



Original Research Article

Recognition of organic rice samples based on trace elements and support vector machines



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ABSTRACT

A simple approach is proposed for the authentication of organic rice samples. The strategy combines levels of concentration of trace elements and a data mining technique known as support vector machine (SVM). Nineteen elements (As, B, Ba, Ca, Cd, Ce, Cr, Co, Cu, Fe, La, Mg, Mn, Mo, P, Pb, Rb, Se and Zn) were determined in organic ($n = 17$) and conventional ($n = 33$) rice samples by quadrupole inductively coupled plasma mass spectrometry (q-ICP-MS) and the variations found in their elemental composition resulted in profiles with useful information for classification purposes. With the proposed methodology, it was possible to predict the authenticity of organic rice samples with an accuracy of 98% when using the 19 original elements. An accuracy of 96% was found using only the elements Ca and Cd.

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1. Introduction

Health concerns and environmental considerations related to the use of pesticides, hormones and veterinary drugs in conventional farming practices have raised public attention to the production and consumption of organic products. Organic farming is an environmentally sustainable approach with viable solutions to a range of problems associated with conventional food production, rural development and animal welfare. In the specific case of organic cereal production, current legislation restricts the use of synthetic fertilizers, pesticides and insecticides. Farming practices should be based on the use of compost or organic waste, readily soluble mineral fertilizers and biological pest control (Capuano et al., 2012).

Due to lower production yields and higher certification costs, organic products tend to retail at higher prices than their conventional counterparts. This fact, associated with their increasing popularity, makes organic products susceptible to fraud. One possible way to differentiate among organic and conventional products is to monitor their chemical composition. Under this perspective, the authentication of organic foods becomes an analytical problem. The studies presented here deal with the authentication of organic rice.

Several analytical strategies exist for the authentication of organic foods of plant origin. These include the measurement of stable isotope ratios such as $^{15}\text{N}/^{14}\text{N}$ (Kelly et al., 2005; Rossman, 2001), metabolomics (Zorb et al., 2006), analysis of phenolic compounds (Wang et al., 2008), copper chloride crystallization (Huber et al., 2010) and infrared spectrometry (Cozzolino et al., 2009). The approach presented here is based on quadrupole-inductively coupled plasma-mass spectrometry (q-ICP-MS) and the differences found in the elemental composition of organic and

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conventional rice. Although ICP-MS has been applied to the determination of metals in rice samples (Capuano et al., 2012; Cheajesadagul et al., 2013; Shen et al., 2013), our literature search reveals no previous reports for the purpose at hand. Our work considers the spectral profiles of rice samples resulting from the determination of three major (g kg^{-1}) and seventeen minor (mg kg^{-1} – mg kg^{-1}) elements. Data analysis was carried out with the aid of a data mining technique known as support vector machine (SVM). Supervised and unsupervised chemometric tools have been used for food authenticity and traceability (Barbosa et al., 2014a,b; Batista et al., 2012; Niu et al., 2011). SVM is a supervised learning model with associated learning algorithms that analyze data and recognize patterns often used for classification and regression analysis (Tan et al., 2006). A literature search has not revealed any reports of its application to data processing of chemical profiles from rice samples. Herein, we demonstrate that the combination of q-ICP-MS with SVM provides a robust analytical tool for the authentication of organic rice samples.

2. Materials and methods

2.1. Rice sampling

Certified organic ($n = 17$) and conventional ($n = 33$) rice samples were purchased from different Brazilian producers (50 different brands) in several cities in the states of Rio Grande do Sul, Santa Catarina, Minas Gerais, Goiás and Tocantins. All organic rice samples were certified by the Brazilian IBD-Agricultural and Food Inspections and Certifications that is accredited by the International Federation of Organic Agriculture Movements. Rice samples (15 g) were separated by quartering as described by the Codex Alimentarius Commission (CAC, 2004) and divided into three plastic tubes. Tube contents were frozen to -80°C and freeze-dried (Liobrás L101, Brazil) and then ground for 3 min in a ball mill (TE 350, Tecnal; Sao Paulo, Brazil) and sifted with a $106\ \mu\text{m}$ sieve (Bertel; Sao Paulo, Brazil).

