

# Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis

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The globalisation of food markets and the relative ease with which food commodities are transported through and between countries and continents, means that consumers are increasingly concerned about the origin of the foods they eat. A growing number of research articles have been published in the last 5 years detailing the use of natural abundance isotope variation and elemental concentrations as geographic 'tracers' to determine the provenance of food. These investigations exploit the systematic global variations of stable hydrogen and oxygen isotope ratios in combination with elemental concentrations, including heavy isotope variations (e.g. strontium-87) and other biogeochemical indicators. This article reviews the developments in the application of multi-isotopic and multi-element methods in the emerging field of 'Food Forensics'.

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doi:10.1016/j.tifs.2005.08.008

## Introduction

There are a number of driving forces for reliable analytical methods to verify the provenance of the food we eat. The UK Food Standards Agency (FSA) has consulted the public on a number of key issues relating to food labelling. The FSA's findings clearly demonstrated that 'country of origin labelling' was 'high on the consumers list of demands for change' (Food Standards Agency, 2001). There is growing enthusiasm among consumers for high quality food with a clear regional identity. The reasons for this vary from (a) patriotism; (b) specific culinary, organoleptic qualities, or purported health benefits associated with regional products; (c) a decreased confidence in the quality and safety of foods produced outside their local region, country or the EU or (d) concern about animal welfare and 'environmentally friendly' production methods. Food scares such as BSE, Foot and Mouth disease, chicken influenza and the malpractices of some international food producers have added to public sensitivity regarding the validity of food origin labelling. As well as heightened consumer awareness there are a number of important legislative driving forces for reliable analytical techniques to verify food provenance.

## EU protected food names schemes

The European Union Protected Food Names Schemes came into force in 1992 (Council Regulation (EEC) No 2081/92, 1992) and offers an independent inspection and labelling system for the protection of food names on a geographical basis, comparable to the French system 'Appellation d'Origine Contrôlée (AOC)' used for wine. There are three schemes; Protected Designation of Origin (PDO), Protected Geographical Indication (PGI) and Certificate of Specific Character (CSC) (also known as Traditional Speciality Guaranteed). PDO is the term used to describe foodstuffs, with a strong regional identity, that are produced, processed and prepared in a specific geographical area using prescribed techniques that may be unique to that region, e.g. Camembert de Normandie, Orkney beef and Umbrian olive oil. Foods with PGI status must have a geographical link in at least one of the stages of production, processing or preparation, e.g. Clare Island Salmon, Sorrento Lemons and Nürnberger Bratwürste. A CSC does not refer to a specific geographical origin, but defines

traditional character, either in terms of production techniques or composition. Manufacturers of Protected foods usually charge a premium for their produce due to increased production costs and consequently economic incentives exist to replace genuine articles with inferior ones for financial gain.

#### Beef labelling regulations

As a result of concerns relating to BSE, Human variant CJD and the impact on the internal market, the European Commission introduced far reaching legislation concerning the labelling of beef. The introduction of EU-wide compulsory beef labelling regulations, from the first September 2000 onwards ([Council Regulation No 2772/1999](#)) were intended to provide European consumers with correct, complete and transparent information to enable them to make an informed choice on the type and origin of beef they purchased. The new beef labelling system was designed to provide full traceability of cattle in the EU. The legislation was introduced in two key stages: (1) which came into force on first September, 2000; introducing labels which showed information readily available at the point of slaughter, e.g. 'slaughtered in' and 'cutting in'; and (2) to apply from first January, 2002—the inclusion of additional precise information about where the animal was born and reared (Commission Press Release DN: IP/00/799, Date: 2000-07-18). The ability to verify production origin in case of suspected mislabelling is extremely valuable to Customs and Trading Standards Authorities.

#### Subsidy fraud-circular trade

Organised crime syndicates throughout Europe have exploited the price-support structure of the European Common Agricultural Policy for financial gain. For example, butter is a product that has been involved in what Customs Authorities call *circular trade*. In practice, this means that when EU produced butter is exported to a 'third' (non-EU country) it attracts a subsidy payment, because of lower market prices prevailing outside the EU. The same consignment of butter is then re-labelled as *Produce of the third country* before being re-imported into the EU. The significance of re-labelling the origin of the butter is that the import tax is much less than the

original subsidy paid on the export. Therefore, by simply re-labelling the geographic origin of butter, a dishonest trader can make a significant financial gain. It has been estimated that this can generate an illegal profit of as much as £30,000 per 25,000 kg consignment of butter ([Balling & Rossmann, 2004](#)).

In the majority of cases paper traceability and livestock tagging systems can guarantee the geographical origin of foods on sale in the retail market. However, the widespread transportation of animals and foodstuffs does present the opportunity for unscrupulous traders to misdescribe the origin of their cargo. The prospect of high profits allied to low risk of detection and the lack of stringent penalties associated with food-fraud has attracted crime syndicates into illegal food trades. Consequently, there is a growing requirement for Enforcement Agencies, such as Customs and Trading Standards, to have access to reliable analytical methods that can verify origin labels on foodstuffs, whether they are part of the Protected Food Names Scheme or some other specific legislation, as in the case of beef, subsidy claims or simply 'suspect' imported produce from inside the European Community or Third Countries.

### Implications of natural abundance stable isotope and elemental variations in food provenance determinations

#### Natural abundance isotope ratios

[Table 1](#) provides a broad overview of the way in which natural abundance isotope ratios can be used for provenance determinations. Many natural phenomena, classed as physico-chemical effects, can lead to isotope fractionation (measurable changes in the ratio of the 'heavy' to 'light' isotope of a given element). For example, evaporation and condensation, crystallisation and melting, absorption and desorption, diffusion and thermodiffusion. As a first approximation natural abundance measurements will provide information on plant 'type' or diet (carbon and nitrogen isotope ratios), and geographical origin (hydrogen, oxygen, sulphur and strontium isotope ratios).

The measurement of the stable isotope ratios of hydrogen and oxygen are applicable to the characterisation of geographical origin because they are strongly latitude dependent. Meteoric water that has passed through the meteorological cycle of evaporation, condensation and

**Table 1. Overview of the way in which the relative proportions of the natural abundance of isotope ratios are affected (or fractionated) in the environment and how this can be exploited for food provenance determinations**

| Isotope ratio                   | Fractionation   | Information                      |
|---------------------------------|---|----------------------------------|
| $^2\text{H}/^1\text{H}$         | Evaporation, condensation, precipitation                            | Geographical                     |
| $^{13}\text{C}/^{12}\text{C}$   | C3 and C4 plants  | Diet (geographical proxy)        |
| $^{15}\text{N}/^{14}\text{N}$   | Trophic level, marine and terrestrial plants, agricultural practice | Diet (geographical proxy)        |
| $^{18}\text{O}/^{16}\text{O}$   | Evaporation, condensation, precipitation                            | Geographical                     |
| $^{34}\text{S}/^{32}\text{S}$   | Bacterial   | Geographical (marine)            |
| $^{87}\text{Sr}/^{86}\text{Sr}$ | Age of the rock and Rb/Sr ratio                                     | Underlying geology, geographical |

precipitation finally constitutes a groundwater that exhibits a systematic geographical isotope variation (Yuntseover & Gat, 1981). Decreasing temperatures cause a progressive heavy-isotope depletion of the precipitation when the water vapour from oceans in equatorial regions moves to higher latitudes and altitudes (Craig, 1961). Evaporation of water from the oceans is a fractionating process that decreases the concentration of the heavy isotopomers of water ( $^1\text{H}^2\text{H}^{16}\text{O}$ ,  $^1\text{H}^1\text{H}^{18}\text{O}$ ) in the clouds compared to the sea. As the clouds move inland and gain altitude further evaporation, condensation and precipitation events occur decreasing the concentration of deuterium. Consequently, the ground water reflects this isotopic gradient from the coast to inland areas (Dansgaard, 1964). The variation of  $^{18}\text{O}$  in the hydrosphere follows an analogous pattern to that of  $^2\text{H}$ . Previous studies have clearly shown that the oxygen-18 and deuterium content of water, consumed by animals, exhibits a strong correlation with the oxygen-18 and deuterium content of organic compounds present in animal products such as milk, butter and cheese (Manca et al., 2001). This correlation is also found in animal tissues and has been exploited by ecologists to determine the migratory patterns of birds (Wassenaar & Hobson, 2001) and insects (Hobson, 1999).

