedra, Arousa, Muros-Noia, Ares-Betanzos). For this, the distribution of 40 elements was determined by ICP-MS in 158 samples of Galician origin and in samples from two Mediterranean regions representative as non-Galician samples. Different supervised pattern recognition techniques (LDA, SIMCA, and ANN) were used that allowed to classify correctly PDO Galician mussels versus non-Galician samples and Galician mussels according to the ría of origin. Cubadda et al. [172] developed an ICP-MS method for the determination of trace elements distribution in marine organisms. The aim of the study was, apart from identifying pollution hot spots, verifying whether it was possible to have an elemental fingerprinting of seafood destined to the fishing market. In the case of mussels, results evidenced that a good separation was achieved between samples collected in three different farming sites. A recent study by Guo et al. [173] evidenced that the trace element distribution in fish muscles can be used as a fingerprint to discriminate among fishes captured in different sea regions. The geographic variability, in fact, was larger than the species variability. Element data were treated with partial least squares discriminant analysis (PLS-DA) and probabilistic neural network (PNN) supervised pattern recognition methods.

Classification of fish by means of elements distribution has been recently reviewed by Lavilla et al. [29].

2.3.6 Fruits and Vegetables

The soil elemental composition can serve as a fingerprint for different crops, providing a useful marker for geographical classification. Fruits and vegetables, which are the foodstuffs more directly linked to soil, reflect well this utility.

Several studies have already shown that the trace element distribution is a powerful marker for classification of fruit and vegetable foodstuffs. The elemental fingerprint given by soil can be affected by various factors such as botanic varieties, fertilization, climatic conditions, and agricultural practices, but several studies [174,175] suggest that the variations of element composition induced by these factors are smaller than the differences between production places when proper elemental markers are selected. As a consequence, in every classification study the proper variables must be selected.

In the category of fruits and vegetables, spices rank among the first places in terms of cost. It has already been cited the fact that saffron from *C. sativus* is perhaps the most expensive food in the world and therefore the ideal candidate for a classification study. D'Archivio et al. [176] analyzed saffron samples coming from three Italian regions, Abruzzo (one among the most important regions in the world producing saffron), Umbria, and Sardinia. Analysis with ICP-MS and LDA allowed discriminating the three geographical provenances; the most significant variables were Li, B, Na, Ga, Rb, Sr, Zr, Nb, Cs, Ba, Sm, and Hf with particular concern to B, Na, Sr, and Rb. These elements can be considered mostly of geochemical origin and therefore characteristic of soil, so that their distribution is not fractionated in the passage from soil to plant. In the already cited study by Brunner et al. [121] on *Szegedi* Hungarian paprika, authors distinguished authentic samples labeled with PDO from foreign paprika products on the basis of both isotopic signature of strontium and trace elements distribution, with main concern to REE.

Bettinelli et al. [177] investigated the link among soil and the different parts of tomato plant for what concerns the distribution of REE. Bontempo et al. [63], in the already cited study on tomato and its derivatives, highlighted the importance of trace elements and in particular of REE in tracing the geographic provenance of these products. Tomato samples from three Italian regions could be discriminated and several trace elements, namely Gd, La, Tl, Eu, Cs, Ni, Cr, and Co, were found to be highly relevant in the classification. Lo Feudo et al. [178] analyzed with ICP-MS tomato samples cultivated in four Italian regions (Apulia, Calabria, Basilicata, and Emilia-Romagna) along two growing seasons; also, a tomato paste sample made in Italy was compared with similar products coming from California, China, and Greece. In both instances, a good discrimination result was obtained on a geographical base, using 32 trace elements as variables and classification with supervised pattern recognition methods (LDA, KNN, and SIMCA).

Classification of hazelnuts from Piedmont was achieved with ICP-MS by Oddone et al. [179] with ICP-MS, using REE as chemical tracers. Authors demonstrated that no fractionation occurred to the original distribution of REE in the passage from soil to fruits (Figure 5), and it was possible to evaluate the differences among hazelnuts from Piedmont, other Italian regions, and Turkey.

Several classification studies on fruits and vegetables based on trace elements determination have been recently issued by a research group working at

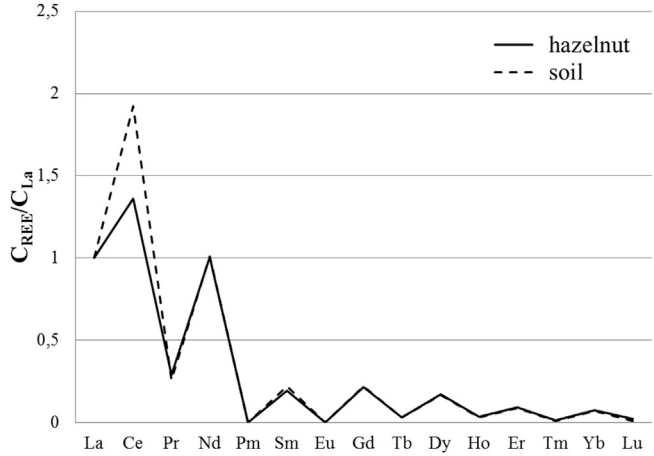


FIGURE 5 Distribution of rare earth elements (REEs) in soil and hazelnuts.

