Application of Isotope Analysis for Food Authenticity and Traceability: Progress and Challenges

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Abstract

With the development of the global food market, food authenticity has become the major concern for consumers. Building an effective food traceability system provides an approach for protecting regional brand, ensuring fair trade competition, and improving consumer confidence. There are several analytical techniques used for determining food authenticity include fluorescence spectroscopy, nuclear magnetic resonance spectroscopy, atomic absorption spectroscopy, gas chromatography mass spectrometry, liquid chromatography mass spectrometry, and isotope ratio mass spectrometry(IRMS). One of the most widely acceptable methods to provide information on the traceability of food is stable isotope ratio analysis, which generally includes various aspects of food productions. This paper reviews the principles of isotope analysis, outlines the requirements and the specific features of the technique in the area of food authentication and traceability, and surveys the applications of isotope analysis in different type of food production, and describes the progress of the development in techniques. It shows that stable isotope analysis has become a powerful tool for food authentication and traceability due to its advantages of high precision and efficiency. The recent progress of isotope analysis use in food authenticity and traceability is concentrated on three aspects: the food adulteration (e.g. juice, honey), the geographic origin traceability of food (e.g. olive oil, dairy productions), authenticity of organic food (e.g. beef, potatoes). The classical approaches investigating hydrogen, carbon and oxygen isotopes as well as strategies including other elements, such as nitrogen and sulfur, are reviewed. In addition, the limitations and future research directions of isotope analysis in food authenticity and traceability are proposed.

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1. Introduction

1.1 Food authenticity and Food Fraud

In recent years, consumers are increasingly demanding informative labels of food provenance and authenticity. Generally, the label or description of food provides its ingredients, geographical origin, processing technology, production years and genetic identity (Woolfe & Primrose, 2004). An authentic food must be the one that strictly complies with a declaration by the producer. The information given by the food label description is essential for consumers to make decisions about their diet and the food they buy. Consumer choices may show their eating customs (e.g. vegetarianism, organic food preferences), health concerns (e.g allergic to some specific components), or religious requirements (e.g. pork prohibition for Muslims and Jews) (Kelly et al., 2005; Laursen et al., 2013).

Many factors determine the overall quality of food, include, but not limited to a nutritional value, freshness, stability, geographical origin, the transportation process, contaminants, and microbiology. The deliberate adulteration and providing misleading information to any part of food supply chain will cause the food fraud. Food fraud is a combined term that is defined as intentional deception using food for economical gain. The common action of food fraud includes: deliberate counterfeiting, mislabeling, adulteration, substitution, addition, dilution, grey market, tampering, mislabel of food ingredients, or food packaging; or false or misguide statements describe about a product with the intention of deceiving consumers (Kamm et al., 2001; Karlsen et al., 2013). For example, organic food fraud is a ‘potential’ problem in a food market (Shears, 2010). As

the trend of purchasing organic food starts to dominate the global market, consumers are increasingly aware of healthier, safer and more environmentally friendly organic production when compared to the conventionally produced foods. The price of organic food is typically much greater than food produced by conventional practices. Substitution with conventional produced food enables the producer to have a motivation for fraudulent activities to gain greater profits (Brown & Sperow, 2005; Giovannucci et al., 2009; Winter & Davis, 2006). Also, the growth of demand and profitable export markets result in production lagging behind supply. The use of fertilizer is a key factor for organic farmers to be considered. The poor efficiency of organic fertilizers may create incentives for farmers to increase yields by planting vegetables with artificial fertilizers and pesticides or mislabelling of conventional vegetables to catch up with rising demands (Vinci et al., 2013). For example, a major case of organic food fraud “Gatto con gli stivali” or “Puss in Boots” in Italy was reported in 2011(Ciolo, 2012). During 2007 to 2011, tons of conventional foods (include vegetables, fruit, and cereal crop) which are intentionally mislabeled as organic foods were imported and sold on the market. About 21 companies were suspected to be involved in this case that cause huge fiscal loss (Tahkapaa et al., 2015).

Another example is the adulteration of meat. The processing techniques of meat provide the opportunity for producers to add water beyond the allowed requirement in cured meat, which is illegal in the UK and USA. Since the amount of added water is not required to state on the food label, some companies take advantage of this legal loophole. In 2008, the company named “Ye Olde Oak” in UK was reported for selling the meat in its ham

with inferior quality. The meat is made up of 55% meat and 37% water. The remaining 8% is additives including gums and polyphosphates, sugar and salt (Shears, 2010).

The global food supply system is expanding, complicating, and lengthening. It was stressed from population growth, rising demands for limited resources and changing diets. In this case, companies need to pay more attention to the potential of food fraud and effectively help their customers discriminate and reduce the fraud risks. Thus, verifying food authenticity plays a key role in ensuring consumer health, protecting consumer rights, preventing fraudulent product and deception in trade competition, keeping sustainable development of national agricultural resources (Badia-Melis et al., 2015).

1.2 Food Traceability

Traceability is clarified as the ability to trace the origin, processing or location of that which is taken into account. It should represent the provenance of materials, the process of production, and the locations the food may be delivered. Food traceability means the capacity to trace a food from the whole process of production and distribution. Traceability allows for actions (like a product recall) be carried out quickly and effectively when something is below the standard. When a potential food safety or quality problem is identified, whether by a food business or a government agency, an effective traceability system can help to protect consumers rights. Traceability allows food businesses to aim at the product which has a food safety or quality problem, reduces the risk to trade and avoid any potential public health problem. It is important for all food businesses to be able to trace products.

There are many modern techniques for food authenticity and traceability, such as Radio-frequency identification (RFID), Near Field Communication (NFC), Isotope analysis, and DNA barcoding. Isotope ratio mass spectrometry (IRMS) has been used to detect fraud in food production since the early 1970s. In recent years, stable isotope analysis has gained increasing attention in control of food quality and provenance due to the high efficiency and precision of this method. Generally, the isotope analysis is focus on three aspects of food authenticity and traceability: (1) Discrimination of food adulteration (2) tracing the geographical origin of food productions (3) verifying organic food.

2. Isotope analysis for food authenticity and traceability

2.1 Principle of isotopic analysis

Isotopes are the atoms having different numbers of neutrons but the same number of protons. Isotopes of a certain element therefore occupy the same position of the periodic table, and consequently, have the same chemical properties but different masses. Generally, isotopes are classified as two types: stable isotope and radioactive isotope (unstable isotope). The nuclei properties of stable isotopes do not change over time while the unstable isotope decrease in mass and decay over predictable periods (Hoefs, 2013; Michener & Lajtha, 2008; Vanhaecke & Degryse, 2012).

Early in 1912, J.J Thomson, a physicist in England discovered the existence of isotopes. However, initially the study of isotopes did not attract much attention owing to the lack

of investigation techniques and the expensive research costs. With the invention of liquid chromatography–mass spectrometry and the discovery of ^{13}C tracking technology, scientists started to use the techniques of isotope analysis (White, 2013). The application of isotope analysis has the advantage of high accuracy and efficiency. As a consequence, isotope analysis has widespread applicability in different fields include food authenticity, medical sciences, geology, and biology (Criss, 1999; Dansgaard, 1964; Fry, 2007; Schauble, 2004).

Isotope fractionation is the key processes which affects the relative abundance of isotopes in natural materials. Two isotopes of an element have similarities in their chemical behavior owing to the same electronic configuration. However, subtle chemical effects (reaction rates and bond strength) result from the difference in mass of isotopes (Hoefs, 2013; Michener & Lajtha, 2008). Bonds with lighter isotopes vibrate faster compared to heavier ones when the atoms have the same bond strength. Faster oscillation means that the molecule has higher vibration energy and less additional energy is needed to break the bonds. Therefore lighter isotopes form more unstable, weaker bonds. Differences in bond strength and in the kinetics processes between isotopes lead to a change in the partitioning of heavy and light isotopes between a source substrate and the products, which are termed as isotope fractionation (Friedman & O'Neil, 1977). There are two basic types of isotope fractionation, kinetic isotope (unidirectional) effects, and equilibrium effects. The equilibrium isotope reaction happens when a reaction approaches equilibrium. In such a system, the heavy isotopes are preferentially enriched in denser phases or the chemical compound with the stronger bonds. Equilibrium isotopic

fractionation is thermodynamically influenced, which means it is determined by temperature but does not depend on how the reaction happens (White, 2013). Kinetic isotope fractionations occur when bonds are broken or rearranged by an irreversible reaction. During this process, the reaction rates are temperature and mass-dependent. The lighter isotopes that have weaker bond strength react more rapidly and preferentially accumulate in the production since their bond are easily broken (Criss, 1999; Schauble, 2004).

Many physicochemical effects (e.g. evaporation, melting, absorption) can influence the variation of stable isotopes abundances. The stable isotope composition of natural materials can be changed by the process of metabolic turnover or the influence of environmental growing conditions, thus leaving a fingerprint in the tissues which reflects the nutrients, feeds and water quality (De Groot, 2004). Tracing these fingerprints can be used as an indication of origin and quality of animal and plants production. The stable isotope ratios show the relationship between light and heavy isotopes of the element in the natural material. The found of isotopic ratios for the elements H, C, N, O and S demonstrate that the lighter isotopes to be the most abundant. For the heavier elements, the ratio between light and heavy isotopes is more balanced (Michener & Lajtha, 2008; Schauble, 2004). Table 1 shows the types of different isotope fractionations in natural materials and the way in which they can be used for food traceability.

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 (Kelly, 2005).

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

Isotopic data are reported in two ways: absolute ratios and relative to standard (delta notation). α notation is the fractionation factor used to report isotope differences between two phases:

$$\alpha_B^A = \alpha_{A-B} = \frac{R_A}{R_B} \qquad \text{Eq. (1)}$$

In fact, the changes in isotope values are typically around the third or fourth significant figure. In order to determine the ratio reliably and accurately, the actual ratio measured in research samples are compared to a standard isotope ratio, and are given as permil deviations from a standard (Baskaran, 2011) :

$$\delta_{Sample} = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \qquad \text{Eq. (2)}$$

The international community uses various standard reference materials for these light elements measurements: VSMOW (Vienna Standard Mean Ocean Water) for $\delta^{2}H$ and $\delta^{18}O$. VPDB (Vienna Pee Dee Belemnite) for $\delta^{13}C$ and $\delta^{18}O$, atmospheric air (AIR) for $\delta^{15}N$ and VCDT (Vienna Canyon Diablo Troilite) for $\delta^{34}S$. Table 2 shows

examples of these standards (Coplen, 1995).

Table 2. Isotopic composition of the primary reference standard (Coplen, 1995)

Primary reference material	Isotope ratio	Accepted value ($\times 10^6$, ppm) (with 95% Confidence interval)
VSMOW	$^{2}H/^{1}H$	155.76 ± 0.10
	$^{18}O/^{16}O$	2005.20 ± 0.43
	$^{17}O/^{16}O$	373 ± 15
VPDB	$^{13}C/^{12}C$	11237 ± 9.0
	$^{18}O/^{16}O$	2067.1 ± 2.1
	$^{17}O/^{16}O$	379 ± 15
AIR	$^{15}N/^{14}N$	3676.5 ± 8.1
VCDT	$^{34}S/^{32}S$	45004.5
	$^{33}S/^{32}S$	8100.0

Fractionations of isotopes are commonly as not evident in the heavier elements, since the mass nuclides are much higher compared to the mass differences of the isotopes. For heavier elements like Pb and Sr, the stable isotope ratios (e.g. $^{87}Sr/\ ^{86}Sr$) often depend primarily on the mineralized element originating from bedrock, sediments and ore bodies which can be used to trace the origin agricultural products, and provide information of the geographical area and the transportation process of a material (Baskaran 2011; Kendall & McDonnell, 2012).