Local agricultural practices and animal diet affect  $^{15}\text{N}/^{14}\text{N}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios respectively.  $\text{C}_3$  plants use the Calvin photosynthetic pathway to assimilate  $\text{CO}_2$ . During this process the plants discriminate against  $^{13}\text{C}$  and therefore possess relatively lower  $^{13}\text{C}/^{12}\text{C}$  ratios than  $\text{C}_4$  plants that utilise the more energy efficient Hatch–Slack pathway. Since,  $\text{C}_3$  plants predominate at higher latitudes and  $\text{C}_4$  plants are more common in warmer climates at lower latitudes (such as the tropics), there is a gradient of decreasing  $^{13}\text{C}/^{12}\text{C}$  in plant material from the equator to the poles, which can also be used as a proxy for geographical origin determination. In addition to  $^{15}\text{N}$  signatures providing information about regional agricultural practices supplementary information may be obtained by measuring stable sulfur isotope ratios. Sulfate reduction does not produce significant fractionation, such that organic sulfur is clearly related to its source. Therefore, the soil or sulphate fertiliser from which it is derived can provide useful geographical origin information.

#### Delta notation

Differences in isotope-effects mentioned in the previous section are usually of the order of a few percent. Consequently, changes in the isotopic ratio at natural abundance levels often occur around the third or fourth significant figure. Isotope ratio analysis therefore requires very precise measurement and this is achieved by measuring the ratio of the heavy and light stable isotopes in the test material and comparing it to a reference compound of nominal isotope ratio. The technique of differential analysis of sample and standard permits very small differences in the

isotopic composition of test samples to be reliably and accurately determined. Thus, isotopic abundance of a sample relative to a reference is normally expressed by the differential Eq. (1):

$$\delta_{\text{ref}} = \left( \frac{R_{\text{samp}} - R_{\text{ref}}}{R_{\text{ref}}} \right) 1000 \quad (1)$$

Which can be simplified to Eq. (2)

$$\delta_{\text{ref}} = \left( \frac{R_{\text{samp}}}{R_{\text{ref}}} - 1 \right) 1000 \quad (2)$$

Where  $\delta_{\text{ref}}$  is the isotope ratio of the sample expressed in delta units (‰, per mil) relative to the reference material.  $R_{\text{samp}}$  and  $R_{\text{ref}}$  are the absolute isotope ratios of the sample and reference material, respectively. Multiplying by 1000 converts the value to *parts per thousand* (‰), or the more commonly used expression *per mil* (derived from the Latin *mille* meaning one thousand and used in an analogous way to *per centum* or *per cent*). In essence the use of Eq. (1) or (2) facilitates the comparison of isotope ratios especially at the natural abundance level when the differences being examined are relatively small.

#### Strontium isotopic ratios

Strontium is a group IIA element, an alkaline earth metal and it has four natural occurring isotopes:  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$  and  $^{88}\text{Sr}$ . Its ionic radius is similar to that of calcium and strontium can substitute for calcium in a wide range of naturally occurring minerals. One isotope,  $^{87}\text{Sr}$ , is formed through radiogenic decay of rubidium-87 ( $^{87}\text{Rb}$ ) with a decay half-life of 49,000,000,000 years (Faure, 1986). Although biological processes, such as assimilation and metabolism by plants and animals may alter stable strontium isotope ratios in a similar fashion as with the S, C, H, O and N isotopes, only the amount of excess radiogenic  $^{87}\text{Sr}$  is evaluated in its use as a geological tracer. Any natural or instrumental mass dependent fractionation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is normalized against an  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194 (Faure, 1986). In this manner the strontium isotopic ratios found in plants, and the animals that eat them, are related to  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the bio-available portion of the mineralised strontium derived from the bedrock, which is the sum of the individual minerals therein, and their geological ages:  $(^{87}\text{Sr}/^{86}\text{Sr}) = f(\text{Rb}/\text{Sr}, t)$ , where  $t$  is the age of the rocks either that of primary crystallization, metamorphosis and/or sedimentary deposition. As a first approximation acidic rocks (e.g. silica rich granites) have high  $^{87}\text{Sr}/^{86}\text{Sr}$ —values due to the high Rb/Sr ratios over time, while basic rocks (e.g. basaltic and carbonate rocks) have relatively lower values. Strontium isotope signatures can therefore be helpful in authenticity determinations, as they have a different scope than the stable isotopes of the light elements. This rationale applies to all natural products including food crops and animal tissues. Thus, ideally if

materials coming from different micro-regions within the same climate zone and therefore having similar  $\delta^2\text{H}\%$  and  $\delta^{18}\text{O}\%$  values, additional Sr isotope ratio analysis may provide an additional level of geographical resolution provided that different lithologies exist with that region.

#### Elemental composition

The multi-element composition of animal tissues reflects, to some extent, that of the vegetation that they eat. The vegetation is the compositional reflection of the bio-available and mobilized nutrients present in the underlying soils from which they were cultivated. Alkaline metals especially Rb and cesium (Cs) being easily mobilised in the soil and easily transported into plants, are good indicators of geographical identity. Trace element availability depends on several factors such as soil pH, humidity, porosity, clay and humic complex etc (Kim & Thornton, 1993). Consequently, the range of soils present and bioavailability mean that elemental composition may provide unique markers in food that characterise geographical origin. It is important to note that the chemical composition of the soil does not necessarily reflect that of the underlying lithology due to the deposition of glacial till during the 'ice-ages'. This is the case for most of Northern Europe, which was covered by glacial till in lowland areas.

#### Geographical origin determination

##### Overview

Multi-element and isotopic analyses have previously been applied to a range of foodstuffs to develop methods that will permit their geographical origins to be determined with varying degrees of certainty. The relevant literature is summarised in Table 2, which shows the various commodity groups investigated, the parameters measured, the instrumental techniques used and the corresponding reference. It should be noted that a vast array of other analytical techniques and parameters have been studied to verify the provenance of regional foods, such as aroma, sugar, phenolic and flavour compound profiling by gas and liquid chromatography; 'fingerprinting' or chemical profiling by  $^1\text{H}$  NMR, near Infra-Red and Fluorescence spectroscopy. These techniques can be extremely powerful tools for food origin determination in their own right and NMR profiling is often reported in the literature in conjunction with multi-element isotopic and trace element analysis (Brescia, Di Martino, Fares, *et al.*, 2002; Brescia, Di Martino, Guillou, *et al.*, 2002; Renou, Bielicki, *et al.*, 2004; Renou, Deponge, *et al.*, 2004). However, the spectroscopic profiling techniques, their reliability and limitations are not the focus of this review.