Dipartimento di Chimica, Università della Calabria (Southern Italy). They studied the distribution of trace elements in Clementine (*Citrus clementina* Hort. ex Tan.) mandarins, one of the most important cultivated varieties in the Mediterranean basin [180]. This variety is cultivated in many countries on different continents, but a world renowned production is the one located in Calabria (Southern Italy), awarded with protected geographical indications (PGI) certification by the European Union as "Clementine di Calabria." Authors were able to discriminate PGI samples of four different Calabrian zones, from non-PGI samples coming from Spain, Tunisia, and Algeria, using supervised pattern recognition methods, such as SIMCA, PLS-DA, and LDA. In another study, they classified samples of Tropea red onion (*Allium cepa* L. var. Tropea), one among the most highly appreciated Italian products, awarded with PGI certification as "Cipolla Rossa di Tropea Calabria," from non-PGI onion samples, i.e., samples coming from cultivation areas located outside the distribution area specified in the production regulations [181]. Authors evidenced the importance of the contribution of REE in the classification.

Tea and coffee are both foodstuffs of vegetable origin with a relevant commercial value. The classification of tea and coffee samples has been attempted by means of trace elements distribution using ICP-MS (in some cases also using ICP-AES). Moreda-Piñeiro et al. [182] were able to discriminate tea samples from Asian and African countries on the basis of element distribution as determined with ICP-AES and ICP-MS. Data treated with supervised pattern recognition techniques (LDA and SIMCA) allowed to distinguish also among teas from China, India, and Sri Lanka. More recently, Pilgrim et al. in the already cited study [127] combined data from ICP-MS and SIA to classify tea samples from different Asian and African countries. Twenty trace elements, among which four REE, were used for application of LDA method.

2.3.7 Animal Products

A very particular animal product is caviar, i.e., roe descending from certain fish species. Caviar is an extremely exclusive and greatly demanded delicacy and therefore one of the most expensive—and most counterfeit—foodstuffs in the world. The most prised caviar is recognized to be that produced from sturgeons of the Caspian Sea, the renowned *caviar Volga*. Perhaps due to the high incomes involved, few analytical studies have been devoted to the classification of caviar; Ebert and Islam [183] used a histological method to identify caviar imitations of Russian sturgeon roe. Rodushkin et al. [184] used the elemental distributions determined by ICP-MS to classify vendace and whitefish caviar samples according to the geographic origin (Sweden, Finland, and USA) and to the type of water in which fish grow (brackish vs freshwater, with brackish caviar being more expensive). Seventy-two elements, from μg/g to pg/g concentrations, were determined. The element distribution in caviar is influenced by its main constituents, i.e., roe and salt, but impurities originating from the caviar preparation and packaging processes can also contribute. Furthermore, contamination during the various analytical stages is possible. To check for this possibility, authors analyzed also samples of unprocessed vendace roe and salt used in caviar production. Elements potentially allowing to establish the sample provenance were As, Ba, Br, I, Li, Mo, Se and Sr while Fe, Al, Ti, and V, even though useful in the discrimination, were reputed to arise during processing and packaging. Particularly useful were element ratios, i.e., Sr/Mg, Sr/Ca, and Sr/Ba that achieved a good discrimination of geographical provenance. In fact, Sr/Ca ratio in otoliths reflects their relative proportion in the ambient water, as showed Bath et al. [185]. Differentiation between caviar from brackish and freshwater sources was accomplished using Sr isotope ratio measurements.

The classification of honey based on geographical or botanical origin has been studied using trace elements distribution in several studies. Minerals could be useful for a classification system, since they can be associated with the soil where Melliferous flora grows. In the passage from soil to honey, however, different sources can contribute to the final elemental composition. Environmental pollution can cause increase of heavy and transition metals concentration. The use of particular fertilizers, rich in REE, in crops can result in anomalous values of these elements' amounts [186]. Chudzinska and Baralkiewicz [187] analyzed with ICP-MS samples of honey of three types (honeydew, buckwheat, and rape) produced in 16 areas of Poland. Data obtained from determination of 15 elements were treated with supervised pattern recognition methods and allowed a good classification according to the regional provenance and to the honey type. Al, Mg, and Zn were the best markers of geographical origin while K and Mn were the markers of honey type. Similar results were obtained by Batista et al. [186] in a study on Brazilian honey samples. In that case Pb, Tl, Pt, Ho, and Er were the most significant variables in the geographical classification. Chen et al. [188] determined 12 elements in 163 Chinese honey samples in order to classify samples according to the botanical origin obtaining a good discrimination between samples of linden, vitex, rape, and acacia honeys.

2.3.8 Products from Cereals

Raw cereals, as fruits and vegetables, are ideal subjects for classification studies using trace elements distribution. Ariyama et al. [140] determined trace elements in rice samples from Japan, China, Thailand, and USA together with isotope ratios of heavy elements. A good classification was obtained, where the most discriminating variables were Rb, Sr, Ba, and Co. Shen et al. [189] studied the correlation between the distributions of trace elements in rice and soil, based on determination of the available fraction of metals. Samples were from four provinces of China. Analysis by means of ICP-MS revealed that most of the elements determined (Mg, K, Ca, Na, Be, Mn, Ni, Cu, and Cd) were significantly different in both soil and rice samples of the four regions. These results were confirmed by LDA chemometric analysis.

Zhao et al. [190] investigated the classification of wheat samples collected from four major wheat-producing regions in China in two subsequent harvests, on the basis of trace elements distribution. Application of LDA to elemental data allowed a good geographical classification.

