



Italian tomato-based products authentication by multi-element approach: A mineral elements database to distinguish the domestic provenance

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ARTICLE INFO

Keywords:

Tomato
Food authentication
Geographical origin
Mineral elements
ICP-TOF-MS
LDA

ABSTRACT

In this study, we propose a novel mineral elements database for the authentication of Italian processed tomato, able to discriminate the domestic provenance from the Chinese, US and Spanish ones. Multi-element analyses by Inductively Coupled Plasma orthogonal acceleration Time-of-Flight Mass Spectrometry (ICP-oa-TOF-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) were used for quantifying 26 mineral elements (Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Co, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, In, Cs, Ba, Tl, Pb, Bi and U) in 183 tomato-based samples of different origin (Italy, China, US and Spain) collected in three different years of production (2013, 2015 and 2017). Linear Discriminant Analysis (LDA) applied to 28 variables (single elements + elemental ratios) allowed excellent separation between Italian and non-Italian tomato samples. Three elemental ratios (Li/Cu, Co/Rb and Sr/Cd) resulted highly effective in identifying the domestic provenance of tomato (100% prediction ability of the model and 98.8% in cross-validation). This result highlighted that ratios between elements were more important than single elements in discrimination.

1. Introduction

In the age of globalization of food markets, the concept of “authenticity” (genuineness and origin) of raw materials has been becoming an increasingly interesting topic for the entire food chain, consumers, and industries. For this reason, the European Community started improving information about the origin of foods, introducing, for some products, the mandatory indication on the label, and allowing members states to make country of origin labelling (COOL) mandatory if consumers feel this information is important (Regulation 1169/2011).

Thus, in 2016 first France and then Italy, in order to increase consumer transparency, extended the requirement of origin declaration to meat and dairy in prepared foods (Decree No 2016/1137, French Decree) and to milk and dairy products (9th December 2016, Italian Decree), respectively.

Afterwards in 2017, Italy further protected “Made in Italy” in the important sector of processing tomato, broadening the mandatory origin on the label to all tomato derivatives other than passata, already regulated by the 17th February 2006 Italian Decree, as well as to tomato-based products composed with more than 50% of tomato (16th November 2017, Italian Decree).

Processing tomato sector in Italy is the basis of the food economy. Italy is, in fact, the first European producer and the third in the world after California and China respectively, with about 5.2 million metric

tons of processing tomatoes produced in 2017 (WPTC, The World Processing Tomato Council, 12 October 2017).

Worldwide, a common fraud against the consumer, known as “Italian sounding”, is the use of geographical names, images and/or brands that recall the “Made in Italy” in market products that are not traceable to Italy. The business turnover of the “Italian sounding” has been globally estimated at exceeding 60 billion euros per year, an amount 2.6 times higher than the current value of Italian exports of agri-food products. This means that, for example, for every box of truly Italian peeled tomatoes there are three whose raw material, though selling as Italian, was cultivated abroad (Monti & Ponzi, 2013).

The interest in the prevention of food frauds has led to the development of analytical techniques able to trace “scientifically” the geographical provenance of food (Danezis, Tsagkaris, Brusica, & Georgiou, 2016; Luykx & van Ruth, 2008). In particular, in the field of the mass spectrometry techniques which are able to analyze bio or mineral elements of food, three kinds of approaches are currently employed: a) the measurement of the variations in the abundances of light stable isotopes (H, C, N, O and S), by Isotope-Ratio Mass Spectrometry (IR-MS); b) the measurement of the variations in the abundances of heavy stable isotopes (Sr, Pb), by Thermal Ionisation Mass Spectrometry (TIMS) or High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS); c) the determination of the elemental composition (multi-element analysis), by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

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The study of the origin of food by multi-element profiling is particularly advantageous as it brings to a high number of variables, which can be used for discrimination (Espineira & Santaclara, 2016).