A common theme of food authentication studies is the requirement for a database of genuine samples to which the 'suspect' test sample can be compared to establish its authenticity. Geographical origin determination is no

exception, but the need to source agricultural products from a wide range of countries is time consuming and costly. Furthermore, in order to constrain an authenticity parameter such as geographical origin there is a requirement for a large number of independent variables to be measured and statistically 'screened' in order to identify key tracers that differentiate the regions or countries of interest. There have been a small number of literature reviews that have dedicated sections of the articles to the application of multi-element and isotope analysis to the determination of the geographical origin. These include Anklam (1998); Horn, Hölzl, Todt, and Matthies (1998); Hölzl, Horn, Rossmann, and Rummel (2004); Kelly (2003); Rossmann (2001). In addition, the multivariate statistical techniques used, in combination with a wide range of analytical methods including multi-element and isotopic analysis, to classify food products according to their geographical and varietal origin has been critically reviewed by Tzouros and Arvanitoyannis (2001).

Measuring elemental concentrations and isotopic variation in premium regional products is arguably the best analytical strategy for accurately verifying geographical origin. This approach is driven by the hypotheses outlined above describing the global variation of isotope abundance of the 'light' bio-elements and 'heavy' geo-elements.

#### Meat

Some of the most recent research into the application of multi-element and multi-isotopic measurements to determine geographical origin has focused on beef and lamb. Hegerding, Seidler, Danneel, Gessler, and Nowak (2002) investigated whether the oxygen-18 content of local ground water, measured by IRMS, was preserved in the tissue water of beef cattle originating from Germany, the United Kingdom and Argentina. Significant differences were observed in the  $\delta^{18}\text{O}\%$  value of tissue water from German cattle ( $n=175$ ) and Argentinian cattle ( $n=42$ ) permitting a reasonably secure classification of origin, for these specific countries, with a single isotopic parameter. However, the natural variation in  $\delta^{18}\text{O}\%$  values did give rise to overlapping outliers in the German and Argentinian data sets and did not provide sufficient resolution to discriminate the UK samples from either the German or Argentinian cattle. Nor did it permit reliable discrimination of northern and southern production regions within Germany. Boner and Forstel (2004) characterised beef from Germany, Argentina and Chile by measuring the  $\delta^{18}\text{O}\%$  and  $\delta^2\text{H}\%$  values of tissue water and  $\delta^{13}\text{C}\%$ ,  $\delta^{15}\text{N}\%$  and  $\delta^{34}\text{S}\%$  values of defatted protein, over a 2 year period. 'Organically' reared German beef cattle were chosen because these animals are generally reared on local pastures and fodder produced on the same farm, which reduces the possibility of confounding factors produced by imported feed materials. The authors

**Table 2. Summary of the relevant literature relating to the use of multi-element and multi-isotopic analysis of food commodities to determine the geographical origin**

| Commodity      | Parameters measured   | Instrumental techniques                                   | Data interpretation       | Reference   |
|----------------|---|---|---------------------------|---|
| Meat           |   |   |                           |   |
| Beef           | $^{18}\text{O}/^{16}\text{O}$   | IRMS  | Univariate, box & whisker | Hegerding <i>et al.</i> , 2002  |
| Beef           | Se  | AAS-hydride generation                                    | Univariate                | Hintze <i>et al.</i> , 2002   |
| Beef           | $^2\text{H}/^1\text{H}$ , $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{34}\text{S}/^{32}\text{S}$   | IRMS  | Box & whisker, PCA        | Boner & Forstel, 2004   |
| Beef           | $^2\text{H}/^1\text{H}$ , $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$   | IRMS ( $^1\text{H}$ , $^2\text{H}$ & $^{13}\text{C}$ NMR) | DA                        | Renou, Bielicki, <i>et al.</i> , 2004   |
| Lamb           | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$   | IRMS  | CDA                       | Piasentier <i>et al.</i> , 2003   |
| Dairy products |   |   |                           |   |
| Milk           | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{18}\text{O}/^{16}\text{O}$   | IRMS  | Univariate                | Kornexl <i>et al.</i> , 1997  |
| Milk           | $^{18}\text{O}/^{16}\text{O}$   | IRMS (1H NMR)   | DA                        | Renou, Deponge, <i>et al.</i> , 2004  |
| Milk           | $^{18}\text{O}/^{16}\text{O}$   | IRMS  | Univariate                | Ritz <i>et al.</i> , 2004   |
| Butter         | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{18}\text{O}/^{16}\text{O}$ , $^{34}\text{S}/^{32}\text{S}$ , $^{87}\text{Sr}/^{86}\text{Sr}$ | IRMS, TIMS  | DA                        | Rossmann <i>et al.</i> , 2000   |
| Butter         | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{18}\text{O}/^{16}\text{O}$ , $^{34}\text{S}/^{32}\text{S}$ , $^{87}\text{Sr}/^{86}\text{Sr}$ | IRMS, TIMS  | DA                        | Balling & Rossmann, 2004  |
| Cheese         | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$   | IRMS (HPLC)   | PCA, CA, LDA              | Manca <i>et al.</i> , 2001  |
| Cheese         | $^2\text{H}/^1\text{H}$ , $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{34}\text{S}/^{32}\text{S}$ , $^{87}\text{Sr}/^{86}\text{Sr}$ , ME  | IRMS. Q-ICP-MS, TIMS, $\alpha$ -spectrometry              | ANOVA, PCA                | Pillonel <i>et al.</i> , 2003   |
| Cheese         | $^2\text{H}/^1\text{H}$ , $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{34}\text{S}/^{32}\text{S}$   | IRMS, AAS (GC, HPLC, NIR, electronic nose)                | PCA                       | Pillonel <i>et al.</i> , 2004   |
| Cheese         | $^{87}\text{Sr}/^{86}\text{Sr}$   | MC-ICP-MS, TIMS   | Univariate                | Fortunato <i>et al.</i> , 2004  |
| Cheese         | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{18}\text{O}/^{16}\text{O}$ , $^{34}\text{S}/^{32}\text{S}$                                   | IRMS (HPLC)   | Box & whisker, CDA        | Camini <i>et al.</i> , 2004   |
| Beverages      |   |   |                           |   |
| Coffee         | ME  | AAS, GF-AAS, EA, NAA                                      | <i>t</i> -test            | Krivan <i>et al.</i> , 1993   |
| Coffee         | ME  | XRF   | PCA                       | Haswell & Walmsley, 1998  |
| Coffee         | $^2\text{H}/^1\text{H}$ , $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$   | IRMS  | LDA, CART                 | Weckerle <i>et al.</i> , 2002   |
| Tea            | ME  | ICP-AES   | PCA, LDA, ANN             | Fernandez-Caceres <i>et al.</i> , 2001  |
| Tea            | ME  | ICP-AES, Q-ICP-MS   | PCA, LDA                  | Moreda-Pineiro <i>et al.</i> , 2001   |
| Tea            | ME  | ICP-AES, Q-ICP-MS   | PCA, LDA                  | Moreda-Pineiro <i>et al.</i> , 2003   |
| Orange juice   | $^{13}\text{C}/^{12}\text{C}$   | IRMS  | Univariate                | Simpkins, Louie, <i>et al.</i> , 2000   |
| Orange juice   | ME  | ICP-AES, Q-ICP-MS   | PCA                       | Simpkins, Patel, <i>et al.</i> , 2000   |
| Cereal crops   |   |   |                           |   |
| Rice           | ME  | ICP-AES, Q-ICP-MS   | PCA, CA                   | Yasui & Shindoh, 2000   |
| Rice           | $^{11}\text{B}/^{10}\text{B}$ , $^{87}\text{Sr}/^{86}\text{Sr}$ , Cd concentration  | Q-ICP-MS, MC-ICP-MS                                       | Binary plots              | Oda <i>et al.</i> , 2002  |
| Rice           | $^{13}\text{C}/^{12}\text{C}$ , $^{18}\text{O}/^{16}\text{O}$ , ME  | IRMS. Q-ICP-MS  | CDA                       | Kelly <i>et al.</i> , 2002  |
| Rice           | $^{87}\text{Sr}/^{86}\text{Sr}$   | MC-ICP-MS   | Univariate?               | Kawasaki <i>et al.</i> , 2002   |
| Wheat          | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$   | IRMS (HR-MAS-NMR)   | PCA                       | Brescia, Di Martino, Fares, <i>et al.</i> , 2002; Brescia, Di Martino, Guil-lou, <i>et al.</i> , 2002 |
| Wheat          | $^{13}\text{C}/^{12}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , ME  | Q-ICP-MS, IRMS  | Box & whisker, CDA        | Branch <i>et al.</i> , 2003   |
| Wine           |   |   |                           |   |
| Wine           | $^{87}\text{Sr}/^{86}\text{Sr}$   | TIMS  | Univariate                | Horn <i>et al.</i> , 1993   |
| Wine           | $^{13}\text{C}/^{12}\text{C}$ , $^{18}\text{O}/^{16}\text{O}$   | IRMS  | Univariate                | Breas <i>et al.</i> , 1994  |
| Wine           | ME, (D/H)1, (D/H)2  | AAS, SNIF-NMR   | ANOVA, PCA                | Day <i>et al.</i> , 1994  |
| Wine           | ME, (D/H)1, (D/H)2  | AAS, SNIF-NMR   | PCA, CDA                  | Day <i>et al.</i> , 1995  |
| Wine           | ME  | Q-ICP-MS  | CDA, PCA                  | Baxter <i>et al.</i> , 1997   |
| Wine           | $^{87}\text{Sr}/^{86}\text{Sr}$ , $^{18}\text{O}/^{16}\text{O}$   | IRMS, TIMS  | Univariate                | Horn <i>et al.</i> , 1998   |
| Wine           | $^{13}\text{C}/^{12}\text{C}$ , $^{18}\text{O}/^{16}\text{O}$ , (D/H)1, (D/H)2  | IRMS, SNIF-NMR  | Univariate                | Rossmann <i>et al.</i> , 1999   |
| Wine           | $^{87}\text{Sr}/^{86}\text{Sr}$   | MC-ICP-MS   | Univariate                | Almeida & Vasconcelos, 2001   |
| Wine           | $^{207}\text{Pb}/^{206}\text{Pb}$   | Q-ICP-MS, TOF-ICP-MS, MC-ICP-MS                           | Univariate                | Barbaste <i>et al.</i> , 2001   |