2.3.9 Organic Food

Laursen et al. [191] investigated the possibility of distinguishing organic and conventional productions of selected vegetables by means of element distribution as determined with ICP-OES and ICP-MS. Wheat, barley, faba bean, and potato were the products studied, cultivated in 2 years at three different locations using both organic and conventional cropping systems. The study was carried out under controlled and comparable conditions for what concerns soil type and climate, so that differences could be due only to the cropping system. Using trace elements as variables, a good discrimination was obtained among organic and conventional products; Cd and Cl were the elements giving higher contribution to the classification, possibly due to trace impurities from inorganic fertilizers used in conventional cropping system. Kelly and Bateman [192] used $\delta^{15}N$ values and trace elements distributions to distinguish between organic and conventional grown tomato and lettuce samples; results were better for tomatoes and poor for lettuces. Systematic differences were found in the concentrations of certain elements, such as manganese, calcium, copper, and zinc, possibly due to the presence of elevated levels of arbuscular mycorrhizal fungi in soils run with organic systems.

2.4 Molecular Ions as Chemical Markers

2.4.1 Strategies of Molecular Analysis

The previous two paragraphs accounted for techniques relying on *elemental* parameters. A classical use of mass spectrometry, however, is the separation and identification of *molecules*. This can be done either using *hyphenated systems*, i.e., interfacing a mass spectrometer with a separative system, or with

stand-alone or *MS-only systems*. Hyphenated systems will be the subject of the following paragraph, while stand-alone systems will be dealt within Section 2.4.3. Both systems are now more than consolidated techniques to identify molecular markers to be used in food classification. General discussions on the application of hyphenated and stand-alone systems in food forensics have been recently issued by Herrero et al. [193] and by Wang et al. [194].

An improvement in the diagnostic power of molecular analysis with MS systems applied to food forensics is the development of advanced *fingerprinting* and *profiling* methods. The concepts of fingerprinting and profiling are not specifically referred to MS since they encompass all the analytical methods that can provide multiple responses from samples; in this sense, techniques such as NMR, vibrational spectroscopies (FT-IR and Raman), electronic spectroscopies (UV–Visible–NIR spectrophotometry) are included together with MS techniques. While traditional methods are focused on identification and quantification of specific compounds in a particular food sample, which is the approach typical of *targeted* strategies, fingerprinting and profiling methods (i.e., *nontargeted* strategies) provide specific information about groups of samples based on their component distribution without need of accurate identification of all molecules. The difference between fingerprinting and profiling is that the latter requires previous knowledge of the samples because it focuses on a specific group of related compounds. Fingerprint/profiling methods call for highly reliable and powerful detection systems such as MS. Moreover, the amount of information given by mass spectral data sets asks for a mandatory chemometric treatment of data with pattern recognition methods [195]. Food forensics studies using fingerprinting/profiling methods based on hyphenated systems are strongly greatly increasing in the last years. The application of these methods has been extensively reviewed by Esslinger et al. [196].

A further improvement occurring in the very last years in the knowledge and potentiality of food forensics resulting from the development of *foodomics*. The new frontier of the application of mass spectrometry to food analysis has an English name but a Spanish father, Alejandro Cifuentes [197]. This discipline results from a powerful interaction among food and nutrition science, advanced analytical techniques (i.e., biomolecular and bioinformatics), with particular emphasis in chemometrics (Figure 6, based on Herrero et al. [193]). Further in-depth analyses on this subject can be found in recent publications [198,199]. Even if the concept of foodomics goes beyond the field of food forensics, one of its main features is the analytical study of foods for compound profiling with the aim of identifying biomarkers useful for food classification. It is clear that mass spectrometry is definitely the core technology for such a task: the depth of information achieved by MS techniques cannot be reached by other techniques. In addition, interfacing of MS with protein and peptide databases has allowed new possibilities of the characterization of biomolecules.

The definition of foodomics encompasses, among others, three main analytical sectors, which have been developed in the last 20 years and have found large

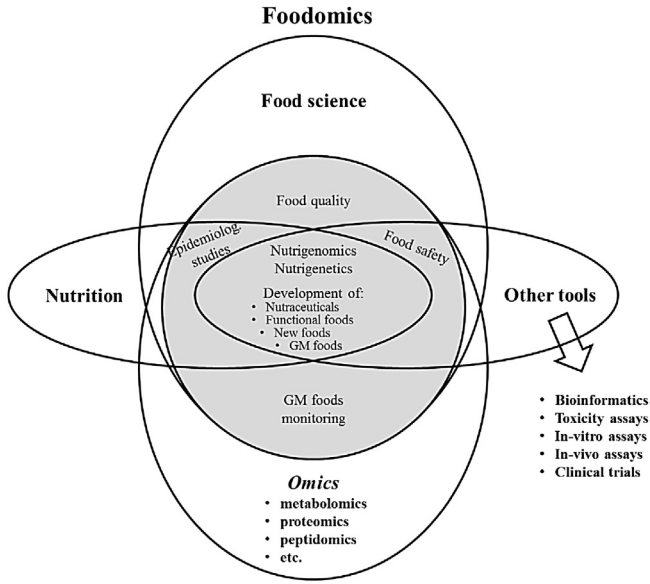


FIGURE 6 The concept of *foodomics*.