From the food authentication perspective, stable isotope analyses can be exploited to trace the geographical origin of plant and animal products, agricultural practice used, as well as to indicate the difference in production techniques and processing methods of certain product types (Badia-Melis et al., 2015).

2.2 Methods and techniques

Isotope ratio mass spectrometry (IRMS) is a useful tool to measure the abundances of the isotopes of natural material. This instrument is made of three basic elements: an ion source, magnetic analyzer and an ion collector (Scrimgeour & Robinson, 2003; Hoogewerff et al., 2003). Only gases are analyzed by the light isotope in IRMS, thus the analytes need to be changed into a gas phase (H_2, N_2, CO, CO_2 and SO_2) which is ready to be ionized. In this case, carbon dioxide is produced from organic compounds through oxidation with copper oxide. Hydrogen is prepared by reaction with a metal like zinc in reductive conversion of water. For the determination of the ^{18}O content of water, another technique with carbon dioxide is used. The ions are separated by a permanent magnet or an electromagnet (Kelly, 2003). Mass and charge determines the radius of deflection. Ions with the same mass to charge ratio have the same deflection radius and heavy ions are deflected less than light ions. This deflection focuses the ions that form several beams that enter the ion collectors. Every beam is quantified using Faraday-cup in ion collectors (Hoogewerff et al., 2003). The discharges of ion currents produce the voltage in the cup that is transformed into digital signal. The application of IRMS to authentication has been used for various food productions such as honey, fruit juices and wine (Kelly, 2003). Scientists used IRMS to differentiate Swiss tomatoes from foreign tomatoes using carbon and nitrogen isotopes. Multi-element isotope analysis like carbon, nitrogen, oxygen, hydrogen was utilized for beef authenticity (Sun, 2008; Boner & Rstel, 2004). Several different interfaces are used to prepared samples for the IRMS, the most widely used are elemental analyzers (EA-IRMS) and gas chromatographs (GC-IRMS) (Werner & Brand, 2001). EA-IRMS involves sample pre-treatment and is appropriate for the analysis of

non-volatile materials (e.g., foods, drugs) even though it shows only an average isotope ratio value of the whole sample. However, GC-IRMS can do isotope analysis of complex mixtures, including useful information and a high identification power (Sun, 2008).

Laser absorption spectroscopy (LAS) has been used for isotope analysis from the 1990s. This relatively small-sized and easy-to-operate technique solves many problems that isotope ratio mass spectrometry has (e.g. high cost, large space requirement, time-consuming chemical conversion) (Wu et al., 2014; Rosario et al., 2010). The principle of this method is that different isotopes in the same molecules absorb light at different wavelengths. Some molecules have strong absorption bands. At appropriate instrumental resolution, the rotational-vibrational absorption features of individual molecules can be found and different isotope compositions are identified (Kerstel, 2005; Aggarwal, 2006). LAS can provide measurements continuously with long time coverage. Through comparison with reference materials, the isotope ratios of the sample can be determined. Laser analysis is often used to determine the $\delta^{2}H$ and $\delta^{18}O$ in ground and surface water (Rao, 2012).

Another commonly used technique for isotope ratio analysis is nuclear magnetic resonance spectroscopy (NMR). NMR take advantages of the phenomenon that nuclei absorb and emit electromagnetic radiation energy at specific resonance frequency in a magnetic field (Renou et al., 2004; Angerosa et al., 1999; Piasentier et al., 2003). All isotopes have magnetic properties, which allow NMR to detect the specific isotope differences for each isotope constitution of this molecule. NMR can analyze isotopes

such as ^{1}H and ^{13}C. The most widely used analyte for NMR is ^{1}H, since it has high sensitivity and isotopic abundance in the natural world, especially for organic compounds. In recent years, ^{13}C and ^{1}H are frequently used to trace the origin of food. A very useful nuclear magnetic resonance spectroscopy to measure specific natural isotope fractionation is SNIF-NMR. This technique can provide information of deuterium within the compound, which is not feasible by IRMS. With this advantage of SNIF-NMR, it is often used to trace the origin and the chemical pathway of formation of compounds containing D isotope (Sun, 2008; Cross et al., 1998). SNIF-NMR was delivered by European Union as an official method to for wine traceability. The sugar from the same the same photosynthesis pathway(e.g. beets and oranges) can be discriminated by D/H analysis using SNIF-NMR (Zhang et al., 2002; Thomas et al., 2010).

2.3 Different isotopes for food authenticity and traceability

2.3.1 Carbon

The element carbon are found in nature consists of 98.89% ^{12}C atoms and 1.11% ^{13}C atoms. The CO_2 produced by organics in the terrestrial soil is rich in ^{12}C but poor in ^{13}C; however, that in the atmosphere has slightly higher ^{13}C levels. The carbon in plants comes from the CO_2 in the atmosphere (Zhang et al., 2002). Plants transform CO_2 into carbohydrates through photosynthesis. An important fractionation effect of carbon stable isotopes occurs during photosynthesis. The fractionation of carbon isotopes inside plants mainly happens when CO_2 enters the chloroplasts of plants, a photosynthetic carboxylation reaction produces the primary product, or the primary product is transformed into the intermediate product in the plants. In the first process, CO_2 passes

through the cell walls of plants through diffusion and enters chloroplasts (Haswell & Walmsley, 1998). Photosynthetic carboxylation reactions fix $^{12}CO_2$ into the primary product of the reaction. During the photosynthetic carboxylation reaction, $^{12}CO_2$ is preferentially absorbed; thus, the $\delta^{13}C$ inside plants is lower. Therefore, the amount of $\delta^{13}C$ in plants is obviously less than that in atmosphere (O'Leary, 1988). Different types of photosynthetic carboxylation reactions can lead to different ^{13}C depletions in plants and result in carbon stable isotope ratio differences. Moreover, factors like temperature, precipitation, and CO_2 concentration also affect the amount of $\delta^{13}C$ in plants.

Owing to the different types of photosynthetic carboxylation reactions, one can divide plants into C_3, C_4, and CAM plants. C_3 plants which follow Calvin cycle are using ribulose bisphosphate (RUBP) carboxylase to fix carbon dioxide, while C_4 plants which follow Hatch-Slack cycle are using phosphoenolpyruvate (PEP) carboxylase to capture CO_2. CAM plants are found in arid areas. They open stomata in the leaves at night to capture CO_2 (Kiriluk et al., 1995). C_3 plants come in a wide variety and grow in warm and humid regions. C_4 plants include corn and sugarcane, which grows in warm and dier environments. CAM plants metabolize CO_2 through sedum acid. They include succulents that grow in arid environments, like orchids, cacti, and dill (Schleser et al., 1999). The ratio of $\delta^{13}C$ in C_3 plants ranges between -34‰and -22‰, averaging is -27±2‰. The ratio of $\delta^{13}C$ in C_4 plants fluctuates between -19‰ and -9‰. The most common is -13±2‰. The ratio of $\delta^{13}C$ in CAM plants which have a wide range, from -38% to -13%, with an average of -17±2‰ (Bender, 1968).

Temperature acts on the $\delta^{13}C$ ratio mainly through impacts on the fractionation effect of carbon stable isotopes in plants. On the one hand, it directly affects the activity of enzymes that participate in photosynthetic carboxylation reactions. On the other hand, it interferes with stoma's absorbing water and CO_2 and the concentration of CO_2 within the air cavity (Stuiver & Braziunas, 1987). Research has shown that plants tend to enrich light carbon isotopes (^{12}C) during the process of organic synthesis. Researchers around the world have focused on the relation between temperature and $\delta^{13}C$ ratio. Most research shows that temperature and $\delta^{13}C$ are negatively correlated: the abundant of $\delta^{13}C$ increase as the temperature falls (Sage et al., 1999). As Farmer indicated, the $\delta^{13}C$ of ulmus americana and the average temperature of summer (from April to September) are negatively correlated (Farmer, 1979). Damesin investigated the relation between the average annual temperature and the carbon isotope composition of four C_3 plants in North China. He found that the $\delta^{13}C$ of all four and temperature change were negatively correlated. Only their sensitivities to temperature change differed. However, researchers have come to the opposite conclusion as well (Damesin et al., 1997). Schleser and colleagues found that the $\delta^{13}C$-T (time) relation was nonlinear. They revealed that it has the characteristics of a parabola, where the inflection point of the parabola corresponds to the best temperature for growing the plant. Thus, we can see that the relation between temperature and $\delta^{13}C$ is complicated. Different situations require different analyses(Schleser et al., 1999).

2.3.2 Nitrogen

Commonly, scientists define the $^{15}N/^{14}N$ in the atmosphere as the standard ratio of $\delta^{15}N$, which means that the $\delta^{15}N$ in the atmosphere is 0‰. In ecosystems, nitrogen isotopes are modified by animals and plants through different processes. In the first process, organisms absorb nitrogen through nitrogen fixation or other ways. In the second process, nitrogen is absorbed and assimilated inside organisms. That is how nitrogen isotopes are distributed and redistributed inside organisms. In the third process, organisms eliminate nitrogen through chemical and physical reactions like denitrification and gas volatilization. The major fractionation effects of nitrogen stable isotopes happen both in the second and third processes (Junk & Svec, 1958; Shearer & Kohl, 1986). The ratio of $\delta^{15}N$ in the soil ranges is between -6‰ and 16‰. The abundance of ^{15}N in nitrogen of the soil is usually higher than that in the N_2 in the atmosphere. During nitrogen fixation, organisms and organizations like rhizobion are able to fix nitrogen can absorb nitrogen directly from the atmosphere. Fractionation effects are not significant during this process. Thus, the $\delta^{15}N$ that enters organisms through nitrogen fixation is similar to the $\delta^{15}N$ in the atmosphere. Nitrogen is transformed and transported inside organisms (Mariotti, 1983). The main reaction is as follows:

$$N_2 \leftrightarrow \text{Organic N} \leftrightarrow NH_4^+ \leftrightarrow NO_2 \leftrightarrow NO_3^- \leftrightarrow N_2O \qquad \text{Eq. (3)}$$

This process includes decomposition, mineralization, and nitrification. The $\delta^{15}N$ produced in mineralization is slightly lower than that of the substrate before mineralization. During nitrification following mineralization, nitrogen fractionation can reach 60‰. Meanwhile, the NO_3^- produced in nitrification reactions will enrich ^{15}N. However, different reactions have different intensities; the fractionation during

nitrification reactions is greater than during mineralization reactions. That is another reason ^{15}N is enriched. On the other hand, the process through which ammonium ions become ions and are denitrificated into waste eliminated from plants, the reaction speed of ^{15}N is slower than that for ^{14}N, which causes more ^{14}N to be released. Thus, the $\delta^{15}N$ of plants and in the soil is generally higher than that of the atmosphere (Choi et al., 2006).

Common organic fertilizers are made from human and animal manure or the combustion of plants through heaping, fermenting, and sterilization. Chemical fertilizers are made from air N_2 through reactions under high temperature and pressure conditions. The nitrogen of organic fertilizers is the organic residue of wastes after fractionation and enrichment (Bateman et al., 2005). The $\delta^{15}N$ values of organic fertilizers are therefore higher than that of the air. The nitrogen of chemical fertilizers comes directly from the air, without any fractionation. Moreover, when plants absorb nitrogen, they take up nitrogen from inorganic nitrogen sources and nitrogen fixation (few plants can utilize molecular nitrogen through nitrogen fixation), rather than from air. Thus, the type of fertilizer can affect the $\delta^{15}N$ of plants. The $\delta^{15}N$ of plants reflects agricultural activity and even the region involved (Broman et al., 1992).