(continued on next page)

Table 2 (continued)

| Commodity                | Parameters measured  | Instrumental techniques               | Data interpretation | Reference                      |
|--------------------------|--|---------------------------------------|---------------------|--------------------------------|
| Wine                     | $^{13}\text{C}/^{12}\text{C}$ , $^{18}\text{O}/^{16}\text{O}$ , (D/H)1, (D/H)2 | IRMS, SNIF-NMR                        | PCA, ANN            | Kosir <i>et al.</i> , 2001     |
| Wine                     | $^{87}\text{Sr}/^{86}\text{Sr}$  | MC-ICP-MS                             | Univariate          | Barbaste <i>et al.</i> , 2002  |
| Wine                     | $^{13}\text{C}/^{12}\text{C}$ , $^{18}\text{O}/^{16}\text{O}$ , (D/H)1, (D/H)2 | IRMS, SNIF-NMR                        | <i>t</i> -test      | Christoph <i>et al.</i> , 2003 |
| Wine                     | $^{13}\text{C}/^{12}\text{C}$ , $^{18}\text{O}/^{16}\text{O}$ , (D/H)1, (D/H)2 | IRMS, SNIF-NMR                        | Univariate          | Christoph <i>et al.</i> , 2004 |
| Wine                     | ME   | ICP-AES, HPIC, ( $^1\text{H}$ NMR)    | PCA, HCA, RDA       | Brescia <i>et al.</i> , 2003   |
| Wine                     | $^{87}\text{Sr}/^{86}\text{Sr}$  | Q-ICP-MS                              | Univariate          | Marisa <i>et al.</i> , 2004    |
| Wine                     | $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ , ME                   | IRMS, ICP-MS?, (classical parameters) | CDA                 | Gremaud <i>et al.</i> , 2004   |
| <i>Other commodities</i> |  |                                       |                     |                                |
| Honey                    | Review   |                                       |                     | Anklam, 1998                   |
| Potatoes                 | ME   | ICP-AES                               | PCA, CDA, ANN       | Anderson <i>et al.</i> , 1999  |
| Vegetable oils           | $^{18}\text{O}/^{16}\text{O}$ , $^{13}\text{C}/^{12}\text{C}$ ?                | IRMS                                  | Univariate          | Breas <i>et al.</i> , 1998     |
| Vegetable oils           | $^{18}\text{O}/^{16}\text{O}$ , $^{13}\text{C}/^{12}\text{C}$                  | IRMS                                  | CA, PCA             | Angerosa <i>et al.</i> , 1999  |

$^2\text{H}/^1\text{H}$ , The ratio of the isotope of hydrogen with atomic mass 2 to the isotope of hydrogen with atomic mass 1;  $^{13}\text{C}/^{12}\text{C}$ , The ratio of the isotope of carbon with atomic mass 13 to the isotope of carbon with atomic mass 12;  $^{15}\text{N}/^{14}\text{N}$ , The ratio of the isotope of nitrogen with atomic mass 15 to the isotope of nitrogen with atomic mass 14;  $^{18}\text{O}/^{16}\text{O}$ , The ratio of the isotope of oxygen with atomic mass 18 to the isotope of oxygen with atomic mass 16;  $^{34}\text{S}/^{32}\text{S}$ , The ratio of the isotope of sulfur with atomic mass 34 to the isotope of sulfur with atomic mass 32;  $^{87}\text{Sr}/^{86}\text{Sr}$ , The ratio of the isotope of strontium with atomic mass 87 to the isotope of strontium with atomic mass 86; ME, Multielement Analysis; ANOVA, Analysis of Variance; ANN, Artificial Neural Network; CA, Cluster Analysis; CART, Classification and Regression Tree Analysis; C(DA), Canonical (Discriminant Analysis); HCA, Hierarchical Cluster Analysis; LDA, Linear Discriminant Analysis; PCA, Principal Component Analysis; AAS, Atomic Absorption Spectrometry; EA, Elemental Analysis (Dumas Combustion); GF, Graphite Furnace; HPLC, High Performance Liquid Chromatography; HPIC, High Performance Ion Chromatography; ICP, AES-Inductively Coupled Plasma-Atomic Emission Spectrometry; ICP-OES, Inductively Coupled Plasma-Optical Emission Spectrometry; INAA, Instrumental Neutron Activation Analysis; IRMS, Isotope Ratio Mass Spectrometry; MC-ICP-MS, Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry; NMR, Nuclear Magnetic Resonance spectrometry; Q-ICP-MS, Quadrupole-Inductively Coupled Plasma-Mass Spectrometry; TIMS, Thermal Ionisation Mass Spectrometry; TOF, Time-Of-Flight; SNIF-NMR, Site-specific Natural Isotope Fractionation-Nuclear Magnetic Resonance; XRF, total reflection X-Ray Fluorescence analysis.