application, among several other fields, in food forensics: *proteomics*, *peptidomics*, and *metabolomics*. Proteomics is the analytical field devoted to the characterization of the proteins expressed in a particular biological system; from the analytical point of view, a major problem is due to the different physicochemical properties of proteins and their large concentration range in real samples. Peptidomics is the analysis of all peptide content within an organism, tissue, or cell, including transient products of protein degradation; in this case, also difficulties arise from the concentration range and the high number of peptidic sequences available in real samples. The applications of proteomics and peptidomics in food forensics have been recently reviewed [200,201]. Metabolomics is focused on the analysis of a metabolome, i.e., the full set of endogenous or exogenous low molecular weight compounds (<1500 Da), which means a large number of different molecules with different chemical and physical properties in a wide concentration range [202]. The term *metabolomics* has been established in the late 1990s. Oliver et al. used the expression *metabolome* for the first time in 1998 [203]. Recalling the concepts of *fingerprinting* and *profiling* expressed before, there are three different ways for analyzing metabolites in a biological system: namely, *target analysis*, *metabolic profiling*, and *metabolic fingerprinting*. Target analysis is the quantitative determination of selected, well-individuated analytes. Metabolic profiling is a nontargeted strategy requiring previous knowledge of the sample, which focuses on the study of a group of related metabolites (e.g., amino acids, alcohols, etc.) or metabolites from a specific metabolic pathway. Metabolic fingerprinting is focused on comparing patterns or *fingerprints* of metabolites among different samples, aiming not to identify

all the involved metabolites but to detect those that can be considered biomarkers. The differences among these approaches have been clarified by Fiehn [204] and reviewed by Dettmer et al. [205]. Due to the great potentialities of metabolomics-based approaches, it is not surprising that several reviews on their applications in the field of food science and nutrition had been recently issued [206–209], with a large number of citations to works of interest in the field of food forensics. Oms-Oliu et al. [210] reviewed the use of metabolomics for classification of plant-derived food. A major part of the cited studies describes the application of MS techniques either in hyphenated or in stand-alone systems. Cubero-Leon et al. [211], in their review work on food classification with metabolomics, showed that the percentage of studies involving mass spectrometry was nearly 50% in the last 10 years, with NMR and vibrational spectroscopy accounting for most of the remaining part.

2.4.2 Hyphenated Systems

In the field of food forensics, a large number of applications have been developed using MS as a powerful detection system coupled with separative techniques. The composition of most foodstuffs results from a complex mixture of dozens or even hundreds of compounds. The application of separative techniques (chromatographic and/or electrophoretic) hyphenated to detection system giving full structural information makes it possible to elucidate the chemical nature of foodstuffs and to develop reliable classification schemes. The hyphenated systems GC-MS and LC-MS have, therefore, a long tradition in the field of food forensics. Interfacing of MS with gas chromatographic systems is historically older and more consolidated, even though limited to the separation of volatile or volatilizable compounds. Nowadays the development of atmospheric pressure ionization (API) sources, such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), which have solved the issues of pressure difference between a liquid phase at high-pressure and low-pressure vacuum regions, has favored the spread of LC-MS-based methods. Applications have been recently reviewed [212–214]. Relatively more recent is the interfacing of MS with electrophoretic systems [215,216] with particular concern to capillary electrophoresis (CE). CE-MS systems have been applied mainly for identification of organic compounds that can play as biological markers in food classification.

2.4.3 Stand-Alone Systems

Besides hyphenated systems, only stand-alone or MS methods have been developed. A list, not necessarily extensive, of the most important stand-alone MS techniques nowadays available must include Pyrolysis (Py-MS), direct infusion of samples by means of ESI-MS or atmospheric pressure photoionization mass spectrometry (APPI-MS), matrix-assisted laser desorption/ionisation–time of flight mass spectrometry (MALDI-ToF-MS), proton transfer reaction–time of flight (PTR-ToF-MS), desorption electrospray ionization (DESI-MS), direct analysis in real time (DART-MS), and secondary electrospray ionization (SESI-MS).

Stand-alone techniques allowed the building of *molecular profiling* procedures and yielded new insight in the identification of molecular markers in food matrices that can be exploited for classification purposes, without need of prior separation. Sample profiling, therefore, can be achieved with similar performances compared to hyphenated systems but in a faster and easier way. These methods have a high potential in food forensics, in particular when coupled with chemometric data treatment. In fact, the spectra obtained can be considered as quantitative fingerprints of the organic components of food samples and, even if simple visual inspection of the spectra usually does not allow identifying prominent peaks that could be used for classification, the use of multivariate pattern recognition methods can yield optimal results. In addition, stand-alone MS methods can request minimal time consumption and low costs (a few minutes are necessary for sample preparation and mass spectrum acquisition) in contrast with traditional methods of molecular biology. The construction of molecular profile databases can integrate methods and provide high-tech tools in large-scale screening for control and authentication of foodstuffs.

A particular system, specifically devoted to the profiling of volatile compounds, is the headspace mass spectrometer (HS-MS). It is a variant of the so-called electronic nose or *e-nose* systems [21,217] in which a mass spectrometer is used as a chemical sensor in order to yield a fingerprint pattern of volatile compounds, which coupled with pattern recognition methods, allows classification of samples according to variety and to other technological features. With respect to classical e-nose systems, based on solid state sensors, the advantage of MS-based e-nose systems lies in the signal reproducibility, higher specificity, and interpretation of the results. In fact, it is possible to obtain information about complex mixtures of volatile compounds even if it is not possible to identify and/or quantify each chemical species. The synergic use of HS-MS with multivariate statistical techniques allows the relevant information for classification and discrimination of the investigated samples to be extracted. Śliwińska et al. [218] have reviewed the applications of artificial senses, including e-noses, in food analysis and classification.