Compared to other ICP-MS instruments, the Inductively Coupled Plasma orthogonal acceleration Time-of-Flight Mass Spectrometry (ICP-TOF-MS) is not very common in laboratories (Thomas, 2004). Anyway, it displays the advantage of being able to analyze, in a very quick way, a large amount of data thanks to the distinctive sampling of ions that occurs almost simultaneously (less than 50 μ s). Other advantages are well described in the literature (Sturgeon, Lam, & Saint, 2000).

The analytical performances of ICP-*oa*-TOF-MS (Inductively Coupled Plasma orthogonal acceleration Time-of-Flight Mass Spectrometry) as instrument suitable to carry out a multi-element analysis at trace and ultra-trace levels have been proved through the determination of more than 50 elements in different kinds of foods and beverages (Husakova et al., 2011). A recent work reports the use of ICP-*oa*-TOF-MS for tracing the geographical origin of vanilla samples by coupling the instrument with Laser Ablation (Hondrogiannis, Ehrlinger, Poplaski, & Lisle, 2013).

Food origin studies applying stable isotope and/or multi-element analysis have been published in a large way. A comprehensive summary of the literature relating to the application of this kind of analysis was reported by Kelly, Heaton, & Hoogewerff, 2005. Regarding vegetable products, more recent studies refer to the origin determination of citrus fruits (Benabdelkamel et al., 2012), coffee (Barbosa, R. M., Batista, Varrique, Coelho, Campiglia., & Barbosa, F., 2014), fruit juices (Bat et al., 2016; Rummel, Hoelzl, Horn, Rossmann, & Schlicht, 2010), hazelnuts (Oddone, Aceto, Baldizzone, Musso, & Osella, 2009), olive oil (Benincasa, Lewis, Perri, Sindona, & Tagarelli, 2007), red onion (Furia, Naccarato, Stabile, Sindona, & Tagarelli, 2011), wheat (Liu et al., 2017), various commercial vegetables (Laursen et al., 2011; Opatič, Necemer, Lojen, & Vidrih, 2017), and tomato-based products (Bontempo et al., 2011; Lo Feudo, Naccarato, Sindona, & Tagarelli, 2010; Trincherini, Baffi, Barbero, Pizzoglio, & Spalla, 2014).

One of the issues that must be taken into account during the assessment of the origin of food is the influence of the production chain of a certain derivative product on chemical markers able to trace the original fresh food (Espineira & Santaclara, 2016).

In the case of tomato (*Lycopersicon esculentum*), studies from literature demonstrate that the geographic discrimination is independent of both the technological process and the harvest period of the fruit (Bontempo et al., 2011; Lo Feudo et al., 2010; Trincherini et al., 2014).

Drawing upon these interesting results, we set up a multi-element analysis by ICP-*oa*-TOF-MS (Optimass9500, GBC Scientific Equipment Pty Ltd., Australia), exploring, as a first approach, the discriminating power of rare earth elements (REEs) on twenty-seven tomato-based products coming from Italy and China.

According to recent literature (Aceto et al., 2013; Farmaki et al., 2012; Guicen, Zhang, Y., Zhang, J., Wang, Chen, Zhang, M. et al., 2016; Oddone et al., 2009), REEs proved to be, in fact, good provenance indicators for food, as no fractionation of the distribution of such elements in soil seems to occur during absorption of REEs ions by plants (Espineira & Santaclara, 2016).

Our preliminary data (not published data) showed a very low content of REEs in tomato samples, according to those described by Spalla et al. (2009). Moreover, in agreement with Lo Feudo et al. (2010), who reported that Ce, Dy, La, Lu, Nd, Sm and Th do not contribute to the discrimination of tomato-based products according to the geographical origin, we found that REEs could not distinguish our Italian samples from the Chinese ones.