suggested that a  $\delta^{13}\text{C}\text{‰}$  value above  $-20\text{‰}$  has been observed as a limit for differentiating between conventionally and Organically reared cattle in Germany, based on the proportion of C4 maize in the diet. However, Organic cattle feed may be outsourced and consequently its composition changed if there is insufficient feed being produced in the local area. The importance of the seasonal variation of  $\delta^2\text{H}\text{‰}$  and  $\delta^{18}\text{O}\text{‰}$  in tissue water was emphasised for the correct interpretation of geographical origin. If the production season was known, beef samples from Northern ( $n=103$ ) and Southern ( $n=65$ ) Germany were correctly differentiated from Argentinian samples ( $n=34$ ) in 95 and 100% of cases, respectively. Elevated  $\delta^{34}\text{S}\text{‰}$  values (median  $+15.2\text{‰}$ ) were shown to be extremely useful in distinguishing the beef samples originating from Chile ( $n=10$ ). A controlled cattle feeding experiment has been conducted by the Institut National de la Recherche Agronomique at three distinct geographical sites in France (Renou, Bielicki, *et al.*, 2004). The study aimed to establish if  $\delta^{18}\text{O}\text{‰}$  of beef tissue water, measured by IRMS, in combination with  $^1\text{H}$ ,  $^2\text{H}$  and  $^{13}\text{C}$  spectrums of extracted beef lipid, measured by NMR, could be used to distinguish the production sites and diet. Discriminant analysis was used to differentiate cattle fed on both the pasture and maize diets at the three

production sites. All pasture fed cattle were well classified, as were 94% of the cattle fed on maize silage. However, the parameters chosen for the discriminant functions were derived from the NMR spectroscopic analysis of the beef lipid fraction. Piasentier, Valusso, Camin, and Versini (2003) investigated the effectiveness of analysing  $\delta^{13}\text{C}\text{‰}$  and  $\delta^{15}\text{N}\text{‰}$  values of extracted lipid and residual protein fractions of lamb meat. Analyses were carried out on 120 samples from 12 lamb types, produced in two distinct regions in each of the countries, Great Britain, Spain, France, Greece, Iceland and Italy. Canonical discriminant analysis was used to evaluate whether lamb meat from the different production origins could be differentiated by its stable isotope ratios. 79.2% of the samples were initially correctly classified and cross validation of the discriminant model reduced this to 67% correct classification of geographical origin.

### Dairy products

Rossmann *et al.* (2000) conducted stable isotope analysis of the light bio-elements ( $\delta^{13}\text{C}\text{‰}$ ;  $\delta^{15}\text{N}\text{‰}$ ,  $\delta^{18}\text{O}\text{‰}$  and  $\delta^{34}\text{S}\text{‰}$ ) and the heavy geo-element, strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) as a means of classifying the origin of butter produced from cow's milk. They discussed these elements in natural cycles, their variations due to climate and

geology, the abiotic and biological fractionation of isotopes and the reasons for regional differences in stable isotope ratios of butter. They reported data from several European countries and from outside the EU. The results indicated that stable isotope ratios and subsequent discriminant analysis based on data for samples of certified origin can enable the reliable detection of the regional provenance of butter. Furthermore, the methodology was subsequently used to successfully prosecute European companies involved in circular trading of butter and illegal subsidy claims (Balling & Rossmann, 2004). The study by Rossmann *et al.* was linked to similar research on milk (Kornexl, Werner, Rossmann, & Schmidt, 1997). In this study, the relative carbon and nitrogen stable isotope abundances in total milk were found to reflect the isotopic composition of the cattle diet and in turn the diet and its isotopic signature was dependent upon geographical and climatic factors. The stability of the isotopic signature of milk was also demonstrated by measuring the isotopic content of milk, casein and whey from one location for more than one year. The observed variations were usually found to be not greater than 1‰. In addition, it was observed that the metabolism associated with milk production produced an enrichment of  $\delta^{18}\text{O}$  in the milk water between +2‰ and +6‰ greater than feeding-water. More recently,  $^{13}\text{C}$  NMR has been employed to determine the proportions of polyunsaturated (PUFA), monounsaturated (MUFA) and saturated fatty acids (SFA) in milk fat and IRMS was used to measure the  $^2\text{H}$  and  $^{18}\text{O}$  enrichment in milk water (Renou, Deponge, *et al.*, 2004). The fatty acid composition was indicative of the cattle diet achieving 100% classification of milks produced from cattle fed on pasture, grass silage and hay at Marcenat, a mountain site in France. IRMS results were found to be more influenced by the production area. A stepwise canonical discriminant analysis showed that high resolution NMR and IRMS are two complementary methods suitable for the authentication of milk according to the cattle feeding regime and geographic origin. In a related study, the effects of the breed of cow on the  $\delta^{18}\text{O}$ ‰ values of milk water were examined when different breeds were kept in the same environment and fed on the same diet (Ritz *et al.*, 2004). The results indicated that the breed of cow influences the  $\delta^{18}\text{O}$ ‰ value of milk water. However, the authors concluded that the effect was negligible in comparison to the observed differences in  $\delta^{18}\text{O}$ ‰ between different diets and production sites. Preliminary results on the analysis of Pecorino Sardo cheese by Manca *et al.* (2001) have demonstrated the usefulness of stable isotope analysis in the absence of  $^{18}\text{O}$  and  $^2\text{H}$  data. The  $\delta^{13}\text{C}$ ‰ and  $\delta^{15}\text{N}$ ‰ of casein and a number of free amino acid ratios (His/Pro, Ile/Pro, Met/Pro, and Thr/Pro) determined by high performance liquid chromatography in samples of ewes' milk cheese from Sardinia, Sicily, and Apulia were reported as parameters independent of maturation time.