In the following sections, the application of hyphenated and stand-alone MS techniques to food forensics is illustrated according to the different food categories. In each section, examples involving hyphenated systems are described firstly and then come examples involving stand-alone MS systems. As the application of classical targeted methods using hyphenated systems is relatively straightforward in food forensics, particular focus will be given to fingerprinting/profiling applications and to methods involving stand-alone MS.

2.4.4 Wine, Fermented Drinks, and Other Beverages

The application of hyphenated systems to wine analysis and classification has a long tradition. Profiling of volatile compounds, polyphenols, and other chemical classes have been used for the classification of wine samples according to geographical origin, grape variety, and aging. Marengo et al. [219] analyzed

with solid phase microextraction (SPME)-GC-MS samples of five different DOC and DOCG wines obtained in Piedmont from Nebbiolo variety: *Barolo*, *Barbaresco*, *Nebbiolo d'Alba*, *Roero*, and *Langhe Nebbiolo*. These wines have different aging periods (respectively 3 years, 2 years, 1 year, 6 months, and no aging). This feature is remarkably reflected in the respective values: *Barolo* and *Barbaresco*, in fact, are among the most prised wines in the world. Using a target approach, it was possible to discriminate the five brands by means of pattern recognition methods (PCA, HCA, Kohonen self-organizing map, stepwise LDA, and SIMCA) according to the aging characteristics. Vaclavik et al. [220] used HPLC coupled to ToF-MS to differentiate red wines of three varieties (Cabernet Sauvignon, Merlot, and Pinot Noir) of various geographical origins (European and the US retail market). A nontargeted metabolomic approach was applied to data: the molecular identification of the compounds separated was not necessary, while ions with identical elution profiles and related m/z values were extracted as molecular features. Data were treated by means of multivariate statistical analysis and yielded a good classification according to varieties. A higher level of confidence for the identification process was achieved by using tandem mass spectrometry. Jaitz et al. [221] developed a rapid LC-MS/MS method for phenols and polyphenols profiling, including three isomeric pairs, in wine samples from 11 Austrian regions, including 6 grape varieties and 5 vintages. A good classification was achieved according to geographical, variety, and vintage features using CDA. Serrano et al. [222] developed an LC method with UV-Vis and fluorescence detection for the differentiation of Spanish PDO wines based on their chromatographic profiles; the most discriminating compounds were then identified by means of MS.

With concern to beer classification, Mattarucchi et al. [223] used a fingerprinting approach with LC-MS to authenticate Trappist beer samples of different brands. In this case, a total of 232 beers were fingerprinted and classified through multivariate data analysis. The selected beer samples were clearly distinguished from beers of different brands; only three samples were wrongly classified when compared with other types of beer of the same Trappist brewery.

In recent years, stand-alone MS techniques have been intensively applied to wine. Fingerprinting with protein or peptides profiles have been proposed. Among the first applications of MALDI-ToF-MS to wine protein characterization, it must be cited in the work by Szilágyi et al. [224], which dates back to 1996. The paper suggested the feasibility of MALDI as an alternative to IRMS or Py-MS for distinction of wines and musts. Chambery et al. [225] applied MALDI-ToF-MS in the analysis of peptide profiles obtained from whole wine protein tryptic digests to the classification of high-quality white wines produced in Campania (Southern Italy). MALDI spectra provided fingerprints of samples that attained their discrimination according to different grape varieties or different winemakers. The qualitative presence or absence of peptide m/z values were used as variables for both types of classification. However, Nunes-Miranda et al. [226] reviewed the methods of protein and peptide profiling, highlighting

some critical points in the possibility of wine authentication. Fulcrand et al. [227] proposed a method involving direct MS with ESI-ToF and MALDI-ToF-MS to determine the profile of polyphenolic compounds and use it as a tool for wines discrimination.

An interesting application of MS in wine analysis is the use of MS-based e-nose systems for profiling/fingerprinting of volatile compounds. In the case of alcoholic drinks, e-nose can be useful in the classification of products according to the varieties or enological features (i.e., aged vs young wines) [21]. With respect to classical e-nose systems based on solid state sensors, MS-based e-nose systems have the advantage of withstanding the high concentrations of ethanol that often interfere with solid state sensors. An example of application to wine classification was issued by Cynkar et al. [228], which used an MS-based e-nose system combined with chemometrics to ascertain the geographical origin of Tempranillo wines produced in Australia and Spain. Capone et al. [229] used solid phase extraction (SPE) to extract volatile compounds from different typical wines from Apulia (Southern Italy). The analysis of the extracts by GC-MS in conjugation with e-nose identified 18 compounds over odor threshold, which were used for further pattern recognition analysis with PCA. By means of PLS-DA analysis, data from e-nose and GC-MS analysis were correlated, establishing the relationships between e-nose response and wine aroma compounds. Vera et al. [230] used MS-based e-nose to discriminate between beer samples produced in different factories. Jelen et al. [231] analyzed raw spirits made from rye, potato, and corn in order to verify the possibility of a classification based on the botanical origin. They used an SPME-MS method in which volatile compounds profiles were determined; PCA and LDA pattern recognition methods allowed a good separation between the three botanical sources. A detailed review on the application of e-noses for the analysis of alcoholic beverages has been published [232].