Research has indicated that different types of chemical fertilizers share similar $\delta^{15}N$ ratios. That is because the nitrogen is coming from a single source, without any processes that fractionate nitrogen isotopes. However, different organic fertilizers may have different $\delta^{15}N$ ratios. For example, the $\delta^{15}N$ of poultry manure is 2.7‰, that of milk cow manure is 4.5‰, and that of pig manure is 11.6‰ (Rogers, 2008). Martinelli (1999) and colleagues

conducted research on cole, barley, and wheat to test the $\delta^{15}N$ when they are not fertilized and when they are fertilized by pig manure, cow manure, and chemical fertilizer (Martinelli et al., 1999). The researchers found that the $\delta^{15}N$ follows the following relation: liquid pig manure > solid cow manure > no fertilizer > chemical fertilizer. They proposed that the abundance of $\delta^{15}N$ is directly related to the type of fertilizer, the form of nitrogen, and the amount of effective nitrogen. Moreover, the amount of fertilizer affects the abundance of ^{15}N in the plants as well (Choi et al., 2006). Bateman (2005) found that the $\delta^{15}N$ of carrots is positively related to the amount of organic fertilizer. When the amount of fertilizer exceeds a certain amount, the $\delta^{15}N$ tended to be similar to the fertilizer $\delta^{15}N$ (close to ±6.5‰) and was negatively related to the amount of ammonium nitrate. With increasing ammonium nitrate, the abundance of ^{15}N decreased (close to ±2.5‰), and the $\delta^{15}N$ value remained about the same when it compared to chicken manure and no fertilizer. This is thought to be due to the fact that carrots absorb less nitrogen from outside nitrogen sources (Bateman et al., 2005).

Biological nitrogen fixation is the only way for the N_2 of the atmosphere to get into ecosystems. Some plants can acquire nitrogen directly from the atmosphere through nitrogen fixation. However, the nitrogen that comes through biological nitrogen fixation does not exhibit significant fractionation, so the $\delta^{15}N$ of non-legumes and other plants that are unable to fix nitrogen (3-4‰) is higher than that for legumes (0-1%) (Vinci et al., 2013) The $\delta^{15}N$ of plants and temperature are positively correlated because temperature affects the activity of microorganisms in soil. When temperature rises, nitrifying bacteria and ammonifying bacteria become more active, leading to faster soil mineralization and

nitrification. In this way, ^{14}N which is more reactive will be consumed more quickly, and ^{15}N will be enriched in the residual soil (Marshall et al., 2007).

Precipitation is an important factor that can affect the $\delta^{15}N$ value of plants. In a lot of areas, the $\delta^{15}N$ of plants rises with lower in average annual precipitation, which means that the $\delta^{15}N$ ratios in arid areas are higher than those in humid areas. However, Rogers (2008) found that this negative correlation only suits non-biological-nitrogen-fixation plants (like rice and wheat). For those plants that are able to fix nitrogen (like legumes), the $\delta^{15}N$ ratios of which do not follow this trend (Rogers, 2008).

2.3.4 Hydrogen and Oxygen

Hydrogen and oxygen of plant and animal tissues are commonly from water. Thus, these two isotope value are affected by the process which have effect on water. The physical and chemical process like evaporation, melting, precipitation can cause the hydrogen and isotope fractionations. The water evaporated from ocean have heavier isotope than the clouds. Heavier isotopes accumulate in the liquid phase and will fall first in the precipitation. From the inland to the high altitude, the rain water gaining more and more heavier isotopes with the physical and chemical process happen. (Craig, 1961; Marshall et al., 2007; Mook & Rozanski, 2000). Commonly, $\delta^{18}O$ and $\delta^{2}H$ values of meteoric water have negative correlation with temperature, and positive correlations with distance from the sea, the altitude/latitude and amount of rain water (Yurtsever & Gat, 1981; Dansgaard, 1964).

Stable oxygen and hydrogen isotope ratio of animal tissues and plants reflects isotope composition of drinking water and feeds for former one and the water irrigated for latter one.(Clark and Fritz, 1997, Schmidt et al., 2001). It is also useful for tracing the geographical origin of meat and vegetable from hydrogen or oxygen isotope values. In addition, $\delta^{18}O$ and $\delta^{2}H$ value of organic compounds present in animal products, such as milk, butter and cheese, also present a close relationship with the isotope value of water consumed by animals, which can provide information for the provenance of these foods.

2.3.3 Sulfur Isotopes

Sulfur is an important non-metallic ore-forming element that exists in all natural environments in the form of reduced sulfur compounds and sulfate. The content of sulfur isotopes changes in a wide range. The most enriched one can have a $\delta^{34}S$ ratios reaching 120‰ and as low as -65‰ (Kelly et al., 2005). Change in sulfur isotopes is mostly caused by two mechanisms. One is the isotopic kinetic effect in the process of sulfate bacterial reduction, and the other is chemical exchange reactions between sulfur compounds and sulfate (Rossmann et al., 2000). Earlier research indicated that under similar climate conditions, $\delta^{34}S$ changes greatly when the geological characteristics are different. The geological characteristics (volcanic or sedimentary and presence of acid or alkaline rocks) of a location can affect its soil $\delta^{34}S$, thereby influencing the plants that grow in the soil (Kelly et al., 2005). Meanwhile, the smoke released by modern industrial technology can affect the soil $\delta^{34}S$ in the form of dry and wet deposition. The use of

fertilizer contains sulfur affects the soil $\delta^{34}S$, too. The change of $\delta^{34}S$ inside animals and plants is not understood as well as that of other elements, but it does not appear to cause significant fractionation. The use of marine derived feed and sulfate-containing splash deposited in the form of aerosols in coastal areas causes the animals in the region to have higher $\delta^{34}S$ ratios (Camin et al., 2007). Thus, the sulfur isotope compositions of organisms are related to their source and can supply certain geographic source information.

2.3.4 Strontium Isotopes

Strontium is an alkaline earth metal element of group IIA and has four isotopes in nature, such as ^{84}Sr and ^{88}Sr. Among them, ^{87}Sr comes from the decay of ^{87}Rb, for which the half-life is 4.9×10^{10} years. The $^{87}Sr/^{86}Sr$ ratio of animals and plants is correlated to the strontium mineralization in the bedrock that organisms can use. Biological processes like absorption and metabolism can change the ratio of stable isotopes such as Sr, C, N, H, O, and S. However, a certain amount of ^{87}Sr that comes from radioactive decay can be used as an index to trace its geographic source (Ghidini et al., 2006). The $^{87}Sr/^{86}Sr$ ratio is determined by the type of rock and soil, rather than human activities, climate, and changes in the production season. Different types of rock have different $^{87}Sr/^{86}Sr$ ratios. For example, the $^{87}Sr/^{86}Sr$ ratio of alkaline rock (basalt and carbonate) is lower and that of acid rock (granite that contents more silica) is higher. This is because the Rb/Sr ratio rises as time passes. Thus, the ratio of strontium isotopes is very helpful for identifying the source of animal and plant production, since different isotopes come from different

regions. When organisms are from similar climates but different regions, which means that they have similar $\delta^{18}O$ and $\delta^{2}H$ levels, their strontium isotope ratio could be a better index, as it can provide petrology information (Kelly, 2003).

2.3.5 Boron Isotopes

Boron has two stable isotopes, ^{10}B and ^{11}B. They have larger relative mass differences, and a chemical isotope effect exists among different boron-containing materials. All those features make boron suitable for isotope ratio analysis. Boron isotope fractionation mainly takes place in aqueous systems, within which boric acid [$B(OH)^{-}$] and borate anion [$B(OH)^{-}_{4}$] will have exchange interactions along with changes in pH value. The ^{11}B of seawater is 40‰ higher than that of other land substances. The adsorption of B clay by the low temperature alteration of oceanic crust and isotopic fractionation caused by carbonate minerals can lead to the enrichment of ^{11}B in seawater. The $\delta^{11}B$ ratio of carbonate is much lower than that of seawater, which means that borate will bind to carbonate structures during deposition. The boron isotope compositions of basalt in different tectonic environments also vary. Beside natural factors, boron fertilizers used in agriculture will affect the $^{11}B/^{10}B$ ratio, which also leads to large differences in boron isotope levels in soil (Coetzee & Vanhaecke, 2005).

3. Current Applications in Food authenticity and traceability

3.1 Discrimination of Adulteration

3.1.1 Juice

There are many reported benefits of fruit and vegetable juices (e.g. vitamins and added mineral content, helpful digestion, strengthen bones, prevention of cancer). In this case, the productions of fruit and vegetable juices have become very popular worldwide and the total volume consumed is growing rapidly. More than 95% of the traded juices belong to the fruit category. Among all the different kinds of utilized fruit for juice, orange and apple dominate the juice trading market (Rossmann, 2001). The economic value and high volume of fruit juice consumed create incentives for traders to adulterate. Typically, the methods used in adulterating juice are: dilution with water and addition of sugars, pulp wash, or addition of other fruit juices. These procedures are used alone, or in a combination that make the authentication of adulteration more difficult. All these types of adulteration pose little threat to the public's health and safety, however, they deceive the customers and create an unfair trading market (Lee, 1984).

Isotope analyses are commonly used in the detection of the undeclared addition of sugar and water in fruit juice. The methods of ^{13}C analysis of sugars are able to detect addition with C_4 sugars. Using apple juice as example, 95% of the soluble solids content of apple are the sugars: fructose, glucose and sucrose. The content range of these three sugar have identified. If the apple juice are adulterated with high fructose corn syrup (HFCS) originating from a C_4 plants which is a cheaper sugar containing 50% glucose and 40% fructose, carbon isotope ratio analysis can detect the $\delta^{13}C$ value changing.(Thomas et al.,

2010).

In 1980, Doner et al. investigated that the mean $\delta^{13}C$ value of apple juice was -25.4‰ by analyzing carbon isotope ratio of 18 varieties of apples. They observed that no significant change of $\delta^{13}C$ with respect to the type of apple or geographical provenance. The result showed that stable carbon isotope ratio analysis can be used to detect adulteration with high fructose corn syrup since the two samples had been shown to have different which is able to be detected and reasonably consistent values (Doner et al., 1980). Doner (1981) then tried to show the linear relationship between $\delta^{13}C$ and the relative content of apple juice in certain mixtures of apple juice and HFCS. Based on the mean value of $\delta^{13}C$ of apple juice, test samples with $\delta^{13}C$ values were greater than -20.2‰ could be treated as adulterated juice with a high percentage of certainty (Doner et al., 1981).