Multivariate statistical analysis performed by applying both unsupervised (principal component analysis and cluster analysis) and supervised linear discriminant analysis demonstrated reliable discrimination for the Pecorino Sardo cheese according to geographical production area. Certain variables were reported as having greater discriminatory power than others, in particular, the variables Ile/Pro, Thr/Pro,  $\delta^{13}\text{C}$ ‰ and  $\delta^{15}\text{N}$ ‰ which resulted in 100% discrimination and classification of the samples by LDA. A comprehensive study of 20 Emmental cheeses was conducted using techniques including IRMS, TIMS, AAS, ICP-MS and alpha-spectrometry (Pillonel *et al.*, 2003). The cheeses were produced in six European regions (Allgau (FRG), Bretagne (F), Vorarlberg (A), Savoie (F), Switzerland and Finland). The parameters measured included  $\delta^2\text{H}$ ‰,  $\delta^{13}\text{C}$ ‰,  $\delta^{15}\text{N}$ ‰,  $\delta^{18}\text{O}$ ‰ and  $^{87}\text{Sr}/^{86}\text{Sr}$ , as well as major (Ca, Mg, Na, K), trace (Cu, Mn, Mo, I) and radioactive elements (Sr-90, U-234, U-238). The discriminating potential of these parameters was assessed using ANOVA and principal component analysis. 'Finland', 'Bretagne' and 'Savoie' cheeses were successfully differentiated using isotope ratios. Concentrations of molybdenum and sodium permitted Emmental cheeses produced in Switzerland, Vorarlberg and Allgau to be successfully differentiated.  $^{90}\text{Sr}$  activity was highly correlated with the altitude of the production zone. A similar extensive study using a wide range of chemical parameters including stable isotope analysis, to detect adulteration and mislabelling, was reported on Raclette Suisse and Fontina PDO cheese by Pillonel, Bütikofer, Rossmann, Tabacchi, and Bosset (2004). The  $\delta^2\text{H}$ ‰ and  $\delta^{34}\text{S}$ ‰ values of the casein fraction from the Raclette cheese clearly differentiated French samples produced in the Northwest and centre/East. The use of four stable isotope parameters  $\delta^2\text{H}$ ‰,  $\delta^{13}\text{C}$ ‰,  $\delta^{15}\text{N}$ ‰ and  $\delta^{34}\text{S}$ ‰ permitted good separation of the Swiss and both French Raclette production areas. It was also observed that the presence of lysozyme and/or natamycin could be used to detect fraudulent imitations of cheese made by 'Raclette Suisse'. PCA of  $\delta^2\text{H}$ ‰,  $\delta^{13}\text{C}$ ‰ and  $\delta^{15}\text{N}$ ‰ was found to give a perfect separation of Fontina PDO, produced exclusively in the Aosta Valley, from two common imitations, 'Fontal' cheese, produced in the North of Italy and Switzerland. The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio of eighteen Emmental-type cheeses has also been measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Fortunato *et al.*, 2004) to determine their geographical origins. The strontium isotope ratios measured by MC-ICP-MS were compared with data on the same samples measured by thermal ionisation mass spectrometry (TIMS). The results agreed within the stated measurement uncertainties for the respective techniques. The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope abundance ratios determined for the Emmental-type cheeses, originating from different regions (alpine, pre-alpine, Bretagne, Finland, Canada, Australia), were consistent with

the local geology of the production areas. Furthermore, the authors reported no difference between 'casein-bound' and 'whole-cheese' Sr isotope, abundance ratios. Multi-element stable isotope analysis has also been applied to a range of different cheeses from three different European Countries (Camin *et al.*, 2004). The cheeses examined were from France (Reblochon and Camembert de Normandie), Italy (Grana Padano, Grana Trentino and Parmigiano Reggiano) and Spain (Manchego and Quesuco de Liebana). The stable isotope ratios ( $\delta^{13}\text{C}\%$ ,  $\delta^{15}\text{N}\%$  and  $\delta^{34}\text{S}\%$  of casein, and  $\delta^{13}\text{C}\%$  and  $\delta^{18}\text{O}\%$  of extracted glycerol) were measured by IRMS. Once again the authors observed that the  $\delta^{13}\text{C}\%$  values of both casein and glycerol were strongly correlated to the amount of maize in the animal diet. The  $\delta^{18}\text{O}\%$  value of glycerol was more dependent on the geographical origin of the cheeses and on climatic/seasonal parameters. Analysis of the isotopic data by stepwise canonical discriminant analysis, permitted around 93% of the European cheeses to be correctly reclassified.

### Beverages

Several investigations have been reported on elemental concentrations in beverages, and these have been driven mainly by interest in mineral nutrition and plant physiology. The first dedicated attempt to link the elemental composition of coffee to its geographical production area was conducted by Krivan *et al.* (1993). The researchers utilized instrumental neutron activation analysis, flame and graphite furnace atomic absorption spectrometry and elemental analysis (dumas combustion) to determine the concentration of 20 elements in green coffee from eight different geographical origins (Columbia, Costa Rica, Cuba, El Salvador, Mexico, Nicaragua, Panama and Papua New Guinea). Manganese was found to be the most significant element to discriminate between the respective coffee production areas in 84% of the mutual *t*-test comparisons. The other elements identified as significant for coffee provenance determination were Co, Cs, Na, Rb and percent C. The potential of using total reflection X-ray fluorescence (TXRF) analysis for multi-elemental profiling of 16 coffees (and seven wines) was investigated by Haswell and Walmsley (1998). Elemental concentrations were quantified versus a vanadium standard. Principal components analysis (PCA) was used to identify which elements were responsible for 99% of the variation in the coffee samples on the basis of 'brand' rather than geographical origin. These were K, Ca, Mn, Fe, Ni, Cu, Zn, Br, Rb and Sr. Star plots were used to show the differences between samples for the key elements. The data demonstrated TXRF potential as a rapid screening and classification technique for coffee samples. The isotopic composition of caffeine extracted from 45 Arabica green coffee bean samples has also been determined to verify geographical origin (Weckerle,

Richling, Heinrich, & Schreier, 2002). The  $\delta^{13}\text{C}\%$  values for caffeine ranged from  $-25.1$  to  $-29.9\%$ ;  $\delta^2\text{H}\%$  from  $-109$  to  $-198\%$  and  $\delta^{18}\text{O}\%$  from  $+2.0$  to  $-12.0\%$ . Classification of the caffeine samples on the basis of provenance by linear discriminant analysis (LDA) led to cross-validated error rates of 7.7% and revealed  $\delta^{18}\text{O}\%$  as the most significant geographical indicator.

A preliminary study to classify fifteen tea samples according to geographical origin using the concentrations of 28 elements, measured by ICP-AES and ICP-MS, was made by Marcos, Fisher, Rea, and Hill (1998). Multivariate analysis of the data by PCA indicated that a distinction could be made between African and Asian and between Chinese and other Asian teas on the basis of trace element composition. In a related paper, the importance of multi-element data treatment, prior to multivariate statistical analysis, by software packages was discussed in relation to tea origin (Moreda-Pineiro, Marcos, Fisher, & Hill, 2001). The study demonstrated that half-range and central value transformations of data prior to multivariate analysis achieved better geographical discrimination than standard data normalisation (i.e. dividing all measured elemental concentrations for a given element by the mean value for that element). These findings were followed by a further study on 85 tea samples from various Asian and African countries (Moreda-Pineiro, Fisher, & Hill, 2003). LDA correctly assigned 91.7–100% of the teas according to their production origin under different identification scenarios. The concentration of 12 metallic elements in 46 tea samples, including green, black, and instant teas, was determined by ICP-AES. A 100% correct classification of the teas into five geographical regions (Kenyan, Chinese, Japanese, Indian and Sri Lanka) was achieved using LDA.

ICP-AES and ICP-MS were used to measure the concentrations of 22 trace elements in 480 samples of Australian and Brazilian orange juices (Simpkins, Louie, Wu, Harrison, & Goldberg, 2000). Principal component analysis of trace elements in reconstituted Australian and Brazilian juices showed a clear differentiation between them with rubidium, barium and boron mainly contributing to the first two principal components. Peel extracts derived from Australian and Brazilian juices were also differentiated and regional differences were apparent for the levels of one or more trace elements in the juices of Australian origin. A similar IRMS study by Simpkins also demonstrated that there were small, but significant regional differences in the  $\delta^{13}\text{C}\%$  value of the soluble solids present in Australian single strength orange juice. (Simpkins, Patel, Harrison, & Goldberg, 2000).