Other stand-alone MS systems were used on alcoholic drinks. With concern to beers, Cajka et al. [233] developed a method based on direct interfacing of SPME to DART-ToF-MS for classification of beer samples from Belgium, the Netherlands, and Czech Republic. This system, together with a more classical SPME-GC-MS system, allowed the characterization of the profile of volatile compounds, which reflect the chemical features typical of different brewing processes. Šedo et al. [234] showed how the application of MALDI-ToF-MS could be used in the classification of beers, allowing to distinguish samples of the same brand but from different breweries. The protein profiles resulted to be highly discriminating, having a strong relation to the brewing materials, technology processes, and sensory characteristics of beer samples. Protein composition of beer depends on the raw materials and the enzymatic reactions that take place in the course of the beer production process.

Among spirits, a major interest has been devoted to characterization and classification of whisky, according to its commercial and traditional value. Aylott et al. [235] applied Py-MS followed by multivariate analysis of the resulting mass spectra to distinguish authentic samples from nonauthentic, in addition

to higher-alcohol congener analysis by GC-MS; Py-MS proved to be reliable as a stand-alone method for whisky classification. An improvement of stand-alone MS methods was later proposed by Møller et al. [236] who used direct infusion of samples with ESI-MS to classify whisky samples from different countries. Authors verified that analysis in negative ion mode yielded the most characteristic whisky fingerprinting mass spectra. Three groups were clearly discriminated: Scotch whiskies, American whiskies, and presumably counterfeit whiskies commercialized in Brazil. Discrimination among single malt and blended Scotch whiskies was also achieved. The proposed method resulted to be a simple and rapid way to check quality and proof of authenticity of whisky samples, with further improvement by means of data treatment with pattern recognition chemometric methods. In addition, application of ESI-MS/MS analysis allowed identifying the most diagnostic anions, which resulted to be simple sugars, disaccharides (indicating the possible use of caramel to adjust color and flavor) and phenolic compounds. Garcia et al. [237], using ESI coupled to ultra-high resolution and accuracy Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), extended the range of diagnostic molecules and further improved the possibility of identifying counterfeit samples. In this case, both positive and negative ion modes yielded useful information.

The Aceto Balsamico Tradizionale di Modena, a high-quality vinegar produced in Emilia-Romagna (Central Italy), is a typical case in which the composition of a foodstuff is so complex that it is hard to find chemical markers for its classification. Its characteristic flavor is the effect of different variables. In such cases, molecular fingerprinting is the best approach for classification. Cocchi et al. [238] used HS-MS, the already cited *e-nose* system, to distinguish correctly aged (and therefore marketable) Aceto Balsamico Tradizionale di Modena products from the ones, which are still undergoing maturation. Classification with supervised pattern recognition methods (SIMCA, LDA) was successful and allowed recognizing the different stages of maturation.

2.4.5 Milk and Dairy Products

Protein profiling is particularly useful in the classification of milk and dairy products. Factors such as genetic and nongenetic polymorphisms and milk processing (i.e., thermal denaturation and proteolysis) can induce variations in the structure of individual proteins, so that milk samples from different species or from different animal breeds of the same species, or resulting from different processes, can be distinguished. Nicolaou et al. [239] analyzed with MALDI-ToF-MS binary and tertiary mixtures of cow's, goat's, and sheep's milks; using supervised pattern recognition methods (linear PLS and nonlinear Kernel PLS) on the protein and peptidic profiles of the samples, they were able to identify the addition of an adulterant milk regardless of milk processing. Yang et al. [240] used two-dimensional gel electrophoresis (2-DE) coupled with MS to acquire protein profiles of milk samples from different animals (cow, goat, camel, yak, and buffalo). The different protein spots acted as specific molecular markers for

identification of milk samples, with particular concern to adulteration; in fact, the animal species could be singled out even in binary mixtures. Cunsolo et al. [241] used MALDI-ToF-MS to identify the fraudulent addition of bovine and caprine milk in raw donkey's milk, a product considered as precious pharma-food thanks to its use in anallergic diets. Extraneous milks were detected by using the protein profiles of some whey proteins as molecular markers. Cunsolo et al. [242] reviewed the applications of MS-based techniques for characterization of milk protein profiles and their use in milk classification.

2.4.6 Vegetable Oils

Given the complexity of the composition of vegetable oils and the high-quality and commercial value of extra virgin olive oils, hyphenated and stand-alone MS techniques can have great potential in their classification. Di Donna et al. [243] developed a method for classification of Italian olives based on the polyphenolic profile as determined with HPLC-MS. Salter et al. [244] used pyrolysis-MS to classify extra virgin olive oils from different regions of Italy and obtained from different olive cultivars. The molecular fingerprints of samples were analyzed with artificial neural network pattern recognition method and allowed a good discrimination of olive oils on the basis of their geographical origin. Vaclavik et al. [245] used high-resolution ToF-MS coupled with DART to determine the comprehensive profiling of triacylglycerols in oils products. Authors were able to discriminate between extra virgin olive oil, olive pomace oil, and olive oil; also, adulteration of extra virgin olive oil with hazelnut oil was achieved.

With concern to e-nose MS-based systems, Oliveros et al. [246] used HS-MS for classification of olive oils of different geographical origin with a fast method of analysis. Samples were from five different Mediterranean areas. Both unsupervised and supervised pattern recognition methods, applied to the profiles of volatile compounds, yielded good results in the classification. Similar results were obtained by Cosio et al. [247] using an e-nose system in combination with artificial neural networks.