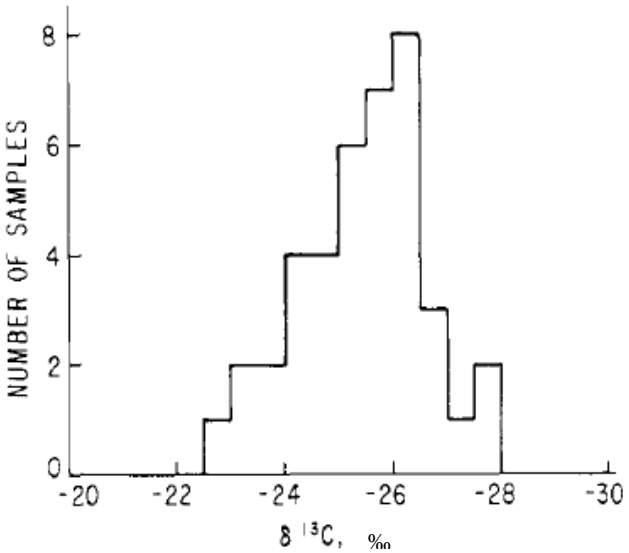


Figure 1. Distribution of $\delta^{13}C$ (‰) values among apple juice

To test whether the $\delta^{13}C$ value of individual components in apple juice consistent for the whole $\delta^{13}C$ value, Lee (1987) conducted an experiment to investigate the $\delta^{13}C$ value of each component of apple juice respectively (sugar, non-volatile acids and phenolic, pulp). They collected a variety of samples from Argentina, Mexico, New Zealand and USA. The mean value of $\delta^{13}C$ for all the samples was -24.2‰, which was consistent with the founding of Doner et al. (1980) The result demonstrated that the $\delta^{13}C$ of each component was relatively the same as those for the corresponding whole juice (sugar, -23.3‰; nonvolatile acids, -27‰; pheolic, -28.8%). In this case, there was no need to detect the $\delta^{13}C$ values separately for each component instead of the whole apple juice to verify the adulteration (Lee & Wrolstad, 1987).

When the source of the sucrose is C_4 plants, it is easy for stable carbon isotope ratio analysis to identify the adulteration, since the $\delta^{13}C$ value is different for juice and cane sugar or HFCS. However, sugar derived from C_3 plants such as beets, has similar $\delta^{13}C$ values for the sugar of many fruits. For example, the ratio of the content for sucrose, glucose and fructose in the orange juice is 2:1:1, which is similar to beet syrup (this make the $\delta^{13}C$ value of beets sugar as similar as orange juice). These facts make stable carbon isotope ratio analysis not adequate for detecting beet sugar addition (Benvenuti & Burgess, 2012). Doner et al. (1987) found that D/H ratio is a good index to show the difference between beet sugar and orange juice sucrose. Compared to beet sugar, the δD value in orange sucrose was significantly higher. The range of δD value of beet sugar was from -178‰ to -108‰, and the mean value was -143‰. However, the mean δD value of

orange juice sucrose was -27‰, with the range from -43‰ to -13‰. They also detected the $\delta^{18}O$ value of the samples; orange juice sucrose has higher $\delta^{18}O$ value than beet sugar. After analysis of this data, a discriminatory formula has been formed to show a 99.99% confidence zone about authentic orange juices. This research demonstrated that δD value has the potential to identify the juice adulteration (Doner et al., 1987; Benvenuti & Burgess, 2012). SNIF-NMR is also now a well-known and effective technique to study the sugar adulteration in fruit juice. Martin et al. (1995) took advantage of this method and converted the fruit sugar into alcohol for analyzing the parameter of D/H in orange juice and beet sugar. When beet sugar was added into orange juice, the parameter was lower than before. Also, the close correlation was observed between the sugar addition percentage and the value of δD. With the increasing of beet sugar, the δD value was lower accordingly (Martin et al., 1995).

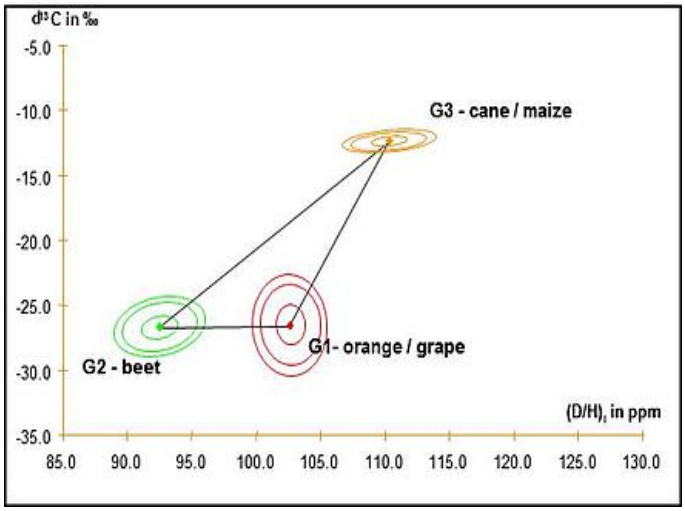


Figure 2. Adulteration triangle: repartition of isotopic ratios on ethanol molecules by SNIF-NMR (Martin et al., 1995)

Determination of $\delta^{18}O$ values of water in fruit juices is used for authentication of adulterated juice, especially in differentiation between directly squeezed and rediluted single strength juices. Authentic juices commonly are enriched in $\delta^{18}O$ and ^{2}H value of water with comparison to water from rediluted products utilizing tap water which is relatively poor in ^{18}O and D values (Simpkins et al., 1999). Bricout and Koziet (1987) found that the $\delta^{18}O$ value of water in juice is 5‰ than the precipitations water. If the juice was added by large quantity of water, the $\delta^{18}O$ value becomes more negative than before (Bricout & Koziet, 1987). Jamin (2003) investigated the isotope fractionation triggered by processing in orange juice. The result showed that the distribution of oxygen isotopes in water was stable during the harvest period, so that it can serve as an indicator of the long-term effect of environmental parameters. They transformed sugar into ethanol and isolated the ethanol for SNIF-NMR analysis, and used ethanol as an internal reference to avoid the any variability (especially temporal or spatial) of observed $\delta^{18}O$ in water. They found that there was a strong correlation between the $\delta^{18}O$ value of water and ethanol. If water was adulterated added to the juice, the correlation changed accordingly. Various market samples from different location were tested by using this methods, the result showed that many samples fall outside the conformity range, which indicated water addition (Jamin et al., 2003).

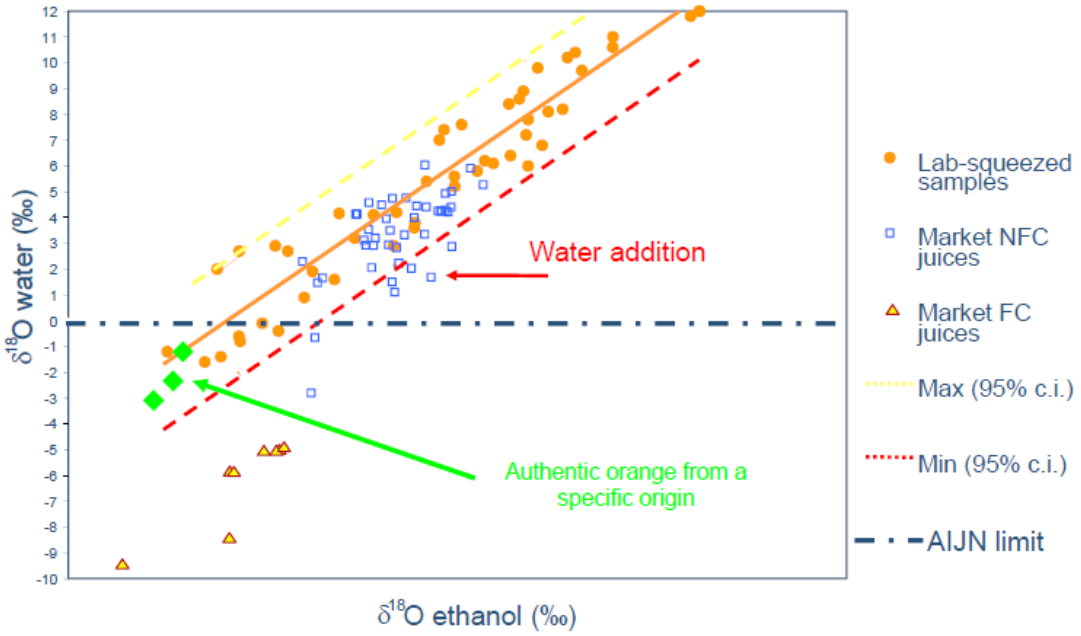


Figure 3. Plot of authentic and market not-from-concentrate orange juice samples in the plane of the $\delta^{18}O$ values of ethanol and water; AIJN, guidelines regarding the minimum values for oxygen and hydrogen isotope ratio value published by Association of the Industry of Juices (Jamin et al., 2003).

3.1.2 Honey

Honey is natural sweet mixture with a special flavor, odor and nutritive value. The sugar content of honey is: fructose, 33.3–43.0%; glucose, 25.2–35.3%; sucrose, 0–2%, other complex sugars like maltose, and trace polysaccharide. The dry weights of honey contain approximately equal amounts of the glucose and fructose. As is similar adulteration methods as juice, honey is therefore susceptible to fraud by adulteration with lower price inverted sugar syrups derived from cane, corn (C_4 plants). The fact is that he flower collected by bees to produce honey originates from C_3 flower. In this case, the C4 sugar addition to honey are more likely to find by the investigation of isotope anlysis. (Bogdanov & Martin, 2002).

White and Doner (1978) observed that the $\delta^{13}C$ of nectars from flower were between -28‰ and -22‰, while the C_4 plants which produce high fructose corn syrup (HFCS), have a $\delta^{13}C$ value between -20‰ and -10‰. They analyzed more than 500 samples of authentic honey from different geographical origin of many countries, and a large number of honey samples were adulterated by different percentages of HFCS. The result shows that samples of honey have a $\delta^{13}C$ value lower than -23.5 ‰ could be classified as authentic honey. If the $\delta^{13}C$ value is higher than -21.5‰, the chance of the honey were adulterated is 99.996%. This method is delivered by Association of Official Agricultural Chemists (AOAC) as an official method of analysis: AOAC 978.17. However, the authenticity of sample honey between -23.5‰ and -21.5‰ can not be evaluated by this methods (White Jr & Doner, 1978; Helrich, 1990).

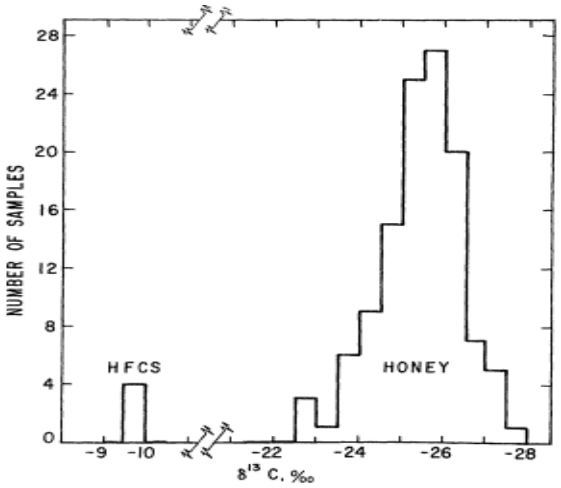


Figure 4. Distribution of $\delta^{13}C$ values among HFCSs and samples of honey (White Jr & Doner, 1978)

Parker found that pulp could be an internal standard substance to analysis the purity of orange juice, due to the differences in $\delta^{13}C$ value of the pulp and sugar in the juice (Parker, 1982). Enlightened by their research, White and Winters (1988) developed an

internal reference technique based on the determination of the $\delta^{13}C$ value of the protein fraction in the honey, to improve the sensitivity of stable isotope ratio analysis (SIRA) in honey authenticity. Compared to the $\delta^{13}C_{honey}$ value, the $\delta^{13}C_{protein}$ values were better for detection. The mean difference between the whole honey and protein fraction was 0.13‰. The result showed that a difference of 1‰ (equivalent to approximately 7% HFCS addition) should be utilized as the limit for determining if a test sample honey was adulterated. This method was adopted by AOAC as official methods: AOAC 991.41 (Helrich, 1990; White & Winters, 1988). Padovan et al. (2003) took advantage of this method to analyze forty honey samples from, eight from Argentina, Canada and the USA. The result showed that $\delta^{13}C_{honey}$ value and $\delta^{13}C_{protein}$ values were differed by more than 1‰ in six Brazil honey, which indicated that they are adulterated (Padovan et al., 2003).

