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

P.R. Trincherini [a,*], C. Baffi [b], P. Barbero [a], E. Pizzoglio [a], S. Spalla [b]

[a] LIMS (Laboratory for Isotope Mass Spectrometry), "L. Cobianchi", Piazza Martiri di Trarego 8, 28921 Verbania, Italy
[b] Università Cattolica del S.Cuore, Istituto di Chimica Agraria e Ambientale, via Emilia Parmense, 84, 29122 Piacenza, Italy

## 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 $\delta‰$ 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 $\delta‰$ values. This technique could be employed in the field of food safety and quality, as a profitable tool for authenticating tomato geographical origin.

© 2013 Elsevier Ltd. All rights reserved.

## 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). $^1H$ 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

---

* Corresponding author. Tel.: +39 (0) 32352562.
*E-mail address:* pierre.trincherini@gmail.com (P.R. Trincherini).

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, & Chadwick, 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 $4.7 \times 10^{10}$ 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 ⩽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.
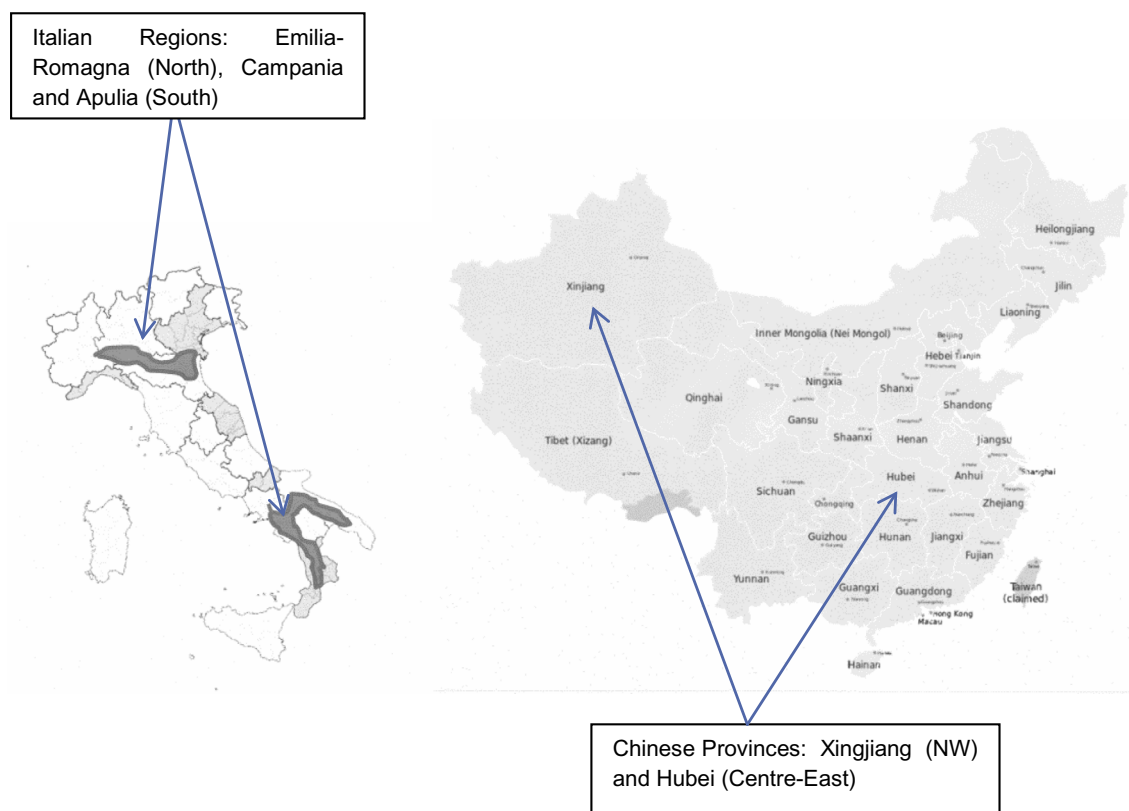
Italian Regions: Emilia-Romagna (North), Campania and Apulia (South)

Chinese Provinces: Xingjiang (NW) and Hubei (Centre-East)

**Fig. 1.** Provenance areas of tomato samples. Left: the Emilia-Romagna Region (north Italy), the Apulia and Campania Regions (south Italy). Right: the Xinjiang (NW) and the Hubei (Central-East) Provinces of China.

- 30 selected samples from the Provinces of Piacenza, Parma and Ferrara; Emilia-Romagna Region, north Italy: samples of berries (1–2 kg of different cultivars) and "passata" (0.5 kg) in glass bottles; year 2010.
- 30 samples from China: double and triple concentrated paste and tomato sauce of 70–200 g in size (Hubei Province) and of 3.0 kg in size (Xinjiang Province), in tinplate packings; year 2011.
- 12 samples from the Region of Apulia, southern Italy: mini-tins of tomatoes in 100 g size tins; year 2011.
- 6 "blind" samples of unknown origin: "passata" and tinned tomatoes (0.5–4.0 kg), in glass bottles and tin cans; year 2011.