2.4.7 Meats

The classification of meat and meat products can be achieved by means of different strategies. Profiling of volatile compounds and lipids is one typical approach. Narvaez-Rivas et al. [248] determined with GC-MS the profile of volatile compounds in samples of Iberian dry-cured hams. Classification according to different pork fattening systems was achieved.

Zaima et al. [249] used a metabolomic approach with MALDI-imaging mass spectrometry in the assessment of beef authenticity. The analysis was carried out on extracted lipids and in few minutes enabled the visualization of the distribution of individual biomolecules. Peaks in the mass range 700–1500 m/z were used for a pattern recognition treatment with PCA; the results allowed obtaining a good discrimination among beef samples from three different areas of Japan.

Among cured meat products, it is highly renowned the quality of Iberian and Italian dry-cured hams. Del Pulgar et al. [250] used the recently developed proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS) technique for the characterization of dry-cured hams produced in Italy (Prosciutto di San Daniele, Prosciutto di Parma and Prosciutto Toscano) and Spain (Dehesa de Extremadura) according to PDOs. Samples were analyzed by direct injection without any pretreatment. Analysis by means of PTR-ToF-MS yielded information concerning the volatile organic profile, which reflects the different manufacturing practices (i.e., rearing system of livestock, salting, and curing process, etc.); data from molecular profiling were treated with PCA that allowed a good classification according to the production processes of the different PDOs. González-Dominguez et al. [251] studied the classification of different types of Iberian ham with other stand-alone MS techniques. Authors analyzed intramuscular fat extracts using two techniques, direct infusion electrospray mass spectrometry (ESI(+)-MS) and flow injection atmospheric pressure photoionization ionization mass spectrometry (APPI(+)-MS). Total lipid profiles (triacylglycerides, diacylglycerides, monoacylglycerides, and free fatty acids) were obtained with simple sample preparation. Data were treated with PLS-DA method that allowed classifying Iberian ham samples according to their feeding systems (traditional feeding based on natural resources vs feeding based on commercial foodstuffs) and provenance.

From a completely different point of view, molecular analysis by means of MS techniques can be used to check for *absence* of meat in particular foodstuffs. *Kosher* is the term for food that may be consumed by Jews according to *halakha* (Jewish law); in a similar way, *halal* stands for food considered permissible to Muslims according to Islamic law. Compliance of food to *kosherness* and *halalness* is very important for Jew and Muslim people and its control is therefore a relevant commercial matter considering the extension of the global Halal food market. Indrasti et al. [252] characterized with two-dimensional comprehensive GC-ToF-MS the fatty acid profile in samples containing animal fat, in order to discriminate among cattle fat, chicken fat, goat fat, and the prohibited lard. Rohman and Man [253] reviewed the analytical methods used in the detection and quantification of pig derivatives in food products to verify compliance to *kosherness* and *halalness* of food destined for consumption by Jew and Muslim people. Among the different methods listed, applications were reported using LC-MS and GC-MS.

2.4.8 Fish

Fish authentication demands for more innovative methodologies since the identification of morphological characteristics, such as the head, fins, skin, or bones, can be lost during processing so that the original fish species cannot be recognized. In addition, globalization and freer markets determined the fact that a growing number of species are used for transformed products. Sophisticated MS techniques using *molecular profiling* can address these needs. Recently, it has been proposed the use of MALDI-ToF-MS for the unequivocal identification of seafood species [254]. This method is based on the evaluation of the mass signals generated from proteins

with molecular weights of about 11 kDa, which can play as specific biomarkers for species discrimination. The applicability of the method was checked by analyzing protein extracts from 25 different seafood species, selected among largely consumed products either of high commercial value or commonly involved in frauds. Authors underlined the fact that this method does not require either preliminary information on the investigated sample or preliminary identification of the proteins generating biomarkers. It was nevertheless evidenced the role of parvalbumins, calcium-binding proteins with molecular weights in the 10,000–12,000 Da range, as progenitors of several of the biomarkers individuated. With concern to processed seafood products, Barik et al. [255] developed a proteomic method for identification of the species of origin based on detection of species-specific sarcoplasmic peptides. The technique used was a combination of 2-DE gel electrophoresis and MALDI-ToF-MS; in addition, LC-MS analysis was performed on the protein spots cut from gel.

2.4.9 Fruits and Vegetables

The classification of fruit and vegetable products can be favored in cases in which foodstuffs are characterized by a wide aromatic or polyphenolic profile. Examples are the characterization of tomato, hazelnuts, coffee, and other items with a marked flavor. Lo Feudo et al. [256] classified samples of fresh tomatoes and triple concentrate tomato pastes of different geographical origin according to volatile fraction profiling as determined with HS-SPME-GC-MS. With a similar metabolomic approach, Jandric et al. [257] classified fruit juices using ultra performance liquid chromatography (UPLC)-QToF MS analysis. Of particular interest are some recently issued studies that illustrated the potentialities of an analytical platform involving sample preparation by headspace SPME, separation by two-dimensional comprehensive GC-MS (GC × GC-MS) and data processing using advanced fingerprinting–profiling approaches. This platform was applied in the classification of coffee samples [258], hazelnuts [259], flavored fruit foods [260], and hazelnuts with comparison to hazelnut-containing sweet pastes [261].

Guo et al. [262] analyzed Chinese apple juices of different varieties and geographical origin with HS-SPME-GC-MS. A fingerprinting approach was followed, using the chromatographic profiles as nonspecific signals and avoiding an a priori identification of the volatile compounds separated. The application of stepwise LDA yielded satisfactory discrimination of the samples according to variety and geographical origin.