Cabanero et al. (2006) used isotope ratio mass spectrometry to determine individual sugar carbon ratio and difference of $\delta^{13}C$ value between sucrose, glucose and fructose ($\Delta\delta^{13}C$). They investigated that the $\Delta\delta^{13}C$ between each sugar are constant in authentic honeys. Fructose and glucose have 0.0 ± 0.3‰ difference, fructose and sucrose have 1.2 ± 0.4‰, and glucose and sucrose have 1.3 ± 0.4‰. The $\Delta\delta^{13}C$ of sample honey sugars which falls outside the range of authentic honey are suspected to be adulterated. This method improves the sensitivity and efficiency of authenticity analysis of honey (Cabanero et al., 2006).

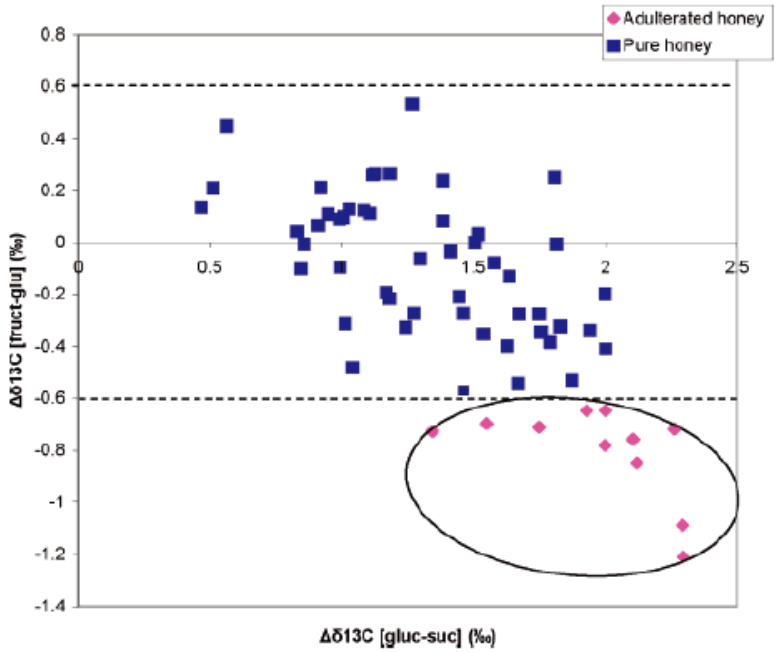
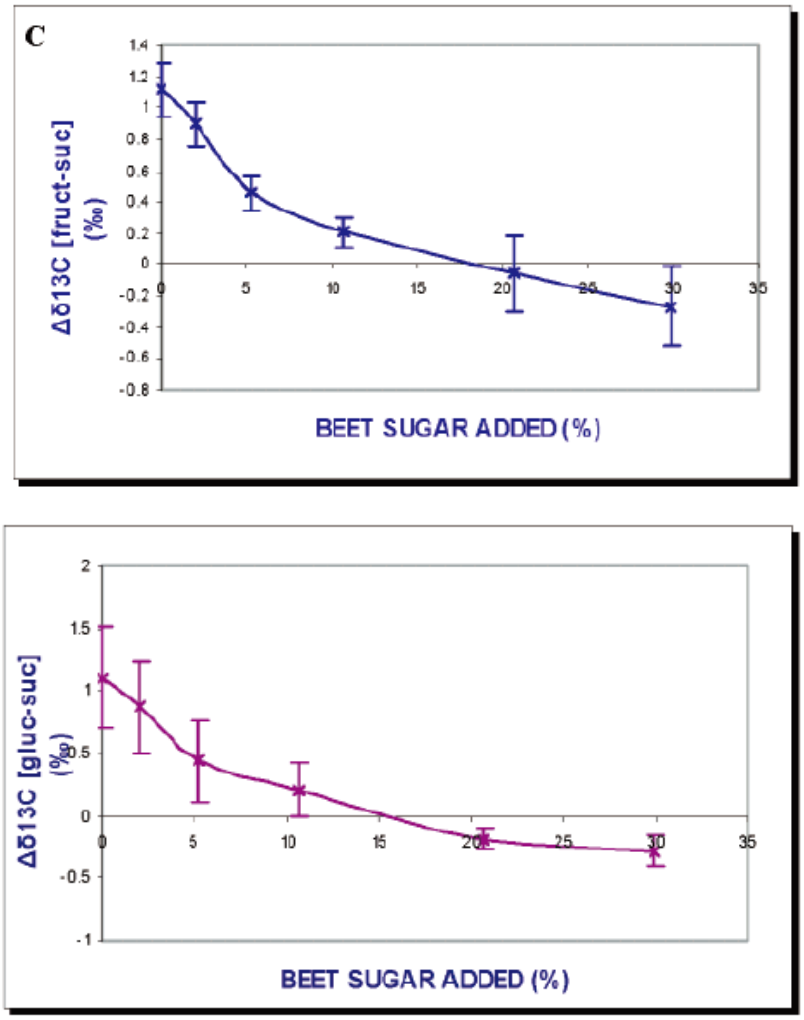


Figure 5. Plot of $\Delta\delta^{13}C_{\text{fructose-glucose}}$ versus $\Delta\delta^{13}C_{\text{glucose-sucrose}}$ value of commercial honeys (Cabanero et al., 2006)

They also detected the adulteration which could not be found by AOAC 991.41. For example, adding 5% of cane sugar shows no significant in difference of $\delta^{13}C_{\text{honey}}$ and $\delta^{13}C_{\text{protein}}$ (less than 1‰). However, the experiments indicated an evidently negative correlation between $\Delta\delta^{13}C_{\text{fructose-sucrose}}$ and $\Delta\delta^{13}C_{\text{glucose-sucrose}}$ and the adding amount of cane sugar. Also, the author conducted the experiments with beet sugar (a C_3 plant) additions to the sample honey, which are hard to distinguish by official methods. Figure 3 shows the changes of $\Delta\delta^{13}C_{\text{fructose-sucrose}}$ and $\Delta\delta^{13}C_{\text{glucose-sucrose}}$ with the increasing addition of beet sugar.



Firgure 6. Plot of $\Delta\,\delta^{13}C_{\text{fructose-sucrose}}$ and $\Delta\,\delta^{13}C_{\text{glucose-sucrose}}$ values versus percentage of beet sugar addition (Cabanero et al., 2006).

3.2 The Geographic Origin traceability of food

3.2.1 Olive oil

There is an increased concentration from consumers around the world on the origin of the purchased vegetable oils. Many branded goods have the label shows high-quality, by particular in virgin and extra virgin olive oil. For the purpose of managing these products quality and tracing the protected denomination of origin (PDO), European

legislation has been employed a Council Regulation (EEC) 2081/92 as a guarantee (White & Winters, 1988). A variety of chemical factors (e.g. fatty acids, iodine value) are used for traceability and authentication, complement with multivariate statistics. However, they do not provide a precise determination of geographical origin to verify the protected denomination. The stable isotope ratios of oxygen and hydrogen, which can offer the accurate and effective analysis to verify the geographical origin, are becoming widely used in traceability of virgin olive oil (Portarena et al., 2014).

Angerosa et al. (1999) carried out the initial research which uses IRMS, to get information about the geographical origin of olive oil samples. They detected the $\delta^{13}C$ value and $\delta^{18}O$ values of whole olive oil, sterols and aliphatic alcohol fractions from olive of Olea europaea L. produced in five Mediterranean countries. The results showed geographical classification of the oils. However, climate change is a disturbing factor. The oil sample from neighboring countries with similar climates did not offer useful information. Recently, more and more evidences show that if these assessments of the geographical origin of olive oil are complement with the information provided from heavy isotope ratios (e.g., $^{87}Sr/^{86}Sr$) and other element information, that a more certain geographical classification of this product can be determined (Angerosa et al., 1999).

The $\delta^{18}O$ values of fatty acids, especially palmitic and oleic acids could be used for determining the quality of oil and its geographical origin when excuted by principal component analysis. Camin et al. (2010) collect over 200 olive oil samples and 300 surface water samples from 8 European locations, and analysed them for hydrogen,

carbon and oxygen stable isotope ratios and other elements. After the multivariate discriminant analysis of the $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$ value and other element data, 95% samples could be accurately classified for their geographical origins (Camin et al., 2010). Macko and Spangenberg (1998) conducted an analysis of the $\delta^{13}C$ value of bulk oil and of individual fatty acids to authenticate the quality and the sources of olive oil. Different oil samples from various sources (e.g. maize, groundnut, hazelnuts, olive, walnuts) from five countries were collected. They found that the range of $\delta^{13}C$ value in virgin olive oil is between -26.5‰ and -35.5‰. Based on the $\delta^{13}C$ values of the whole oil, palmitic acid and oleic acid, the principal components analysis results effectively differentiate the virgin olive oil, the low grade of the edible olive oils, and other sources oils. In addition, the chemical and thermal factors could cause the isotope discrimination which lead to higher oleic acid $\delta^{13}C$ values or higher quantity of ^{13}C in residual bulk oil. These factors need to be taken into account when the authenticity is assessed (Spangenberg & Macko, 1998).

3.3.2 Wine

Since wine always has the high economic value compared to other agricultural products, there are more articles published which studied the geographical origin of wine. For the determination of the geographical origin of wine, $\delta^{13}C$ and $\delta^{18}O$ values of ethanol and water in wine are detected. West et al. (2007) recognized the relationships between wine water $\delta^{18}O$ and climate change. They also investigated the precipitation $\delta^{18}O$ ways of the grape growing sites of three states. Compared to the standard tap water $\delta^{18}O$‰, the estimation of the origin of the wine is shown (West et al., 2007).

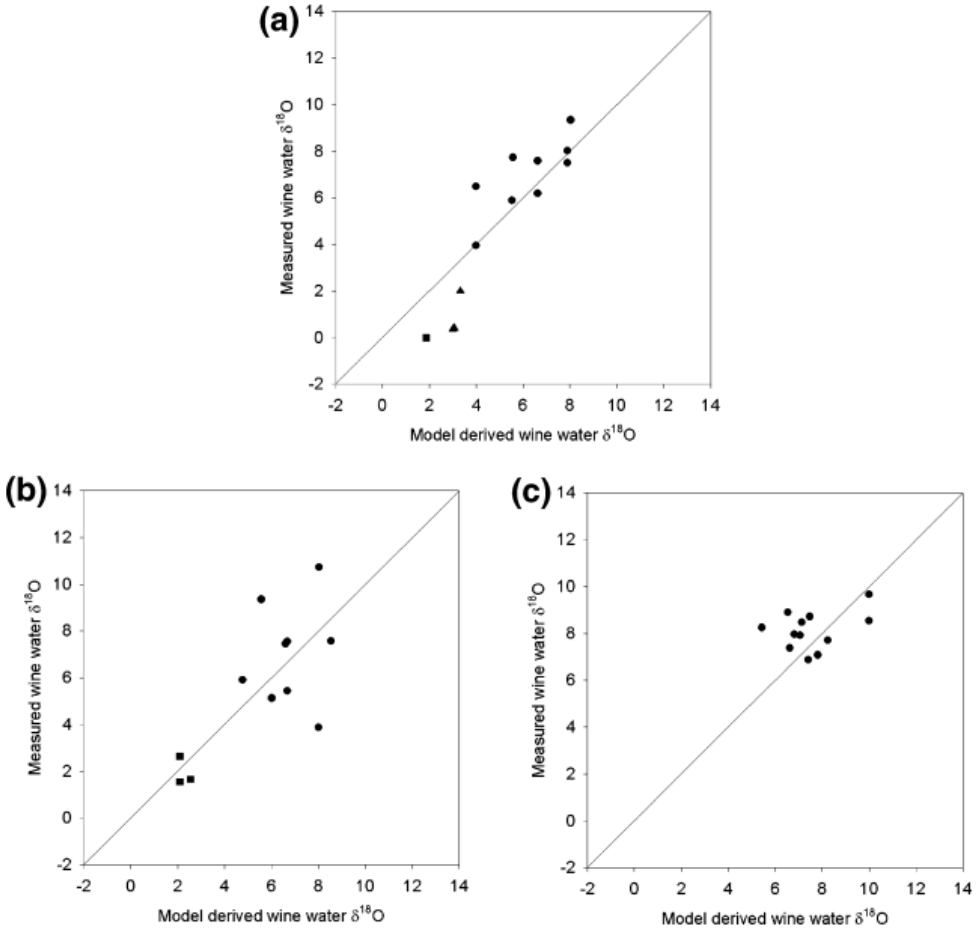


Figure 7. Wine water $\delta^{18}O$ data versus multiple-regression model predicted wine water $\delta^{18}O$ for (a) Chardonnay, (b) Pinot Noir, and (c) Zinfandel grape varieties from the 2002 vintage. California samples are shown as circles, Oregon samples as squares, and Washington samples as triangles (West et al., 2007).