### Cereal crops

The distinction of the geographic origin of Japanese brown-rice samples by their multi-element concentrations was studied by Yasui and Shindoh (2000) using ICP-AES and ICP-MS. Thirty-four kinds of unhulled rice samples

were collected from 27 different locations. Nine elements (Mn, Zn, Fe, Cu, Rb, Mo, Ba, Sr, Ni) were used in a PCA that permitted distinction of rice samples cultivated in the Tohoku/Kanto area from those in Hokuriku, and those in Tohoku from those in the Kanto regions. Kelly *et al.* (2002) reported the use of IRMS and ICP-MS to determine the origin of rice samples cultivated in the USA, Europe and Basmati regions (India and Pakistan). Nine key parameters ( $\delta^{13}\text{C}\%$ ,  $\delta^{18}\text{O}\%$ , boron, holmium, gadolinium, magnesium, rubidium, selenium and tungsten) were identified by stepwise canonical discriminant analysis and permitted 100% discrimination between rice samples from these production origins. The authors observed high levels of boron ( $>2.5\ \mu\text{g/g}$ ) associated with rice samples from America and notably high levels of holmium were found in rice samples from the state of Arkansas. European rice samples generally contained relatively high levels of magnesium and Indian/Pakistani samples were characterised by relatively low  $^{18}\text{O}$  abundance, characteristic of the relatively high altitude at which Basmati rice crops were cultivated and irrigation with Himalayan water. Multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been used to characterise the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of rice cultivated in Australia, California, China and Vietnam (Kawasaki, Oda, & Hirata, 2002). The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios of the Chinese and Vietnamese rice samples ranged from 0.710 to 0.711 and were slightly higher than the majority of the Japanese samples. Australian rice exhibited the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of all the rice examined, ranging between 0.715 and 0.717. Conversely, the Californian rice had a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.706. The Sr isotope ratios were determined with a precision of  $<0.01\%$  (RSD, repetitions=60). The study clearly demonstrated that strontium isotope ratios can provide unique information for the estimation of rice provenance. Oda, Kawasaki, and Hirata (2002) extended this work on rice by combining  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, measured by MC-ICP-MS, with boron isotope ratios ( $^{11}\text{B}/^{10}\text{B}$ ) and cadmium concentrations measured by ICP-MS. Sixty-eight rice samples cultivated at different sites in Japan (44), California (15), China (4), Australia (3), Korea (1) and Vietnam (1) could all be distinguished using only  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, or  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in combination with  $^{11}\text{B}/^{10}\text{B}$  or cadmium concentrations.

The geographical origin of durum wheat semolina was differentiated using the natural abundance isotopic ratios of carbon, oxygen and nitrogen from samples produced in Italy, Canada, Turkey and Australia (Brescia, Di Martino, Guillou, *et al.*, 2002). The relationship between isotopic content and the latitude was confirmed. In an additional study including the spectroscopic technique proton high-resolution magic angle spinning nuclear magnetic resonance ( $^1\text{H}$  HR-MAS NMR) analysis of two cultivars of durum wheat produced in different Italian geographical areas were differentiated according to cultivar and geographical origin using multivariate statistics (Brescia, Di Martino, Fares, *et al.*, 2002).

Branch, Burke, Evans, Fairman, and Briche (2002) conducted a preliminary investigation using ICP-MS analysis of Cd, Pb, Se and Sr and stable isotope analysis of  $\delta^{13}\text{C}\%$  and  $\delta^{15}\text{N}\%$  to identify the country of origin of commercial wheat samples cultivated in North America (9), Canada (7), France (3) and Germany (1). Discriminant analysis correctly predicted the origin of all the wheat samples. However, the concentration of selenium and the  $\delta^{13}\text{C}\%$  values were consistently higher in USA/Canadian samples than in European samples and the use of  $\delta^{13}\text{C}\%$  data alone was found to be sufficient to correctly determine the origin of all twenty wheat samples analysed in this study.

## Wine

A much larger number of studies, using multi-element and multi-isotopic analysis, have been conducted on the provenance of wines. This is due to the relatively high value of wine compared with other agricultural products and the fact that higher quality production from particular regions has long been recognized through the AOC and other similar European national legislation. Some of the earliest research relates to the use of strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), measured by thermal ionisation-mass spectrometry (TIMS), to determine the provenance of wine. Using this technique Horn, Schaaf, Holbach, Hoelxl, and Eschnauer (1993) distinguished wines grown in different regions within a given country (e.g. France and Italy). The variation of  $\delta^{18}\text{O}\%$  of wine water with production region has been recognized for some time (Breas, Reniero, & Serrini, 1994) and this measurement has been formally included in the official European wine database since 1996 (Commission Regulation No 1932/97). The main factors affecting the variation of  $\delta^{18}\text{O}\%$  of wine water for authentic EU databank wines have been discussed by Rossmann *et al.* (1999). The official European method for detecting illegal chaptalisation of wine (addition of sugar to grape must prior to fermentation) has been in place since 1991 and is based on measuring the  $^2\text{H}/^1\text{H}$  ratio at the methyl and methylene positions of ethanol by deuterium magnetic resonance spectroscopy (Commission Regulation No 2348/91). This technique is known as Site-specific Isotope Fractionation measured by Nuclear Magnetic Resonance (SNIF NMR<sup>TM</sup>). The  $^2\text{H}/^1\text{H}$  ratio at the methylene position of ethanol,  $(\text{D}/\text{H})_2$ , relates mainly to the  $^2\text{H}/^1\text{H}$  ratio of the fermentation water derived from the grapes and consequently the geographical origin of the wine. Day, Zhang, and Martin (1995) combined  $(\text{D}/\text{H})_2$  data with multi-element data from 165 authentic grape samples collected in well-defined vineyards of France situated in Alsace, Burgundy, Beaujolais and the Loire Valley. The approach was also applied to smaller production areas or Appellations (Cotes de Nuits, Cotes de Beaune, Cotes Chalonnaises and Maconnais). Discriminant analysis classified the samples into typical Appellations with nearly 100% efficiency. The separation of 112 Spanish

and English wines according to geographical origin was achieved by inductively coupled plasma mass spectrometry (ICP-MS) analysis of 48 elemental concentrations (Baxter *et al.*, 1997). The data was examined using canonical discriminant analysis. This was able to unequivocally identify the production origin of Spanish wines from three different regions (Somontano, Rioja and Cariñena). It was also possible to completely differentiate English and Spanish white wines. The authors found that if red and rose wines were included in the Spanish set, the English and Spanish populations could be distinguished with 95% accuracy. The elements identified as providing the majority of geographical separation were Cd, Cr, Cs, Er, Ga, Mn and Sr. The authenticity and geographical origin of wines produced in Slovenia were investigated by Ogrinc, Kosir, Kocjancic, and Kidric (2001) using a combination of IRMS and SNIF NMR methods. Grapes and wines produced in the three different wine-growing regions of Slovenia in 1996, 1997, and 1998 were analysed. The stable isotope data were evaluated using principal component analysis and linear discriminant analysis. Discrimination between coastal and continental regions was achieved with the deuterium/hydrogen isotopic ratio of the methylene site in the ethanol molecule (D/H)<sub>2</sub>, which relates mainly to the fermentation water from the grapes and  $\delta^{13}\text{C}\text{‰}$  values. Furthermore, inclusion of  $\delta^{18}\text{O}\text{‰}$  in the PCA and CDA resolved the two continental regions Drava and Sava. Almeida and Vasconcelos (2001) reported the use of quadrupole ICP-MS to determine the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of eight Portuguese wines, from five regions, and two from the French region Bourdeaux. The results suggested that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measured by Q-ICP-MS was a promising fingerprint of wine origin, however Quadrupole ICP-MS is generally accepted as being insufficiently precise to routinely use the technique for geographical origin assignment (Barbaste *et al.*, 2001). TIMS or multi-collector magnetic sector field ICP-MS are generally accepted as the methods of choice for measuring  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Barbaste, Robinson, Guilfoyle, Medina, & Lobinski, 2002).

