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Precise determination of strontium isotope ratios by TIMS to authenticate tomato geographical origin

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ABSTRACT

Thermal Ionisation Mass Spectrometry (TIMS) was applied to discriminate a total of 118 tomato samples (berries, "passata", tinned tomatoes, sauce, double and triple concentrate) coming from two different countries. The TIMS technique gave significantly different results for the $^{87}Sr/^{86}Sr$ ratios and δ‰ values between Chinese and Italian tomato samples, irrespective of the treatment type. This technique proved to be a "robust" method, suitable for a precise discrimination of the two geographical origins. TIMS was able, within the Italian samples, to discriminate different geographical production areas, by virtue of different $^{87}Sr/^{86}Sr$ ratios and δ‰ values. This technique could be employed in the field of food safety and quality, as a profitable tool for authenticating tomato geographical origin.

1. Introduction

The authentication of the origin of food products, through a precise determination of the different geographical origin, can answer important questions concerning food safety, food quality and consumer protection. In this regard the European Union (EU) has issued some regulations concerning the protection of food names: protected designation of origin (PDO), protected geographical indication (PGI) and traditional specialities guaranteed (TSG) (Mout, 2004). The regulations now in force in the EU are 510/2006 for PDO and 509/2006 for PGI; in 2002 an anti-fraud legislation (178/2002) was introduced; in 2006 the EU regulation 1898/2006 was added. These indications are particularly important in EU countries, where there has been a long tradition of associating certain food products with particular regions (Luykx & van Ruth, 2008); at present, in EU countries, no legislation exists for governing and checking the import of plant foods, unlike the import of foods of animal origin which is ruled by EU Regulation 882/2004. This fact, together with the different legislation in force in the "global" wider tomato trade market, allows illegal behaviour, such as food fraud, which can damage both trade and human health. For the future a globally-accepted legislation with severe monitoring actions and penalties should be adopted; it should be based on shared "robust" methods, set up and validated in terms of internal precision and external accuracy, independent of the "labelling".

The analytical approaches for determining the geographical origin of food products date from 1980s; they have been subdivided into four groups: mass spectrometry techniques (IRMS, ICP-MS, PTR-MS, GC–MS), spectroscopic techniques (NMR, IR, fluorescence and atomic spectroscopy), separation techniques (HPLC, GC, CE) and other techniques, including DNA technology and sensor analysis (Luykx & van Ruth, 2008). The most employed approach for establishing the geographical origin of food compounds seems to consist in a combination of the above methods; nevertheless, for a single food, fresh or processed, in a single laboratory, the results obtained by a validated analytical method could profitably support the legislator's decisions.

As far as tomato authenticity is concerned, numerous studies have been developed in recent years (Arvanitoyannis & Vaitsi, 2007). Magnetic Resonance Imaging (MRI) spectroscopy has allowed the distinction between PGI fresh cherry tomatoes and non-PGI ones (Sequi, Dell' Abate, & Valentini, 2007). ^{1}H NMR (nuclear magnetic resonance) spectroscopy, in combination with multivariate analysis has differentiated the metabolite content of Chinese and Italian tomato pastes (Consonni, Cagliani, Stocchero, & Porretta, 2009; Consonni, Cagliani, Stocchero, & Porretta, 2010). Inductively coupled plasma mass spectrometry (ICP-MS) in combination with linear discriminant analysis (LDA), soft independent modelling of class analogy (SIMCA) and K-nearest neighbours (KNN), have been employed to discriminate different geographical

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zones for fresh tomatoes and triple concentrated tomato paste (Lo Feudo, Naccarato, Sindona, & Tagarelli, 2010). Until now, no study has been published concerning the discrimination of the geographical origin for tomato with the use of thermal ionisation mass spectrometry (TIMS).

This technique has been successfully employed in hydrology (Chaudhuri, 1978), in geochemistry and cosmochemistry (Dickin, 1995; Faure, 1986; Huchon, Taylor, & Klaus, 2001), in Anthropology (Evans, Chenery, & Montgomery, 2012; Latkoczy, Prohaska, Watkins, Stingeder, & Teschler Nicola, 2001), for forensic purposes (Beard & Johnson, 2000; Rummel, Hoelzl, & Horn, 2007) and it has been applied in the food field to authenticate the origin of wines, vegetables, dairy products and beef (Barbaste, Robinson, Guilfoyle, Medina, & Lobinski, 2002; Horn, Schaaf, Holbach, Holzi, & Eschnauer, 1993; Rossmann et al., 2000; Rummel et al., 2012; Swoboda et al., 2008). It takes advantage of the principle according to which, during growth, plants absorb nutrients from the soil without any interference, such as isotopic fractionation (Stewart, Capo, & Chadwich, 1998). Good correlations were observed between the concentration profile of heavy metals in plant foods and in the soil where they were grown, which were even better for fresh foods than those derived from metabolic processes (Fortunato et al., 2004).