In 1993, Horn et al. shows the process of tracing the origin of high-quality wine from different regions in France and Italy, using strontium isotope ratios ($^{87}Sr/^{86}Sr$) (Horn et al., 1993). Almeida (2001) investigated the $^{87}Sr/^{86}Sr$ ratio in ten samples of different sites of Portuguese and French. In order to test if significant differences occur in the values of the ratio $^{87}Sr/^{86}Sr$ value in all of the samples, they used the least significant difference (LSD).

Thus, the Sr isotope ratios are shows the decreasing pattern. The result demonstrates that there are some significant differences among wines sample of different locations. For example, samples from two regions of Portuguese have lower Sr isotope ratios than other regions of Portugues. In addition, North Eastern Portugal wine has statistically different and higher $^{87}Sr/^{86}Sr$ value than the other wines sample. These experiments suggest that the $^{87}Sr/^{86}Sr$ ratio is a useful signature of wine provenance (Almeida, 2001). Coetzee (2005) used $^{11}B/^{10}B$ ratios derived from red wines in different wine regions in France, Italy, and South Africa. Also, white wines from three South African regions are investigated for the differences. The result shows that mean $^{11}B/^{10}B$ ratios in red wines of these three countries were found to be different between 0.5 and 1.5%. South Africa wines have the highest mean $^{11}B/^{10}B$ ratios and Italy wines have the lowest ratios (Coetzee, 2005).

The $\delta^{13}C$ values determination by IRMS and ^{2}H-NMR analysis of the methyl group as described for wine are also used to determine the origin of acetic acid (Schmid et al., 1981). The $\delta^{13}C$ values are commonly used to detect the adulteration of apple vinegar by the adulteration of cheap acetic acid. This acetic acid is usually come from corn starch fermentation. It is typical to apply both hydrogen and carbon isotope analysis because C_3 plants (beet sugar, potato or grain starch) also have to be considered as sources for cheap acetic acid (Krueger, 1984). The deuterium value of acetic acid as calcium salt can be provided by IRMS. Recently, the determination of both $\delta^{13}C$ and $\delta^{2}H$ values by GC-IRMS are gaining more attention which may become the easiest way to get stable isotope ratios for authentication of origin of acetic acid (vinegar) (Perini et al., 2014).

3.2.2 Dairy Production

Isotope analysis is commonly used to determine the provenance of dairy production. By comparison to plant materials, dairy production has more protein, and lipids which are generated from animal metabolism. Additionally, the enrichment of nitrogen and sulfur in dairy products makes them suitable for isotope analysis. In addition, the feeds of animals which produce dairies are come from plants materials, in this case, the determination of dairies geographic origins need to combine the stable isotope parameters of the plants feeds and isotope fractionation effects during animal metabolism (Drivelos & Georgiou, 2012; Chung et al., 2014).

Determining the geographical origin of dairy products through measuring $\delta^{18}O$, $\delta^{15}N$, $\delta^{13}C$ value, $\delta^{34}S$ value, $\delta^{2}H$ and $\delta^{87}Sr$ values for dairies are feasible. Kornexl(1997) detected the changes of $\delta^{13}C$ and $\delta^{15}N$ value of milk from different regions of Bavaria. The result showed that the type of feeds was a primary factor affecting $\delta^{13}C$ and $\delta^{15}N$ value. The $\delta^{13}C$ of milk from grassland regions typically showed relatively negative values than the ones from the regions dominated by crop cultivation. Climate change and the soil conditions also have effects on the $\delta^{15}N$ values (Kornexl et al., 1997).

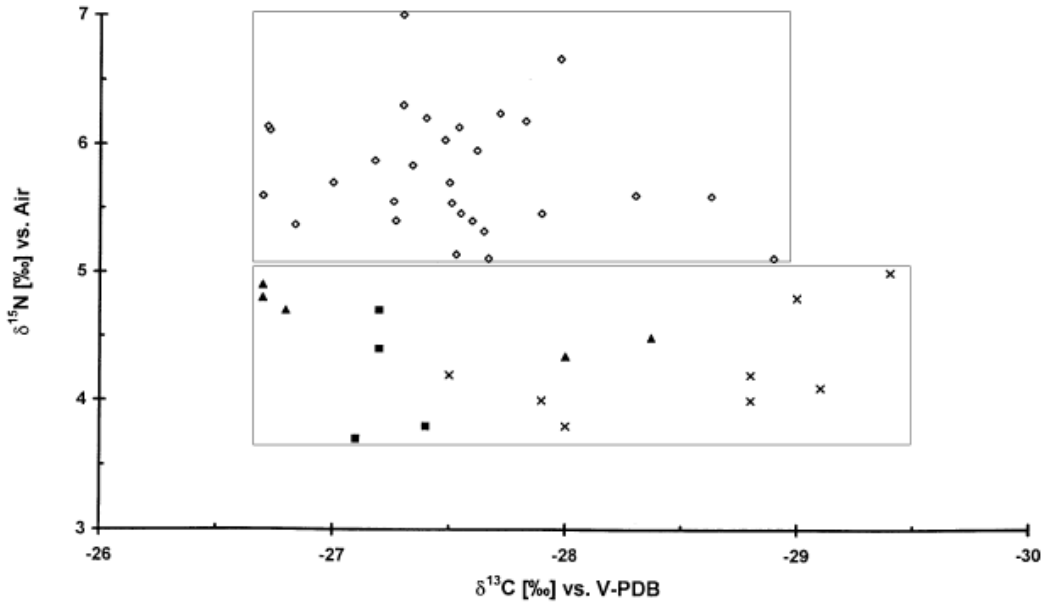


Figure 8. Combined $\delta^{13}C$ and $\delta^{15}N$ values of unskimmed milk samples from farms in northern (▲), southern (◇), eastern (×), and alpine (■) regions of Bavaria. The cattle diets were based on grass and hay ($\delta^{13}C$= -27 to -30‰, $\delta^{15}N$= 0 to +3‰), bruised grain ($\delta^{13}C$= -26 to -28‰, $\delta^{15}N$ = 2.5 to 6‰), and stacked corn (mainly in the wintertime, $\delta^{13}C$= -12 to -14‰, $\delta^{15}N$= 4 to 6‰); the relative amounts were unknown(Kornexl, 1997)

In recent years, Knobbe et al. (2006) studied the influence of animal feeding systems on isotope ratios in milk. The researchers measured C and N stable isotopes in milk and cow urine under different feeding systems. The $\delta^{13}C$ value in milk and urine depends on different feeds from C_3 or C_4 plant materials. The $\delta^{13}C$ value in both milk and urine from feeding with C_3 grasses was much lower than that by feeding with corn. Compared to urine, $\delta^{13}C$ value was slightly lower in milk. In the grass fed test group, $\delta^{13}C$ values in milk and urine were higher than that of the feeds. In the corn group, the ^{13}C content in urine had a similar range as the feeds. However, the ^{13}C content in milk was lower than that of feed. In addition, the $\delta^{15}N$ values in urine were different since the N needs to be balanced for longer time, while $\delta^{15}N$ values in milk were not significantly different in the two feeding systems(Knobbe et al., 2006).

The $\delta^{18}O$ value and $\delta^{2}H$ also can be used for determining whether the sample comes from mountainous or plain area. Renou et al. (2004) used NMR and isotope ratio mass spectrometry to identify geographic sources of milk. Discrimination analysis results showed that high frequency nuclear magnetic resonance (NMR) and isotope ratio mass spectrometry technology can complement each other for identifying geographical source of milk and cow feed. In that study, $\delta^{18}O$ and $\delta^{2}H$ value of the milk from mountainous regions were evidently higher than the one from the plain lands, except for the $\delta^{2}H$ from grass fed cow which were opposite. The types of cow feeds (pasture, grass silage, hay) were obviously distinguished by $\delta^{18}O$ and $\delta^{2}H$ values at mountain site, while the differences were not significant on plains (Renou et al., 2004). Ritz (2005) points out that milk cow variety may affects the isotopic composition, however, the influence was very minor, which could not weaken the ability of $\delta^{18}O$ value to distinguish different feeds and place of origin(Ritz et al., 2005).

There are many other studies on stable isotope of milk. However, fewer studies are focus on cheese and butter. Manca et al. (2006) analyzed the characteristics of several stable isotopes in Sardinia on traditional cheese (made from cow milk in local free feeding or pasture), industrial cheese (made from cow milk in intensive farming) and imported cheese (made from raw milk imported from other countries). Variance analysis and multiple comparison results showed that $^{13}C/^{12}C$， $^{34}S/^{32}S$ and $^{18}O/^{16}O$ have differences among three cheeses, while $\delta^{15}N$ and $\delta^{2}H$ have smaller differences. Principal component analysis and cluster analysis results showed that industrial cheese and imported cheese had similar isotope characteristics. Within the group of local dairy samples of local

cheeses, no significant differences were found in the C, N, and O isotope ratios linked to area of production. Isotope analysis methods can be used for distinguishing the imported cheeses from local traditional cheeses so as to achieve the goal of protecting product origin (Manca et al., 2006). Fortunato et al. (2004) distinguished cheeses of different regions (Alps, Tania, Finland, Canada and Australia) with isotope ratio mass spectrometry methods, $^{87}Sr/^{86}Sr$ seemed to be very effective in determining the origin of cheeses (Fortunato et al., 2004). Pillonel et al. (2003) use $\delta^{15}N$, $\delta^{2}H$, $\delta^{13}C$ and $\delta^{87}Sr$ values to distinguish cheeses from six different regions of Europe(Allgau, Bretagne, Finland, Savoie, Swizerland, and Vrarlberg) and found that the $\delta^{87}Sr$ values provided information that further subdivided the regions (other than $\delta^{15}N$, $\delta^{2}H$, $\delta^{13}C$ values) according to their geological conditions. The mean $\delta^{87}Sr$ values of Finland (4.85‰) are clearly different than other regions which are between –1.64‰ and –1.00‰. The reason of the higher values was that Finland is the only region with an older acidic rock beds. The principal component analysis successfully discriminated the cheese from Finland, Bretagne and Savoie except for other two regions (Pillonel et al., 2003).

