Food Research International 77 (2015) 299–309

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Monitoring the authenticity of organic rice via chemometric analysis of elemental data

Endler Marcel Borges [a,b,c,*], Jane Mary Lafayette Neves Gelinski [b], Vanessa Cristina de Oliveira Souza [c], Fernando Barbosa Jr. [c], Bruno Lemos Batista [d]

[a] Departamento de Química, Universidade Regional de Blumenau (FURB), Campus 1, Rua Antônio da Veiga, 140-Victor Konder, 89012-900 Blumenau, SC, Brazil
[b] Universidade do Oeste de Santa Catarina (UNOESC), Núcleo Biotecnológico, Rua Paese, 198, Bairro Universitário — Bloco K, CEP 89560-000, Videira SC, Brazil
[c] Laboratório de Toxicologia e Essencialidade de Metais, Faculdade de Ciências Farmacêuticas de Ribeirão Preto (FCFRP), Universidade de São Paulo (USP), Avenida do Café s/n, Monte Alegre, 14040-903 Ribeirão Preto, SP, Brazil
[d] Universidade Federal do ABC, Centro de Ciências Naturais e Humanas, Santo André, SP, Brazil

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 25 May 2015
Accepted 3 June 2015
Available online 6 June 2015

Keywords:
Chemometrics
ICP-MS
Multi-element fingerprinting
Organic food
Quality control
Rice

ABSTRACT

50 rice samples (18 organic and 32 ordinary) from Brazil were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) for 20 elements (As, B, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, P, Pb, Rb, Se and Zn) to identify significant differences between the two types (organic and ordinary) of rice. Concentrations of As, B, Ba, Co, Cr, Cu, Mn, P and Zn were found to be higher in ordinary versus organic rice, while K, Ca, Mo, Rb and Se concentrations were lower in ordinary versus organic samples. The remaining investigated elements (Cd, Ce, Fe, La, Mg and Pb) exhibited statistically equivalent concentration in the two types of rice. Principal Component Analysis (PCA), Soft Independent Modeling of Class Analogy (SIMCA), Hierarchical Cluster Analysis (HCA) and K-nearest neighbors (KNN) statistical techniques of the elemental fingerprints were readily able to discriminate organic from ordinary samples and can be used as alternative methods for adulteration evaluation.

1. Introduction

Organic farming is a holistic approach to agriculture and food systems based on agro-ecosystem health, soil fertility, reduction of inputs, and locally to regionally adapted farming systems (FAO, 2001; Kahl, Załęcka, Ploeger, Bügel, & Huber, 2012). Under this prospective, the process that leads to a commercial product should be able to maintain the organic integrity and vital qualities of the original agricultural produce. Opposed to the use of fertilizers, the holistic agricultural approach recommends the application of biological and mechanical methods to food production (Załęcka et al., 2014; Zikeli, Rembiałkowska, Załęcka, & Badowski, 2014).

Organic farming has grown rapidly on a global scale. Currently, there are approximately 370 million ha of land operating under certified organic management that generate a turnover of organic products amounting to 60 billion US dollars (Zikeli et al., 2014). Based on the benefits that organic farming brings to the environment and human health, governments around the world are prone to subsidize organic farmers that follow legal standards of organic quality. By following appropriate protocols of organic farming and labeling organic products accordingly, organic farmers have been able to increase consumer trust (Zikeli et al., 2014).

In addition to ecological considerations, certification of organic products requires a series of precautions. These include the detoxification of the soil in areas under transition from chemical to organic agriculture and the absence of chemical fertilizers and pesticides (Barbosa, Batista, Varrique, Coelho, Campiglia & Barbosa, 2014; Barbosa, Nacano, Freitas, Batista & Barbosa, 2014; Brenton, Edwards-Jones, & Jensen, 2009; Granato, Branco, Nazzaro, Cruz, & Faria, 2010; Kahl et al., 2012; Ponte & Gibbon, 2005; Zielinski et al., 2014). The “certified label” adds market value to organic products, which makes the authentication process relevant under the perspective of possible fraud. Since the differences among organic and ordinary products are not visible to the naked eye, systematic control of the authenticity of organic food products still relies on chemical analysis (Barbosa, Batista, Varrique, Coelho, Campiglia and Barbosa, 2014; Brereton, 2013; Kahl, Baars, et al., 2012; Kahl, Załęcka, Ploeger, Bügel, & Huber, 2012). However, authenticity of organic products in most countries and products is only assessed by means of