In nature Strontium is present with four stable isotopes: ^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr, where the isotope composition varies according to the β-decay of ^{87}Rb, which turns into ^{87}Sr with a half-life decay time ($T_{1/2}$) of 4.7×10^{10} years. The Rb–Sr combination generates different ^{87}Sr/^{86}Sr isotopic ratios which, reflecting only the variations in the amount of radiogenic ^{87}Sr present in the sample, depend on the age and on the pedological characteristics of soils where they naturally occur, namely their geographical origin. The net result is that the strontium isotopic composition of a sample yields information about provenance or geological interaction, unobscured by local temperature variations or internal biological processes (Capo, Stewart, & Chadwick, 1998). These results were confirmed by data of Sr isotopic ratios carried out on a high number of European mineral waters, where the different ^{87}Sr/^{86}Sr ratios observed (range 0.7035–0.7777) were significantly affected by different rock types, after being permeated by waters (Voerkelius et al., 2010).

The possibility to discriminate different geographical origins within small ranges of variation of the ^{87}Sr/^{86}Sr isotope ratios, requires high precision of the measurement and this can be reached by the thermal ionisation mass spectrometry (TIMS) technique. For food traceability, sector field mass spectrometry with plasma source (SF-ICP-MS), both with single and multiple collectors (MC-SF-ICP), was used for solid samples, while SF-ICP-MS and the TIMS technique were employed for water samples. TIMS is recognised as the most precise technique, although it is time consuming, because it lacks isobaric interference of a molecular nature which forms during the ionisation processes in the spectrometers with plasma sources; moreover TIMS is very suitable for dealing with an investigation based both on the discrimination between isotope ratio values $\leqslant$0.1% and on an internal precision of the measurement better than 0.005%. In all isotope techniques, before measurement, it is essential to separate Sr from Rb, in order to eliminate the isobaric interference caused by ^{87}Rb which is always present, although with variable concentrations, in samples from geological environments, and therefore also in the samples of food chains closely bound to them. The tomato (*Licopersicum esculentum*) is a plant belonging to the family of the *Solanacee*. Botanically, it is an ovary, with seeds of a flowering plant; therefore it is a fruit or, more precisely, a berry with a typical red colour. Tomatoes can have beneficial effects on human health, due to the presence of antioxidants such as carotenoids (lycopene and β-carotene) and polyphenols (flavonoids and hydroxyl cinnamic acids). About 1700 tomato varieties are registered in the world, but only 100 of them are responsible for 70% of total world production. In Italy 300 tomato varieties are registered but only 60 of them are used every day (http://www.zipmec.eu/en/Vegetables-production-and-processing-trade/tomatoes-history-production-trade.html). World production of fresh tomatoes in 2012 was 33 million tons (M t) (World Production Estimate of Tomato Processing – WPTC., 2012), a quarter of which is devoted to industrial processing. Italy (4.5 M t) is the leading producer among the Members in Mediterranean Area (AMITOM) (13.8 M t) and the second producer in the world, preceded by California (11.7 M t). China, with 3.2 M t, is the third world producer, having acquired this position in only 15 years (World Processing Tomato Council, WTO, 2012). As far as exports of tomato are concerned, China is the world leader, followed by Italy. The biggest market for Chinese exports is the EU 27 area. China started to export in 1995, firstly, to the neighbouring nations of the Far East (Japan, Philippines, Korea), then, in the subsequent 15 years, to EU countries (Italy, Germany, UK) and Russia. After 2004 Chinese producers opened up new markets for their products, especially in North and West Africa. China has also become a transformer of tomato by virtue of new installations sited near Gansu and in Mongolia and it is the only nation in the world not subjected to any law concerning tomato cultivation so it can produce GMO tomatoes too. As regards tomato processing, in Italy, in 2012, the Regions of Apulia and Emilia-Romagna have devoted 34% and 33% of the national utilised agricultural area (UAA) for tomato cultivation, representing 37% and 31%, respectively, of the total Italian production. China, is the main supplier (52.9% of the total) of semi-manufactured tomatoes for Italy; in these last 10 years imports of concentrated tomatoes from China have increased fourfold (+272%). Tinplate packings of tomato concentrate, of over 200 kg, are unloaded from Chinese ships; this product is processed again and packed as an Italian product; this is possible because, by virtue of the legislation in force, the indication of the origin of the cultivated product is not compulsory on the containers for sale, the mark of packaging being enough. The Chinese tomato product is characterised by a very competitive price but, lacking in most of the qualitative and organoleptic characteristics of the Italian tomato products, it is often used to blend the Italian product; in this way it supplements the national supply. The risk is that often this mixed product can be marketed with the wording "made in Italy".

The aim of this study was to verify the suitability of TIMS as a "robust" technique for the authentication of the geographical origin of processed or fresh tomato samples coming from China and Italy, through a discrimination based on a precise determination of the ^{87}Sr/^{86}Sr ratios. This may allow us to build up isotopic clusters, relative to Chinese and Italian tomato products, irrespective of the type, e.g. fresh or processed, so as to enable a sure geographical assessment of the place of origin for unknown samples whether Chinese or Italian.

2. Experimental

2.1. Samples

Fig. 1 shows the geographical distribution of the total 118 tomato samples, listed below following a chronological sampling time order:

- 40 samples from the Province of Piacenza, Region of Emilia-Romagna, north Italy: berries, double and triple concentrated tomato paste, in tins; years 2006–2008.