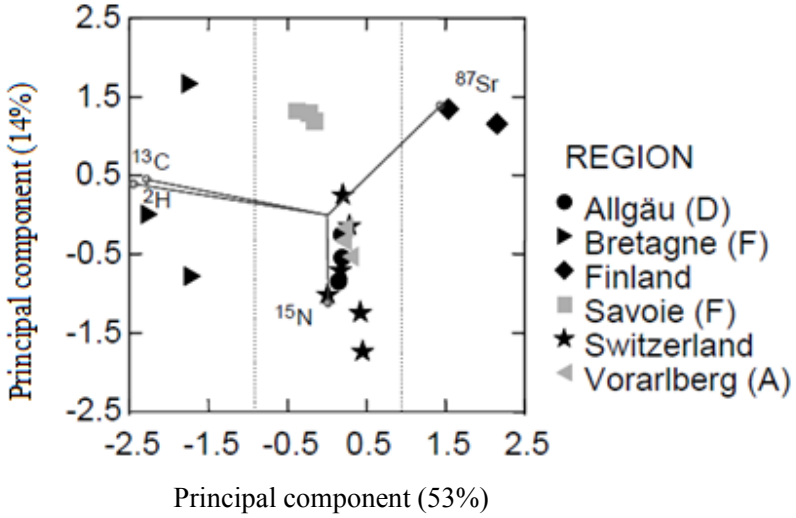


Figure 9. Principal component Analysis of parameters $\delta^{15}N$, $\delta^{2}H$, $\delta^{13}C$, $\delta^{87}Sr$. Separation of the group Finland, Savoie and Bretagne (Pillonel et al., 2003).

There are increasing numbers of studies for determination of geographical sources of dairy products with isotope techniques. Different isotope indexes can be measured aiming at different milk products. The $\delta^{13}C$ value and $\delta^{15}N$ value in full milk, casein and whey, the $\delta^{13}C$ value in milk lactose and the water $\delta^{18}O$ value in milk are usually measured for raw milk (Kornexl et al., 1997). For cream, the $\delta^{13}C$ value in full cream, $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$ and $\delta^{87}Sr$ values in cream protein as well as $\delta^{18}O$ value in cream water are usually measured. In addition, although some studies have reported that the $\delta^{18}O$ value in raw milk and cream water has significant differences among different regions, the results are prominently affected by season. For example, water $\delta^{18}O$ value in milk during spring and winter is prominently lower than the samples during summer and autumn (Rossmann et al., 2000). Therefore, when the $\delta^{18}O$ value in water is used as an index for isotope analysis, seasonal factors should be taken into account. In the study of cheese, $\delta^{13}C$, $\delta^{15}N$,

$\delta^{34}S$ and $\delta^{87}Sr$ values in casein, $\delta^{13}C$ and $\delta^{18}O$ value in cheese and $\delta^{18}O$ in water are usually determined. The $\delta^{18}O$ value in water is not a powerful parameter for verifying cheese authenticity because water can be easily adulterated during cheese making process (Pillonel et al., 2003).

3.2.2 Meat

Multi-isotope measurements have been adopted to trace the Protected Designation of Origin (PDO) of meat. The tissue water in the beef is related to meteoric water and ground water. Boner and Rstel (2004) collected beef samples from various farms in Germany, Argentina and Chile to detect the $\delta^{18}O$ value and $\delta^{2}H$ in the water of beef tissues due to the well-known pattern of $\delta^{2}H$ and $\delta^{18}O$ in meteoric water and ground water. The experiment demonstrated that δD value and $\delta^{18}O$ value were decreasing from south to north. The D/H value falls from about –45 to –85‰ and $\delta^{18}O$ value falls from –7‰ to ‾ 12‰ . The mean value of $\delta^{2}H$ in southern Germany was between -56‰ and -55‰, while the one in northern German were -36‰. Therefore distinct differences can be expected, modified by the seasonal influences. In north German, the average $\delta^{18}O$ value (-3.7‰) is slightly different from that of -5.9‰ in south German. As a consequence, utilizing isotope ratio of D/H and $^{18}O/^{16}O$ to trace the geographical origin of beef is practical (Boner & Rstel, 2004).

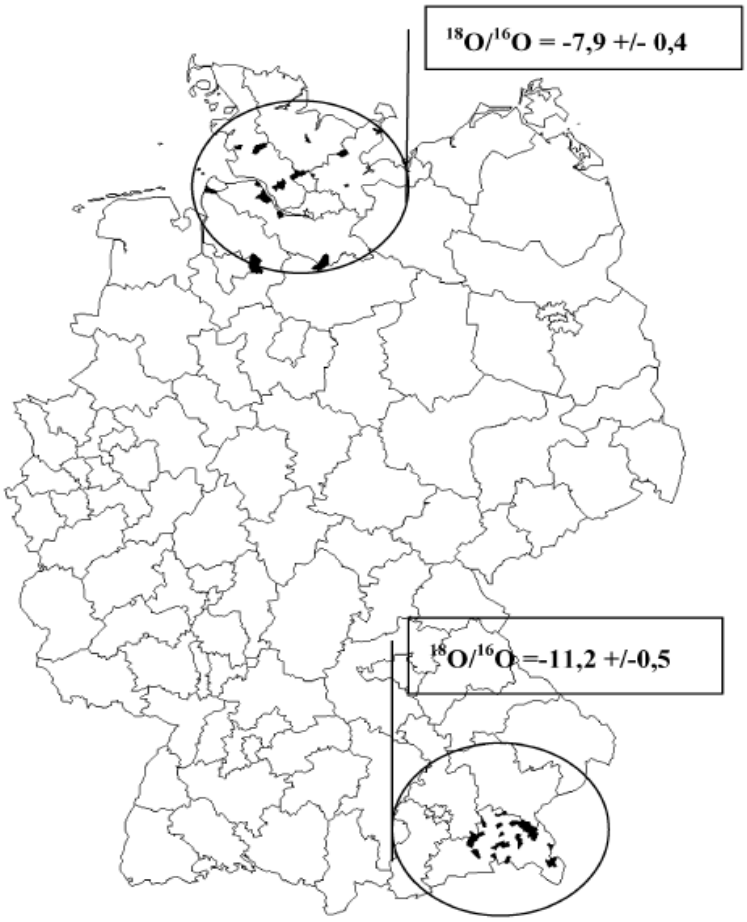


Figure 10. Geographical origin of the north German and south German samples.
The isotope ratio of oxygen in groundwater based on the study by Forstel et al (Boner & Rstel, 2004).

However, D/H and $^{18}O/^{16}O$ are strongly affected by seasonal factors; other parameters maybe needed to support the beef provenance results. $^{34}S/^{32}S$ data and $^{15}N/^{14}N$ in raw protein shows the significant difference in different farm locations in Germany.

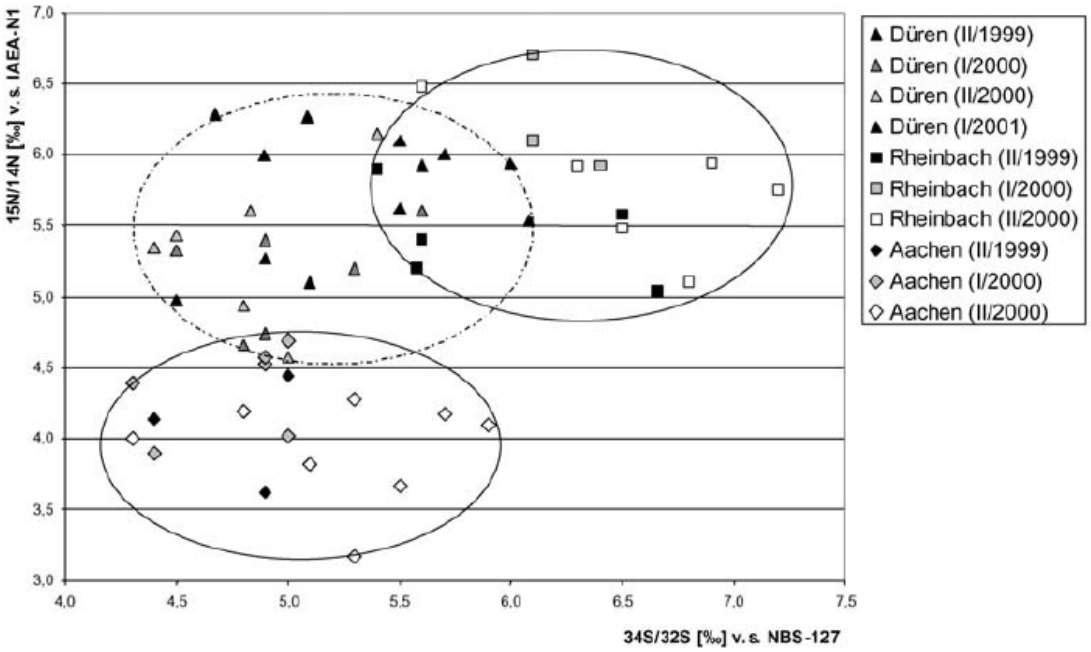


Figure 11. Local geographical pattern of the stable isotopes nitrogen and sulfur: *I* Jan – Jun, and *II* Jul – Dec. The samples belong to the three farms: Aachen, Dueren and Rheinbach (Boner & F O Rstel, 2004)

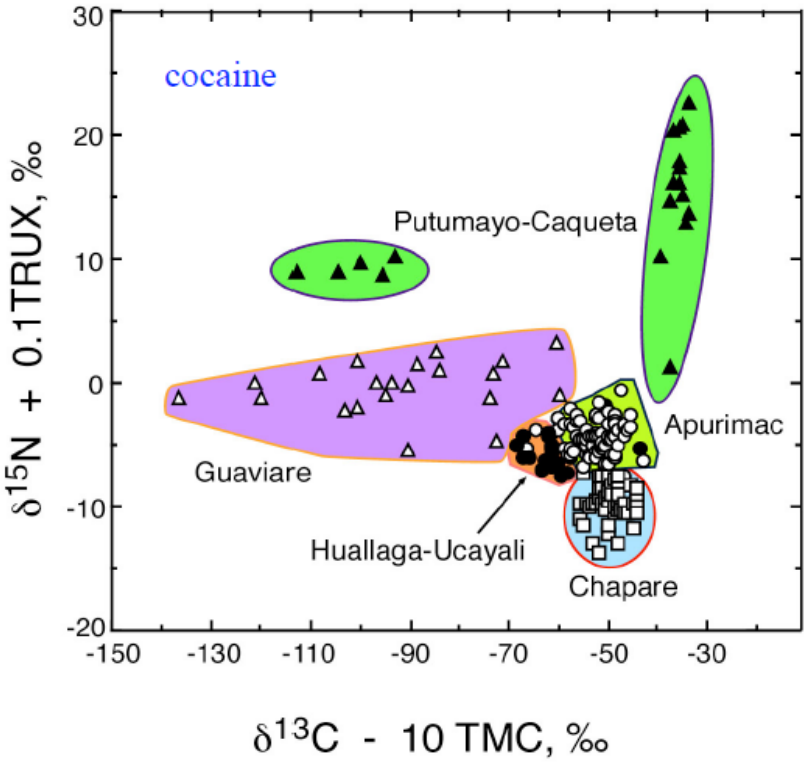
Schmidt et al. (2005) conducted an experiment to detect the origin of beef from different countries in Europe and America by carbon and nitrogen isotope analysis. It was concluded that there are notable difference of $\delta^{13}C$ and $\delta^{15}N$ value between Europe and America, which indicates the different diets for cattle. Irish and other European samples were fed on materials originating from C_3 plants, since their mean $\delta^{13}C$ value are close to the on in C_3 plants (-27‰). The beef samples from US and Brazilian had $\delta^{13}C$ value as similar as C_4 plants (-13‰), which showed that the cattle have almost exclusive C_4 foodstuffs diets, likely maize (Schmidt et al., 2005).