---

* Corresponding author at: Departamento de Química, Universidade Regional de Blumenau (FURB), Campus 1, Rua Antônio da Veiga, 140-Victor Konder, 89012-900 Blumenau, SC, Brazil.

E-mail address: marcelborgesb@gmail.com (E.M. Borges).

http://dx.doi.org/10.1016/j.foodres.2015.06.008
0963-9969/

certifications, and no analytical parameters are applied (except in some particular food commodities and countries) (Manning & Soon, 2014).

This article deals with the use of inductively coupled plasma (ICP) mass spectrometry (MS) for the analysis of twenty chemical elements in rice samples. Rice is one of the most important staple food crops for almost half of the world's population (Cheajesadagul, Arnaudguilhem, Shiowatana, Siripinyanond, & Szpunar, 2013; Vlachos & Arvanitoyannis, 2008). It also possesses the main source of calories and protein for humans, particularly in Asia, America and some European countries. According to the Food and Agriculture Organization (FAO), developing countries are the main player in the world rice trade (Cheajesadagul et al., 2013; Vlachos & Arvanitoyannis, 2008). The high sensitivity and relatively high salt tolerance of ICP-MS, associated to its accuracy of analysis and compound-independent element response make this technique a leading approach for the identification and determination of trace elements in a wide range of samples (Ammann, 2007; Husted et al., 2011).

Analytical efforts on the authenticity of foods have been focused on the geographical origin of agricultural products (Husted et al., 2011; Karoui & De Baerdemaeker, 2007; Luykx & Van Ruth, 2008), botanical/cultivar type and the presence of adulterants (Kelly et al., 2002). Multi-elemental and multi-isotope analyses via ICP atomic emission spectroscopy (ICP OES) have been particularly useful to determine the geographical origin of foods (Kelly, Heaton, & Hoogewerff, 2005). Although the multi-elemental and multi-isotope compositions of rice have been used to differentiate its origins (da Silva et al., 2013; Gonzálvez, Armenta, & de la Guardia, 2011; Kawasaki, Oda, & Hirata, 2002; Kelly et al., 2002; Kokot & Phuong, 1999; Li et al., 2013; Suzuki, Chikaraishi, Ogawa, Ohkouchi, & Korenaga, 2008), our literature search revealed no previous reports on ICP-MS for discrimination of ordinary and organic rice samples. Thus, we demonstrate, here, that the combination of ICP-MS spectral fingerprints and chemometric algorithms provides a robust approach for comparison of rice samples and for verifying the authenticity of organic rice.

2. Material and methods

2.1. Instruments

The determination of trace elements in rice samples was carried out by using an ICP-MS (ELAN DRCII, PerkinElmer, CT, USA) with high-purity argon (99.999%, White Martins, Brazil). The instrumental parameters and optimized conditions are shown in Table 1.

Table 1
Instrument settings for q-ICP-MS.

Instrument	Elan DRCII (PerkinElmer SCIEX)
Nebulizer	Meinhard®
Spray chamber	Cyclonic
Torch injector	Quartz for clinical sample (2.0 mm)
Auto lens	On
RF power (W)	1100
Gas flow rates (L min^{-1})	Nebulizer 0.56–0.98; plasma 15; auxiliary 1.2
Interface	Platinum cones
Sampler	1.1 mm
Skimmer	0.9 mm
q-ICP-MS (standard mode)	^{75}As, ^{11}B, ^{137}Ba, ^{44}Ca, ^{111}Cd, ^{140}Ce, ^{59}Co, ^{52}Cr, ^{65}Cu, ^{57}Fe, ^{39}K, ^{139}La, ^{24}Mg, ^{55}Mn, ^{98}Mo, ^{31}P, ^{208}Pb, ^{85}Rb, ^{82}Se and ^{66}Zn
Internal standard	^{103}Rh
Scanning mode	Peak hopping
Integration time (ms)	2000
Replicates	3
Sweeps	40
Readings	1
Dwell time (ms)	50
Lens voltage (v)	6.0
Sample uptake rate (mL min^{-1})	1.0
Correction equations	
Zinc = ^{64}Zn − (0.035247 × ^{60}Ni)	
Selenium = ^{82}Se − (1.007833 × ^{83}Kr)	
Antimony = −0.125884 × ^{125}Te	