Sabatino et al. [263] developed a hyphenated method using HPLC with both diode array and MS detectors for authentication of saffron. The high specificity of MS allowed the unequivocal identification of characteristic markers of adulterants (e.g., safflower, marigold, turmeric, etc.).

With concern to coffee, Arruda et al. [264] analyzed with HS-SPME-GC-MS coffee samples harvested in different maturation stages and treated by different processes. Profiling of volatile compounds, with more than 110 molecules, allowed to discriminate both the maturity stage and processing type used. Garrett et al. [265] analyzed green beans of *arabica* coffee of different cultivars

and geographic provenance by means of direct infusion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) and a metabolomic approach. The application of PCA and PLS-DA pattern recognition methods to data from the identified metabolites allowed discriminating samples according to both genetic and geographical features.

2.4.10 Animal Products

Radovic et al. [266] applied the potential of Py-MS for the authentication of honey samples according to the botanical origin. Ten unifloral types were tested: acacia, chestnut, eucalyptus, heather, lime, rapeseed, sunflower, citrus, lavender, and rosemary. Using discriminant function analysis (DFA) as supervised pattern recognition method, the data obtained allowed a good discrimination among the different botanical sources but not among the geographical provenances. More recently, Wang et al. [267] used MALDI-ToF-MS to determine the geographic origin of honey samples according to the protein pattern, in order to overcome the limitations of other parameters such as volatile trace compounds, saccharides, or trace elements in the classification. Protein profiling has already shown its potential in the botanical classification of honey [268]. In this work, honey samples from Hawaii and other regions in the world were analyzed and their MALDI-ToF-MS protein ion mass spectra were transformed into protein ion mass spectral barcodes, which allowed a robust and accurate comparison with the mass spectral database library generated by authors with dedicated software. Classification with PCA of protein fingerprints, expressed as barcodes, allowed separating honeys of different geographical and floral origins.

2.4.11 Products from Cereals

Studies on cereals and bakery foods are not very common. Bianchi et al. [269] characterized the profile of volatile compounds in samples of PDO Altamura bread, a renowned bakery food produced in Apulia (Southern Italy). The influence of different baking modes was also evaluated. Beleggia et al. [270] determined with HS-SPMR-GC-MS the profiles of the volatile components in semolina and pasta samples obtained from four durum wheat cultivars, evidencing differences among the different cv employed. Dinelli et al. [271] used HPLC interfaced with ESI-TOF-MS to highlight differences in the profiles of phenolic compounds in modern and old common wheat varieties. Pattemore et al. [272] used MALDI-ToF-MS for identification of cereal varieties. Authors identified single nucleotide polymorphism (SNP)-based markers.

2.4.12 Organic Food

Levandi et al. [273] analyzed different varieties of conventionally grown spring and winter wheat and of organic wheat with an untargeted metabolomic strategy using HPLC-ESI-MS/MS. The results of pattern recognition treatment with PCA allowed discriminating between conventional and organic wheat varieties.

Zörb et al. suggested an analytical approach based on 2D gel electrophoresis coupled with MALDI-ToF-MS to determine the protein profile in wheat grains and to distinguish organic and conventional wheat products [274]. A selected number of proteins were isolated that could be useful as markers.

A field of particular concern is the one of *transgenic foods*, a term which is referred to food products containing or derived from genetically modified organisms (GMO). GMOs are the well-known organisms derived from recombinant DNA technology which have found wide applications in many fields, among which agriculture. The use of GMOs is of course prohibited in the production of organic foodstuffs in legislations all over the world, therefore proper analytical strategies are needed in order to recognize their fraudulent (or in many cases involuntary) application. These strategies rely mostly on gene expression profiling, protein profiling, or metabolic profiling, recalling the use of MS techniques. Examples of applications are on maize [275,276] and soybeans [277]. This matter has been recently reviewed by Valdés et al. [278].

A slightly different concept is one of the healthy products: this includes foods, dietary supplements, and nutraceutics that can positively affect human health and wellness. Phytochemicals have been proposed as health promoters. Several commercial products containing phytochemicals are submitted for evaluation of health claim. Evaluation must be sustained by an increase in the knowledge on phytochemicals' bioactivity and their impact in health, which can be obtained by means of analytical platforms based on MS techniques [279].

3. CONCLUSIONS AND FUTURE TRENDS

The contribution of mass spectrometry in the field of food forensics has been well demonstrated by the huge number of applications developed in the last years. Several approaches have been issued, concerning hyphenated systems versus stand-alone MS systems, different strategies (targeted vs nontargeted methods) and different ways of sample introduction. The advantages of MS techniques against traditional techniques are apparent in terms of robustness, completeness of information, and fastness of application, which means reduced costs of analysis also.

The prospects of the application of MS techniques to the classification of foodstuffs are almost limitless. There is no doubt that mass spectrometry had features well-suited to become the ideal tool for food certification. In particular, a huge improvement of knowledge in this field will be given by the close interaction of MS analysis, bioinformatics, availability of large databases, and all the advanced "omics" technologies. These potentialities could now be applied to build robust and reliable procedures for insertion in national and international regulations. Unfortunately in many countries, with particular concern to those with large-scale industry, the matter of food forensics has to face the interest of great producers. It would be hard to explain why, at present, only in few cases

MS techniques were indicated as methods of choice in official national regulations. At the end, therefore, limitations in the possible developments will be rather a politic-economic matter than a technical or scientific one.

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