Piasentier et al. (2003) collected 12 lamb types from France, Greece, Italy, Spain, United Kingdom and Iceland which are fed on milk, grass, and grass combined with other

concentrated feeds. Multivariate analysis was used to differentiate between countries, animal feeding methods or correlation of these parameters. The results indicated that there were significant differences in $\delta^{13}C$ values of raw protein and fat for lambs having different diets and locations. Also, the mean $\delta^{13}C$ values in raw protein are usually 5‰ higher than fat. The $\delta^{15}N$ values were independent of feeds and the differences were only related to the cultivated varieties of lamb (Piasentier et al., 2003). Camin et al. (2007) also found that isotope ratios of H, C, N, and S were effective tools to predict the origin of lambs, since all of the isotope ratios varied in different location. For example, the high deuterium content for lamb in Greece are closely related to the high deuterium content of precipitation water and ground water of the eastern Mediterranean (Camin et al., 2007).

3.2.3 Cocaine

Cocaine was the most widely used narcotic drug. In this case, the determination of the geographic origin of illicit cocaine are gain more investigation by isotope forensic studies. In 1999, Ehleringer et al. analyzed the carbon and nitrogen stable isotope content in cocaine samples of different geographical origins. Ehleringer et al. (2000) measured $\delta^{13}C$ and $\delta^{15}N$ of coca leaves to partition sources to five regions. The coca leaves sample from Putumayo and Caqueta regions of Colombia were distinguished from each other by their ^{13}C content. Also, those from the Huallaga and Ucayali Valleys from the Apurimac Valley of Peru can be separated by ^{13}C value. Coca leaf from Bolivia has significantly less $\delta^{15}N$ value than the leaf from Peru. The $\delta^{15}N$ value in coca leaves is higher in Colombia and lower in coca grown in the Chapare Valley of Bolivia (Ehleringer et al., 2000; Ehleringer et al., 1999).



Firgure 12. $\delta^{13}C$ and $\delta^{15}N$ of coca leaves, Trux, truxilline; TMC, trimethoxycocaine (Ehleringer et al., 2000)

The authors used bivariate mean and standard deviation parameters to estimate the frequency. Based on this result, they correctly identified the countries of origin of these coca-leaf samples. They detected the origin of cocaine by giving a sample to the place of which it has the highest probability. They used this method and found the precise geographical origin of ninety percent of the coca-leaf samples. Almost all of the cocaine in South America is derived from one of these 5 regions (figure). Also, these locations have a temperature decrease from the wettest regions in the north and driest in the south. This means that nutrient pattern in tropical forest places (especially the coca growing regions) are more open than in drier and temperate locations, which affects the range of

coca-leaf $\delta^{15}N$ values (Ehleringer et al., 2000).

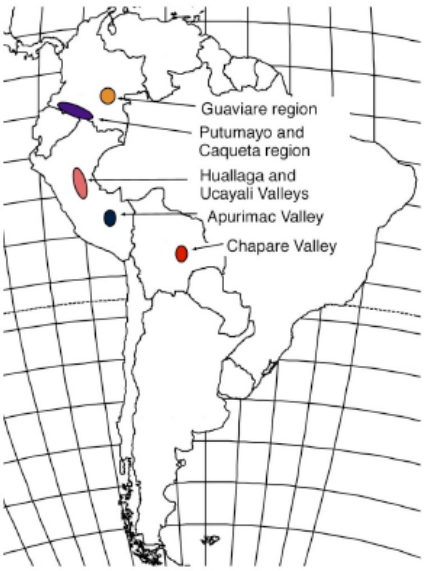


Figure 13. Five regions of cocaine growth (Ehleringer et al., 2000)

3.3 Authenticity of Organic food

Organic food production is commonly more expensive than conventional food, and was added benefits of increasing safety and healthy. Unlike conventional agriculture, synthetic fertilizers and pesticides are usually not allowed in organic regimes. Organic fertilizers are typically a combination of animal manures and plants debris. Biological pesticide control, selected cultivated varieties and crop rotation are also used in an organic system (Laursen et al., 2013). European Community Council Regulation (834/07, 889/2008) has delivered some practical standards to manage the label and the quality of organic productions (Ciolo, 2012)

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Nitrogen isotope analysis is the most common way to authenticate organic productions.

Plants nitrogen isotope ratios are closely related to the different fertilizer types applied to soil. Generally, organic fertilizers such as composted animal manures or plants debris, have higher $\delta^{15}N$ values than synthetic nitrogen fertilizers. Accordingly, higher $\delta^{15}N$ level of compounds containing nitrogen is detected in organically vegetables. However, sometimes a mixture of $\delta^{15}N$ from organics and inorganics in the soils condition may make $\delta^{15}N$ analysis more complicated. The carbon isotope fingerprints also shows a difference of fertilizers (Rapisarda et al., 2010). The C isotope fractionation of plants is controlled by Rubisco carboxylation during photosynthesis. The N supply from fertilizers may indirectly influence the water use efficiency by affecting stomatal conductance, which causes changes of Rubisco carboxylation. Therefore, the N supply modifies the carbon isotope composition (Kelly & Bateman, 2010). The $\delta^{13}C$ values are sometimes lower in organic vegetables in some studies, because higher microbial activity leads to higher soil respiration in organic farmland. The $\delta^{18}O$ value in leaf water of plants depends on evapotranspiration which may be affected by plant density and growth rates. Since organic farming sometimes differs from conventional ways in these aspects, oxygen isotope may identify the difference. In addition, the different $\delta^{34}S$ values in organic and mineral fertilizers may cause sulfur isotope ratios differences (Bateman et al., 2007).

However, Rogers found that the $\delta^{34}S$ and $\delta^{18}O$ value in organic cabbage, onion and lettuce has no significant differences from conventionally grown ones (Rogers, 2008). One the other hand, the $\delta^{15}N$ value was higher, while the $\delta^{13}C$ value is lower respectively. Camin et al. (2007) reported that the $\delta^{15}N$ (7.17‰) value of organic potatoes was markedly higher than conventional ones. In addition, using the lowest $\delta^{15}N$ observed for

organic samples (+4.3‰) as threshold value for evaluation in the organic samples, 15% of conventional potatoes were misclassified (Camin et al., 2007). Georgi et al. (2005) conducted an experiment to analyze the $\delta^{15}N$ value for long living term (e.g.pumpkin, egg plant, corn > 80 days) and shorter living term (e.g. tomato, broccoli, zucchini, cucumber < 80 days) organic plants respectively. The stable nitrogen isotope analysis was found to be more effective for short living term vegetables, which have more significantly differences with conventional ones(Georgi et al., 2005). Mihailove et al. (2014) concluded that lettuce, potatoes and tomatoes using organic fertilizers have higher $\delta^{15}N$ values than plats raised using synthetic fertilsers. However, the $\delta^{18}N$ value of organic vegetables is lower. This result demonstrated that $\delta^{18}N$ had potential to identify the organic foods (Mihailova et al., 2014). Rapisarda prepared two types of organic oranges samples (Navelina and Taroco,) and detected $\delta^{15}N$ in protein , amino acids of orange pulps and protein (Navelina, 6.21‰; Taroco, 6.67‰) was obviously higher than the conventional ones (Navelina, 4.43‰ and Taroco 5.53‰). The $\delta^{15}N$ value in amino acids was also higher (Rapisarda et al., 2005).

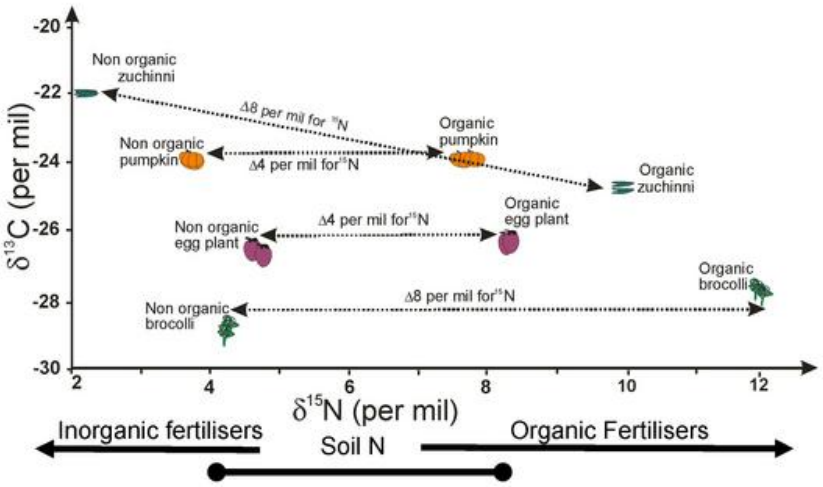

Figure 14. The $\delta^{15}N$ and $\delta^{13}C$ value of some common plants (Georgi et al., 2005)

Currently, the isotope analysis focused on the differences of feeds to identify the organic animal production. The $\delta^{13}C$ value of the C_3 plants feeds (e.g. grass, hay, soybean) was relatively low, while that of the C_4 plants feeds (corn, sorghum) was high. Molkentin et al. (2007) reported that organic milk and traditional milk could be distinguished through analyzing C stable isotope in milk due to different corn contents in cow feed. The $\delta^{13}C$ value was -26.6‰ or higher in traditional milk fat, the value was lower in organic milk, and the lowest value was -28.0‰. They use a $\delta^{13}C$ value above -26.6‰ as the standard to authenticate 269 milk samples for 3 organic farms and 3 conventional farms. The result shows that the accurate rate to identify the organic milk was 99%. In addition, there was no significant difference in $\delta^{34}S$ value between organic and conventional milk (Molkentin & Giesemann, 2007). Barhar et al. (2008) found the different $\delta^{13}C$ value between organic and conventional Irish beef. The organic beef has lower $\delta^{13}C$ which was between -26‰ and -28‰. For the conventional beef, $\delta^{13}C$ is between -25.52‰ and 23.8‰) and has wider range. These data showed that conventional cows were fed on more concentrated feeds than the organic ones fed on organic grass(Bahar et al., 2008).

4. Conclusion

Isotope analysis has proven to be a powerful tool in the authenticity and traceability of food productions. The techniques of isotope analysis have advantages of: high precision in the methods which can provide clear and strong evidence for food authentication that cannot be obtained using other analytical techniques, the need for small samples, and the fact that the same technique can be used for almost any type of food productions. Isotope analysis has been applied in food studies as recorders of various environmental, chemical

and biological processes. The sensitivity of the methods shows that it is not only hard to subvert, but often need high cost to do so if the adulteration has used the isotopic enriched ingredients. Another limitation to the application of the technique of food authentication and traceability is the lack of large information of isotope abundances in food productions. Also, natural isotope variability, complexity of the chemical structure of the analyzed food material, and the impact of a wide range of external factors can lead to large uncertainties to the result of isotope ratios data. Thus, more robust analyses need to be used for the reliable verification of food authenticity. Recent technological advances in IRMS have introduced a possibility to perform simultaneous rapid analyses of multiple isotope ratios. The use of multi-element isotope analyses combine with other analytical methods (e.g. mult-element analysis, DNA barcoding and chemometrics) have been reported to provide higher discriminative power and are currently gaining increased attention in food traceability studies. Although several advances have been made in the use of isotope analysis in food authentication, more studies are required to continue the improvement of the various approaches discussed in this paper. With the new and complex deception methods grow, further development of isotope analysis is needed to keep pace.

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