2.2. Reagents

High-purity deionized water (resistivity $18.2\ \text{M}\Omega\ \text{cm}^{-1}$) was generated with a Milli-Q water purification system (Millipore RiOs-DI™; Massachusetts, USA) and used throughout the procedures. With the exception of nitric acid (HNO_3), all other chemicals were of analytical-reagent grade purity. HNO_3 (Synth; Sao Paulo, Brazil) was purified in-house with a quartz sub-boiling still from Kürner Analysentechnik (Rosenheim, Germany). Triton® X-100 and hydrogen peroxide (H_2O_2) were acquired from Sigma–Aldrich (Missouri, USA). Aqueous solutions of rhodium ($1000\ \text{mg L}^{-1}$, internal standard) and multi-element standard mixtures containing Cu, Zn, Mg, B, P, Mo, As, Pb, Cd, Mn, Se, Co, Cr, Ba, Rb, Fe, Ca, La and Ce with $10\ \text{mg L}^{-1}$ individual concentrations were obtained from PerkinElmer (Connecticut, USA).

2.3. Sample digestion, solution preparation and analysis

All operations were performed in a class-1000 clean room. Plastic bottles, vessels and conic tubes were cleaned by soaking for 24 h in 15% (v/v) HNO_3 , rinsed five times with Milli-Q water and dried in a class-100 laminar flow hood (Veco; Sao Paulo, Brazil) before use. All solutions were prepared in a class-100 laminar flow hood. Sample digestion was carried out in closed vessels with the aid of a microwave oven decomposition system (model Ethos D, Milestone; Bergamo, Italy). The digestion procedure followed the protocol previously validated by Nardi et al. (2009). Briefly, an accurately weighted mass (250 mg) of rice sample, in triplicate,

was mixed in a PFA digestion vessel with 5 mL of HNO_3 (20%, v/v) and 2 mL of H_2O_2 (30%, v/v). The mixture was subjected to digestion according to a five-step program with the following temperature ($^\circ\text{C}$)/ramp (min): ~ 20 to $160^\circ\text{C}/4.5$ min, $160^\circ\text{C}/0.5$ min, 160 to $230^\circ\text{C}/5.0$ min; $230^\circ\text{C}/15$ min and 230 to $30^\circ\text{C}/20.0$ min (cooling). After cooling down to room temperature, all digested solutions were brought to 25 mL final volumes with Milli-Q water. All solutions were then spiked with the internal standard (Rhodium) to a $10\ \mu\text{g L}^{-1}$ final concentration. Stock solutions for q-ICP-MS analysis were prepared by dissolving the multi-element standard mixture solution with Milli-Q water. Working solutions were prepared by serial dilution of stock solutions with 4.0% (v/v) HNO_3 and kept at room temperature until further use.

Quantitative analysis was performed via the calibration curve method. Calibration curves were built with a minimum of five concentrations of standards per element. The limits of detection (LODs) were calculated as three times the standard deviation (S_B) of 20 consecutive measurements of the reagent blank multiplied by the dilution factor used for sample preparation (200 mg of sample/25 mL of final volume).

The nonparametric Mann–Whitney test was applied to evaluate possible differences between chemical elements in organic and conventional samples. Differences were considered significant when $P < 0.05$.

2.4. Instrumentation

q-ICP-MS measurements were carried out with a Perkin-Elmer instrument equipped with a standard reaction cell (DCR-ICP-MS ELAN DRCII, CT, USA). The sample introduction system consisted of a quartz cyclonic spray chamber and a Meinhard® nebulizer connected to the peristaltic pump of the spectrometer with Tygon® tubes. The q-ICP-MS was operated with a platinum sampler and skimmer cones purchased from Perkin-Elmer. The peristaltic pump of the q-ICP-MS was set at 20 rpm. Other instrumental parameters and experimental conditions are summarized in Table 1. High-purity argon (99.999%, White Martins, Brazil) was used throughout.

Table 1
Instrument parameters for the q-ICP-MS.

Torch injector	Quartz (2.0 mm)
Spray chamber	Cyclonic (Quartz)
Sample Uptake/Peristaltic pump speed	$1\ \text{mL min}^{-1}/20\ \text{rpm}$ (tygon tubes 0.76 mm black-black)
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 , ^{138}Ba , ^{44}Ca , ^{114}Cd , ^{140}Ce , ^{53}Cr , ^{59}Co , ^{65}Cu , ^{57}Fe , ^{139}La , ^{24}Mg , ^{55}Mn , ^{98}Mo , ^{31}P , ^{208}Pb , ^{85}Rb , ^{82}Se , and ^{64}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 = $^{64}\text{Zn} - (0.035247 \times ^{60}\text{Ni})$	
Selenium = $^{82}\text{Se} (1.007833 \times ^{83}\text{Kr})$	

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