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Analytical Methods

The application of stable isotope ratio analysis to determine the geographical origin of wheat

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ABSTRACT

In this work, in order to discriminate the geographical origin of wheat, $\delta^{13}C$ and $\delta^{15}N$ values of 35 wheat samples originated from different regions were determined, using the method of element analyser–stable isotope ratio mass spectrometry. The results indicated that wheat from Australia, the USA, Canada and China could be potentially discriminated by using analyte $\delta^{13}C$ and $\delta^{15}N$. $\delta^{13}C$ values of wheat were ranged from −25.647‰ to −22.326‰, the $\delta^{15}N$ values of 35 wheat samples were calculated between 1.859‰ and 7.712‰. Moreover, the results illustrated regional distributions of $\delta^{15}N$ values of wheat as Australia > The USA > Jiangsu province of China > Shandong province of China > Canada. So $\delta^{13}C$ and $\delta^{15}N$ analysis would be potentially useful for rapid and routine analyses of geographical origin of wheat, even the cereal grains. In order to confirm the discrimination capability of $\delta^{13}C$ and $\delta^{15}N$, a follow-up work will use this method to analyse a larger set of samples.

1. Introduction

In recent years, mislabelling and adulteration are still two of the most serious problems in many areas of food market, they not only infringe the rights of the consumers, but also threaten the livelihood of honest traders (Guyon et al., 2014; Nietner, Haughey, Ogle, Fauhl-Hassek, & Elliott, 2014; Tosun, 2013, 2014). Under this kind of phenomenon, consumers are increasingly attracted to foodstuffs that declare not only their composition but also their geographical origin, such as products with a Protected Denomination of Origin (PDO). As these products command a premium price, origin mislabelling is always a tempting fraudulent practise (Federica Camin, Anaisabel Blanch Cortes, Michéle, & Giuseppe Versini, 2004).

With the improvement of people's living standards, the safety and authenticity of food are becoming more and more important. Several kinds of ways were adopted to ensure the authenticity of the food, for example, in Japan, the polished rice, when packaged, requires labels indicating cultivar, cultivation area, and year of production in accordance with the Japanese Agricultural Standard (JAS) Law. However, the geographical origin and rice cultivar cannot be distinguished by image analysis, leading to authenticity problems such as the addition of inferior rice to premium rice and mislabelling (Yaeko, Yoshito, Nanako, Naohiko, & Takashi, 2008). China is a cereal grains importing country, as the figures showed, the imports of wheat in 2012 was 3.42×10^6 tons. In this case, in order to prevent the addition of inferior wheat to premium wheat, a simple and fast analytical method which identifies them is required to resolve these authenticity problems.

To protect consumers against such types of fraud, efficient analytical tools able to demonstrate and characterise the authenticity problems of foodstuffs were also established. For most food products, the authenticity can be distinguished by botanical-cultivar origin, the absence of adulterants, and especially geographical origin. In the case of wheat, even the cereal grains, the determination of authenticity is a more complex problem as they can depend on both geographical origin and cultivar. Recently, the relationship between chemical compositions and cultivation areas has been evaluated by fatty acid compositions and strontium and boron isotope ratios (Kitta et al., 2005). In addition, rice cultivars have been identified powerfully by gene analysis using polymerase chain reaction (PCR) (Ohtsubo, Nakamura, & Imamura, 2002). Besides, trace element analysis has also been used as a rapid tool for discrimination of cultivation areas (Yasui & Shindoh, 2000). However, these methods require numerous purification steps, which is not only time-consuming, but also increases the risk of sample contamination and the loss of analyte.

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For a long time, element analyser–isotope ratio mass spectrometry (EA–IRMS) has always been widely used to trace the origin of organic materials in biochemistry field, geochemistry field, archaeology field, petroleum chemistry field, and so on (Ambrose & DeNiro, 1986; Hayes, Freeman, Popp, & Hoham, 1990; Rozanski, Araguás-Araguás, & Gonfiantini, 1992). In recent years, it has also become increasingly important as a tool for food authenticity problems (Longobardi, Casiello, Sacco, Tedone, & Sacco, 2011). Generally, the isotopic compositions of plant materials reflect various factors such as isotopic compositions of source materials (e.g., CO_2, H_2O and NO_2) and their assimilation processes as well as growth environments, especially the climate and altitude. Moreover, the fertilizer and farming ways from different kinds of origins may also affect the isotopic compositions of plant materials. Therefore, characteristics of the isotopic compositions have been widely used to investigate the authenticity of food materials. For example, the adulteration of honey (Cabañero, Recio, & Rupérez, 2006), juice (Eric, Frédérique, Rebeca, & Miche, 2005), and wine can be identified by differences in the carbon, nitrogen or oxygen isotopic compositions between authentic and adulterated products. In addition to these, the geographical origin of meat (Schmidt et al., 2005), dairy products (Ritz et al., 2005), and cereal crops can also be traced by using the EA–SIRMS method.