A discussion of the relationship between meteorological data and the isotopic composition of wines, from Franconia in the context of chaptalisation and geographical origin, has been presented by Christoph, Rossmann, and Voerkelius (2003). The wines were produced in the region of Franconia and Lake Constance between 1992 and 2001. Factors such as the amount of rainfall immediately prior to grape harvest were shown to have a significant effect on interpretation of  $\delta^{18}\text{O}\text{‰}$  and  $\delta^2\text{H}\text{‰}$  data. A follow-up study examined the same isotopic parameters in Hungarian and Croatian wines produced between 1997 and 2001 (Christoph *et al.*, 2004). The paper discusses the main analytical parameters and controls for authentication and traceability of wines in Europe and 'Third Countries'. The Hungarian wines

exhibited little or no isotopic variation with the growing region. However, the Croatian wines showed significant differences in  $\delta^{18}\text{O}\text{‰}$  values between continental and coastal cultivation caused by the hot and dry climate near the Adriatic Sea. The characterisation of Swiss wines using multi-element concentrations, isotopic ratios and classical parameters (e.g. %v/v ethanol, pH, total acidity, volatile acidity, malic acid, fructose, tartaric acid, lactic acid, succinate, citric acid, glycerol, 2,3-butandiol, dry matter and relative density) were combined in the geographical characterisation of Swiss wines (Gremaud, Quaile, Piantini, Pfammatter, & Corvi, 2004). Multivariate analysis permitted differentiation of four main production zones. These were defined as Tessin, Valais, Romandie and Alemanique. A fifth zone (Graubunden) was differentiated in the 2001 vintage. The results demonstrated that the variables  $\delta^{18}\text{O}\text{‰}$  of the wine water, strontium, rubidium, and %v/v ethanol, were the most significant for provenance determination.

### Other commodities

There has been an increased awareness by consumers across Europe regarding the origin of the vegetable oils they buy. There are many branded goods declaring provincial high quality characteristics and this is especially the case for extra virgin olive oil (EVOO). A large number of chemical and sensory parameters, such as fatty acids, triglycerides, unsaponifiable matter, iodine value and so on, have been combined with multivariate statistics, but they do not provide a secure classification of geographical origin to verify PDO labelling (Aparicio, 1999). This is where geographical classifications based on the stable isotope ratios of oxygen and hydrogen, when combined with other multi-element data, offer the best analytical strategy for accurately verifying the geographical origin of cultivation. Initial research into the use of  $^{18}\text{O}$ -pyrolysis continuous-flow IRMS, to obtain information about the geographical origin of olive oil samples, was carried out by Angerosa *et al.* (1999). They determined the  $\delta^{13}\text{C}\text{‰}$  and  $\delta^{18}\text{O}\text{‰}$  values of whole olive oil, sterols and aliphatic alcohol fractions from fruits of *Olea europaea* L. produced in Greece, Italy, Morocco, Spain, Tunisia, and Turkey. The results permitted provincial classification of the oils. However, there was some misclassification observed for oil samples coming from neighbouring countries with similar climates.

### Conclusions

Currently, trace element and isotope ratio analysis offers the most promising hypothesis driven approach to establish the geographical origin of food. However, it is important to mention some common limitations and reservations that are

highlighted in the literature and some general methodological considerations.

Firstly, rapid profiling techniques (e.g.  $^1\text{H}$  NMR) and classical parameters, such as the concentration of specific organic compounds in food, should not be overlooked as they often provide invaluable additional information to aid interpretation. For example, the concentration of beta-carotene in dairy products indicates if the milk used in production was collected during periods of pasture feeding. This in turn may provide production-season information in temperate zones and ensure that appropriate meteorological data is applied in the interpretation of  $\delta^{18}\text{O}\%$  and  $\delta^2\text{H}\%$  data. A number of research articles reviewed above are described as 'preliminary' as the authors acknowledge the relatively small numbers of authentic samples they have included in their studies of geographical origin. Is the number of samples in the database sufficient to be a true reflection of the commercial sample population they will ultimately be compared against? Paradoxically, as databases are expanded and the number of samples analysed increases the natural variation in elemental composition and isotope ratios increases so that geographical origin interpretation actually becomes more complex, due to natural variation and overlap in measured parameters from the authentic sample populations. Authentication strategies involving the use of multi-isotopic and multi-elemental parameters have been facilitated by increasingly rapid measurement procedures. The use of 'high productivity techniques' such as multi-element continuous-flow IRMS and multi-collector ICPMS enable large quantities of data to be rapidly generated. In principle, the most powerful methods are generally those that combine as many of the elemental and isotopic signatures as possible, into a multi-dimensional authenticity matrix where natural variation is more readily constrained and detection of mis-description is difficult to subvert. Consequently, this analytical approach demands proper data pre-treatment. Procedures such as normalisation, transformation, weightings, prior probabilities etc play an important role in the interpretation of the data with multivariate software packages. It is then critical that the robustness of the multivariate model is tested with techniques such as cross-validation and 'blind-testing'.

It is extremely important to quantify the repeatability and reproducibility of multi-element and multi-isotopic measurements. In order to make meaningful origin assignments it is necessary to know the measurement uncertainty so that differences in elemental concentrations, or isotope ratios, for commodities from different geographical origins can be deemed as statistically-significant or not. Control of long-term measurement repeatability with matrix matched in-house reference material is essential if authentic databases are to be established over a number years. Furthermore, if databases are to be developed on a European-scale for

enforcement purposes, in the same way as the wine databank, then long-term reproducibility is also of paramount importance.

In the case of meat origin, there are many other confounding factors that must be considered during the construction of authentic comparative databases. The protein turnover-times in muscle tissue means that isotopic signatures will have a lag-time before they reflect changes in feeding regime and changes in feed water as a result of livestock movement, often prior to slaughter. The homogeneity of elemental and isotope signals between different cuts of meat, or tissue types, from the same animal also needs to be firmly established and characterised. As with food markets, the globalisation of feed markets and the desire to obtain cheap sources of feed may mean that certain elemental and isotope signals will not reflect the region of production. It is therefore important to recognize these restraints on geographical interpretation until they have been characterised by appropriate controlled feeding experiments. Similarly, it is important not to use geographical models that are heavily dependent on trace element markers from manufacturer's processes as this could lead to uncontrollable variations. However, this does raise the alternative possibility of anti-fraud, isotopic or elemental labelling of premium food products that do not pose a threat to consumers.

In the longer-term, it is hoped that a deeper understanding of how meteorological and geochemical signatures are transferred into food systems may obviate the need for expensive comparative databases of authentic foods. Ultimately, this would allow the generation of isotopic and multi-element *maps* for foods from different geographical locations, which could be incorporated into traceability systems. For the moment though, there is a need for comparative databases to be established for premium foods and for these to be used as benchmarks in ongoing scientific developments in the near future. Overcoming the need for comparative databases in food provenance determinations will be an extremely challenging task.

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