2.2. Reagents

With the exception of HNO_3, all reagents were of analytical-reagent grade. HNO_3, was purified in a quartz sub-boiling still (Kürner Analysentechnik) before use. High purity deionized water (resistivity 18.2 MΩ cm) was generated with a Milli-Q water purification system (Millipore, Bedford, MA, USA) and used throughout. Rhodium, iron, magnesium, zinc and copper (1000 mg L^{-1}) and multi-element (10 mg L^{-1}) standard solutions were obtained from PerkinElmer (Shelton, CT, USA). Triton® X-100 and tetramethylammonium hydroxide solution (TMAH) 25% (w/v) in water were purchased from Sigma-Aldrich (St. Louis, USA).

2.3. Sampling and analytical procedures

Certified organic (n = 18) and ordinary rice (n = 32) samples were obtained from the Brazilian retail market. All organic rice samples were certified by the Brazilian IBD-Agricultural and Food Inspections and Certifications, i.e. a government entity that is accredited by the International Federation of Organic Agriculture Movements. Aliquots of rice samples were stocked in propylene metal-free Falcon® tubes (Becton Dickinson) and freeze-dried (−80 °C) until further use.

In order to quantify 20 chemical elements (As, B, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, P, Pb, Rb, Se and Zn) in rice, we used the ICP-MS method proposed by Sucharova and Suchara (2006). Concentrations of these elements are provided in Table S1 of the Supplementary material. A solution of rhodium 10 μg $L^{-1}$was used as the internal standard. All samples were white rice.

Sample preparation was carried out according to the method proposed by Batista, Grotto, Rodrigues, de Oliveira Souza, and Barbosa, (2009), it consist of 100 mg (weight) of rice in a closed vessel and digest it with 8 mL of 20% (v/v) HNO_3 and microwave energy. This digested solution was made up to 50 mL in Polypropylene vials with Milli Q® water. Samples were then calibrated against aqueous standards prepared in 10% (v/v) HNO_3.

The accuracy and precision of the ICP-MS method were verified with two Standard Reference Materials from the National Institute of Standards and Technology (NIST), namely SRM 8415 Whole Egg Powder and SRM 1568a Rice Flour. All concentration values were found to be in good agreement with the reference values.

2.4. Data analysis

PCA, HCA, SIMCA and KNN were performed using Pirouette Version 3.11 from Infometrix, Inc. (Woodinville, USA). Before applying PCA, HCA, SIMCA and KNN, all variables were “autoscaled”.

Looking at the data, it is seen, that some variables are measured in numbers that are much larger than the others. For example, P is mg/kg, whereas, Ce and La are μg/kg. If this difference in scale is not handled, then the PCA model will only focus on variables measured in large numbers (Bro & Smilde, 2014). It is desired to model all variables and there is a preprocessing tool called auto-scaling, which will make each column have the same ‘size’, so that, all variables have an equal opportunity of being modeled (Bro & Smilde, 2014). Auto-scaling means that from each variable, the mean value is subtracted and then the variable is divided by its standard deviation. Thus, our data was auto-scaled before applying PCA (and other chemometric tools like, HCA SIMCA and KNN) (Borges, 2014; Borges & Collins, 2011).

For the HCA, Euclidian distances and Incremental linkages were used. For PCA, correlations were used. For SIMCA, probe threshold 0.950, 20 maximum factors and Local scope were used. KNN was carried