All the samples were collected by the staff of a private processing tomato firm (Mutti S.p.A., Montechiarugolo, Parma, I) and by the personnel of the Institute of Agricultural and Environmental Chemistry (IAEC, Catholic University, Piacenza, I) according to the sampling times listed above. In order to guarantee the maximum correspondence between "passata" and berries, for the set of 30 tomato samples selected from north Italy, a particular sampling scheme with georeferenced samples was adopted. The other samples were obtained directly or through commercial trade channels, making sure they were representative of the geographical area of provenance. After preliminary treatments such as quartering, blending and freeze-drying, carried out in the IAEC laboratory, the samples were sent to the Laboratory for Isotope Mass Spectrometry (LIMS; Verbania, I) for dissolution, chemical pre-treatment and isotope measurements.

### 2.2. Materials: reagents and standard solutions

HNO₃ (Traceselect), analytical grade reagents (H₂O₂) and high-purity deionised water, Milli-Q (18.2 MΩ) from Millipore (Sigma–Aldrich, St. Louis, MA, USA) purified by a ping-pong sub-boiling © Teflon distillation system, were used for sample dissolution procedures. Glassware was rinsed by overnight immersion in a solution of $HNO_3$ (10% m/v), followed by rinsing with deionised water. The SRM 987 ($SrCO_3$ isotopic) from the National Standards and Technology (NIST) (Gaithersburg, MD, USA) was used for external precision measurement (RESD) and method validation. Except for freeze-drying and dissolution, all the other lab operations were carried out under Class 100 clean conditions (Aquaria, MI, I). FEP (fluorinated ethylene propylene) containers were used for the storage and treatment of the samples, according to a well-documented and certified procedure (Trincherini et al., 2003).

### 2.3. Instrumentation

The instrumentation for sample preparation consisted in a freeze-dryer (mod. Mini Fast 680, Edwards, Norfolk, UK) for lyophilisation, in a closed microwave oven (MILESTONE, Montoe, CT, USA) or in a simple digestion under controlled atmosphere for chemical dissolution, in an atomic absorption spectrometer (VARIAN *Mod220*; Varian Australia Ltd, Mulgrave 3170, Victoria, Australia) for the determination of Sr and Rb concentrations in digested samples, and in a Sr-resin 50–100 μm from EiChrom Europe (Triskem, Bruz, F) for Sr–Rb separation. The instrumentation for isotope analysis consisted in a Finnigan 262 VMC mass spectrometer (*Finnigan*, Thermo Scientific GmbH, Bremen, D), able to focus the following masses: $^{84}Sr$, $^{85}Rb$, $^{86}Sr$, $^{87}Sr$ and $^{88}Sr$, and equipped with 5 Faraday cups placed in a variable multicollector, with extensive optical geometry, but corresponding to a system that has a conventional geometry, with a 64 cm deflection radius.

The measurements were carried out on the "zone refined" rhenium (Re) filaments (H. Cross Co., Moonachie, NJ, USA). An advanced software for data acquisition was installed by Spectromat

GmbH, Bremen, D. Parameters such as mass calibration and gain calibration, were performed for the multicollector daily. The instrument can accept a block of thirteen samples with two reference isotopic standards (SRM NIST 987) as continuous accuracy control. Together with over 100 tomato samples, 35 samples of isotopic standard were measured with a final value of 0.71031 ± 0.00003, equivalent to an internal precision better than 40 ppm and an external precision comparable with the certified value.

## 3. Measurements

### 3.1. Sample pre-treatment

In the IAEC lab all samples, except the liquid ones, after quartering, were submitted to a mixing procedure before freeze-drying, carried out for two days at $T = -40\ °C$, with the use a freeze-dryer. Then samples were ground by using agate mortar and pestles to obtain a fineness of 1–2 mm. Subsequently they were sent to LIMS lab, in polyethylene bottles, for analysis.