Generally, the isotopic compositions of plant materials reflect various factors such as isotopic compositions of source materials and their assimilation processes as well as growth environments. The carbon isotopic composition of plant materials strongly depends on the carbon fixation process such as the C-3, C-4 or crassulacean acid metabolism (CAM) cycle (Guler et al., 2014; Wang et al., 2015). Different photosynthesis pathway of plants presents biological discrimination effect on the carbon fixation process, which can cause the difference of $^{12}C/^{13}C$ in different kinds of plants, resulting in the $\delta^{13}C$ values of plants in C-3 cycle and C-4 cycle were −22‰ to −33‰ and −10‰ to −20‰, respectively, while that of plants in CAM cycle was wider. Unlike carbon isotopic composition, the nitrogen isotopic composition mainly depends on soil nutrition (Elflein & Raezke, 2008; Kropf et al., 2010; Meints, Shearer, Kohl, & Kurtz, 1975). In conclusion, EA–SIRMS can be regarded as a useful and potential method in identification of geographical origins of many kinds of food and cereal crops.

In our work, we determined stable carbon and nitrogen isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$ values) of 35 wheat samples from different regions by using elemental analyser–stable isotope ratio mass spectrometry (EA–SIRMS), in order to develop a simple and rapid method to discriminate geographical origin of the wheat.

As stable isotope analyses will potentially discriminate cultivation areas of wheat, even the cereal grains and the recent spread of EA–SIRMS facilitates rapid and routine analysis of the elemental and stable isotopic compositions of organic materials, the EA–SIRMS method will become an important tool for discriminating the geographical origin of cereal grains, especially wheat.

2. Materials and methods

2.1. Samples

35 wheat samples were obtained from Guangdong Institute of Cereal Science Research (Guangzhou Guangdong, China), which are originated from the USA ($n = 5$), Australia ($n = 5$), Canada ($n = 5$) and Jiangsu province ($n = 10$) and Shandong province ($n = 10$) of China, respectively. All samples were dried and ground to a fine powder before analysis. In order to avoid cross contamination, all the equipments used for drying and grinding were completely cleaned before the preparation of each sample.

2.2. Standards

The δ notation is used to describe the isotopic difference between the sample and an international standard, which was defined as the following formula (1),

$$\delta^{13}C(‰) \text{ or } \delta^{15}N(‰) = (R_{sample}/R_{standard} - 1) \times 1000 \quad (1)$$

Where R_{sample} is the isotope ratio (i.e., $^{13}C/^{12}C$, $^{15}N/^{14}N$) of the sample, and $R_{standard}$ is that of the reference materials. Variations in stable isotope ratios were reported as parts per thousand (‰) deviation from internationally accepted standards: Vienna Pee Dee Belemnite (V-PDB) standard for carbon, atmospheric nitrogen (AIR) for nitrogen. Each sample was analysed three times and values were averaged. The analysis was repeated if the difference between the two values was higher than 0.20‰ for $\delta^{13}C$ and $\delta^{15}N$. Moreover, for each run at least one in-house standard (casein for carbon and nitrogen) was analysed to check the accuracy of the analysis. In this paper, the casein was chosen as the standards of carbon and nitrogen isotope.

2.3. Measurement

The carbon and nitrogen isotope ratios of all samples were measured by elemental analyser–stable isotope ratio mass spectrometry (EA–SIRMS) using a DELTA V PLUS IRMS (Thermo Electron Corporation) interfaced with a Flash 2000 element analyser (Thermo Electron Corporation). All samples and standard materials were measured after the balance of reference gases, the standard deviations (SD) of reference gases, CO_2 and N_2, were less than 0.06‰ ($n = 10$) and 0.08‰ ($n = 10$), respectively.

2.4. The $\delta^{13}C$ analysis

The powdered cereal grains and wheat were weighed 1 mg into a small tin capsule (3 mm × 2 mm × 5 mm). Then the capsule was folded and compressed to contain the sample and minimise any air present. The prepared samples were introduced into the elemental analyser using an auto-sampler. The stable carbon isotopic composition is recorded in the delta (δ) notation relative to the VPDB standard. The CO_2 reference gas was calibrated against a casein reference material and was found to have a value of $\delta^{13}C = -26.98‰ \pm 0.15‰$ ($n = 10$) (Cabañero et al., 2006). This gas was used as reference gas for all the measurements. The linearity region for the isotope amount ratio n ($^{45}CO_2$)/n ($^{44}CO_2$) as a function of the intensity of $m/z = 44$ was 4 to 10 v. Only analyses within this range were used in the final values (Li et al., 2011). Each sample was analysed a minimum of three times and the mean value was adopted.

2.5. The $\delta^{15}N$ analysis

The cereal grains and wheat (1 mg) were weighed and analysed in a similar way to the samples used for carbon isotope analysis. Due to the increased amount of sample, the dilutor must be switched on just prior to the elution of the CO_2 peak and switched off immediately after to prevent the detector from being overloaded with CO_2. The $\delta^{15}N$ composition is reported relative to a reference gas pulse of known $\delta^{15}N$ composition. And the N_2 reference gas was also calibrated against a casein reference material and was found to have a value of $\delta^{15}N = +5.94‰ \pm 0.20‰$ ($n = 10$). Each sample is analysed a minimum of three times and the mean value was adopted. All samples were analysed over a period of 18 months, with replicate samples analysed throughout the entire period to ensure reproducibility of results.