Thus, in our subsequent study (Fragni, Trifirò, & Nucci, 2015), we checked the possibility to trace by multi-element analysis the provenance of forty-one different processed tomato products (juices, passata, double and triple concentrates) coming from Italy, China and Spain, focusing our attention to other micro-elements different from REEs.

As a good discrimination between EU and Chinese samples was

obtained, in this work we implemented previous results analysing other 128 tomato samples of known origin (Italy, China, US and Spain), with the final aim to build a robust mineral elements database for the Italian tomato authentication.

In all 169 samples, twenty-six mineral elements (Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Co, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, In, Cs, Ba, Tl, Pb, Bi and U) were considered; the twenty-two micro-elements (Li, Be, Al, V, Cr, Mn, Co, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, In, Cs, Ba, Tl, Pb, Bi and U) and the other four macro-elements (Ca, K, Mg, and Na) were quantified by ICP-*oa*-TOF-MS and ICP-OES (Vista MPX, Varian), respectively.

Spectral interferences occurring during analyses with ICP-*oa*-TOF-MS were studied, and the usefulness of Linear Discriminant Analysis (LDA) for building the classification model was evaluated.

Finally, by way of example, 14 “Italian sounding” commercial tomato samples coming from the US with labels that recalled the “Made in Italy” were analyzed and classified in the built LDA model.

2. Experimental

2.1. Chemicals and reagents

Reagents used for samples mineralization and preparation of all solutions necessary for ICP analyses, HNO₃ (69%, m/v) and H₂O₂ (30%, m/v), were ultra-pure grade (Ultrex II, Baker). All solutions were prepared with high-purity deionized water (0.05 μ S/cm, Purelab Ultra ELGA).

ICP-TOF-MS analyses: Multi-element solution containing Li, Al, V, Cr, Mn, Co, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, Cs, Ba, Tl, Pb and U (10 mg/l, Spex CertiPrep, Claritas) was used to prepare the calibration standards in 1% HNO₃; Be, In and Bi mono-element solutions (1000 mg/l, PlasmaCAL, SCP Science) were 1000-fold diluted for obtaining internal standard solutions of Be, In and Bi (1000 μ g/l) in 1% HNO₃ to be added both to calibration standards and to mineralized samples.

Instrument tuning was carried out with a 10 μ g/l solution containing Ba, Be, Ce, Co, In, Mg, Pb, Rh, and U (Spex CertiPrep Claritas, 10 mg/l).

For spectral interferences recognition, mono-element solutions of Ca, K, S, and P (1000 mg/l, TraceCERT[®], Fluka) were opportunely diluted; anhydrous beads of NaCl (99.999% trace metals, Aldrich) were used for the assessment of chlorine interferences.

ICP-OES analyses: Multi-element solution containing 100 mg/l of Ca, K and Na and 10 mg/ of Mg (TraceCERT[®], Fluka) was used to prepare the calibration standards in 1% HNO₃.

Instrument tuning was carried out with a solution containing 5 mg/l of Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Mo, Sr and Zn and 50 mg/l of K (Vista Cal, Varian).

2.2. Samples

The 169 samples used for building the mineral elements database, consisted of tomato juices, passata, semi-concentrated, double and triple concentrated tomato pastes collected in three different years of production (2013, 2015 and 2017). Tomato samples came from Italy (N = 140), China (N = 17), US (N = 4) and Spain (N = 8). Most of the Italian, as well as foreign products of known origin (Chinese and American), were kindly provided by “Ministero delle Politiche Agricole Alimentari e Forestali (MiPAAF)” and “Agenzia delle Dogane”; all Spanish and some Italian and Chinese samples were brought to Italian supermarket and/or provided by food companies. Finally, 14 samples of “Italian sounding” tomato passata of unknown origin came directly from US companies. In Table 1 all processed tomato samples divided by type and origin are listed.

2.2.1. Samples preparation

Before elements quantification, samples and suitable blanks were mineralized in triplicate by a wet acid digestion (Wheal, Fowles, &

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