For digestion, a 250–300 mg of freeze-dried sample was dissolved by using both a microwave assisted digester and chemical mineralisation working under a controlled atmosphere. In both cases, 2–3 mL of $HNO_3$ (Traceselect) and, sometimes a few drops of ultrapure $H_2O_2$ were added as digestion reagents. As far as the dissolution completeness and the results of the determination of the isotopic ratios are concerned, no difference was observed between the above two methods, except for a shorter time for the assisted digestion. After evaporation to dryness, the residue was dissolved again in 10 mL of 8 M $HNO_3$ and the solution thus obtained was transferred to a Sr-resin column, where Sr was fixed, then eluted with 0.05 M $HNO_3$ and finally eliminated as a leachate. The most suitable conditions for Rb/Sr separation had previously been established by measuring, by AAS, the concentrations of Sr and Rb in an initial series of 40 digested tomato samples. The Rb/Sr concentration ratio showed values close to 1 for 63% of the samples, between 0.5 and 1 for 15% of the samples and <4 for the remaining 22% of the samples; Sr concentration values ranged from a minimum of 1 ppm to a maximum of 12 ppm, with an average value of 5.30 ppm. The separation procedure was optimised using the specific Sr-resin described above, following a separation procedure optimised to a well-known and documented method (Fortunato et al., 2004; Swoboda et al., 2008; Trincherini et al., 2003). At first the resin was conditioned with $HNO_3$ (about 1% w/w) for at least 12 h, during which the supernatant $HNO_3$ was replaced at least twice. Once employed, the resin can be utilised again, subject to an accurate series of washings with $HNO_3$ (about 1% w/w) and rinsing with ultrapure and redistilled water. Some tests carried out on the recycled resin using the certified standard SRM 987 served to ascertain the complete absence of the Sr previously employed. The measurement of Sr and Rb concentrations by AAS was necessary to fix the aliquot of the sample to be loaded on the resin in conformity with EiChrom Recommendations (EiChrom; Horwitz, Chiarizia, & Dietz, 1992), according to which the resin should be charged with 10–20% of the maximum capacity, i.e. about 10 mg mL$^{-1}$. The volume of the sample was reduced to 5 mL and the washing of the resin was done with 2–3 mL $HNO_3$ 6–7 mol L$^{-1}$. At the end the eluate containing Sr was submitted to dry evaporation, recovered with 50 μL of $HNO_3$ 1% and, later on, reduced at the time of the deposition on the filament. Following experimental optimisation of volumes and concentrations, the separation of Sr–Rb can achieve very good results but hardly ever 100%. In particular, in some samples where the Rb/Sr ratio is equal to 1.5–2.0 or more, the eluate can include significant traces of Rb. This element can strongly affect the measurement of the isotopic ratio inducing a positive drift, as can be seen in Figs. 2a and 2b.

In Fig. 2a the value of the $^{87}Sr/^{86}Sr$ isotopic ratio is assumed to be equal to 0.7100, for the total absence of Rb; increasing amounts of Rb (expressed as the % Rb/Sr ratio) can strongly modify the measurement of the $^{87}Sr/^{86}Sr$ isotopic ratio. By extrapolation of the dashed area the precision and the acceptable Rb/Sr percentage values can be better observed, with no mathematical corrections as in Fig. 2b, necessary for the present investigation.

### 3.2. Isotopic ratio measurements

The mass spectrometer TIMS (Finnigan 262 VMC) was equipped with a multicollector system able to focus the following masses: $^{84}Sr$, $^{85}Rb$, $^{86}Sr$, $^{87}Sr$ and $^{88}Sr$. Since mass 85 is present only in the Rb and not in Sr isotopic composition, it can be monitored continuously without any interference and the $^{87}Rb$ value can be deduced from the $^{85}Rb$ value since the $^{85}Rb/^{87}Rb$ ratio is about 3. Inside the spectrometer, the heating program for filaments of emission and evaporation (the sample is deposited on the latter) allows us to "burn" Rb traces and to check the total absence of signal at mass 85. Only at this point is it possible to begin the data acquisition concerning isotopic $^{87}Sr/^{86}Sr$ ratio values. The long-lasting stability of the signal produced by ions emitted by filaments is responsible for the high precision of the measurement obtained by this technique where, once the best separation has been set up, the measurement process is no longer subject to any interference. The software of the instrument foresees a series of fundamental calibrations, among which, in particular, the detector scan of each Faraday cup and the vision of their alignment (Fig. 3). The stability of the peak shape, especially the top one, differentiates the measure carried out by use of isotopic ratios by TIMS from that obtained by any other instrument, ICP-source mass spectrometers included. Rosner (2010) accurately analyses the problems involved in the measurement of the isotopic ratio $^{87}Sr/^{86}Sr$ when an ICP-source is used. They are very complex and difficult to solve when a quadrupole sector is used, but partially remediable when a double focussing (DF) mass spectrometer equipped with a multicollector (MC) is used. Also in this instance, however, the presence of non-eliminable ions (Kr$^+$), partially non-eliminable ions (Rb$^+$) and of molecular interferent ions, originated from the matrix composition, requires mathematical corrections which are not always and not necessarily univocal. The certified standard SRM 987 (NIST) was used to ensure quality both as an internal standard and as a check for instrumental functionality, with the criterion of two standards at the least for every ten samples. The series of results ($n = 36$) gave a value of the internal precision, the relative internal
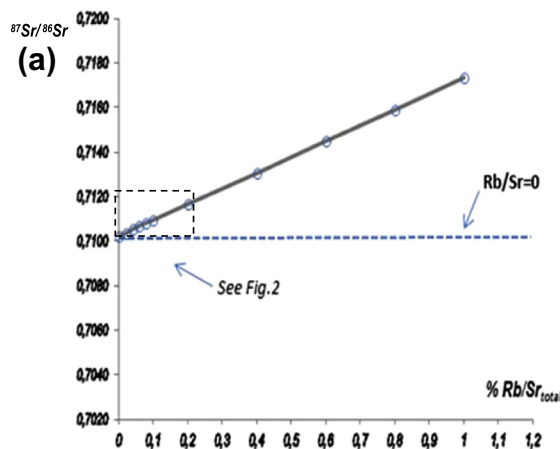


**Fig. 2a.** Changes in the $^{87}Sr/^{86}Sr$ isotopic ratio according to the increasing amounts of Rb added.
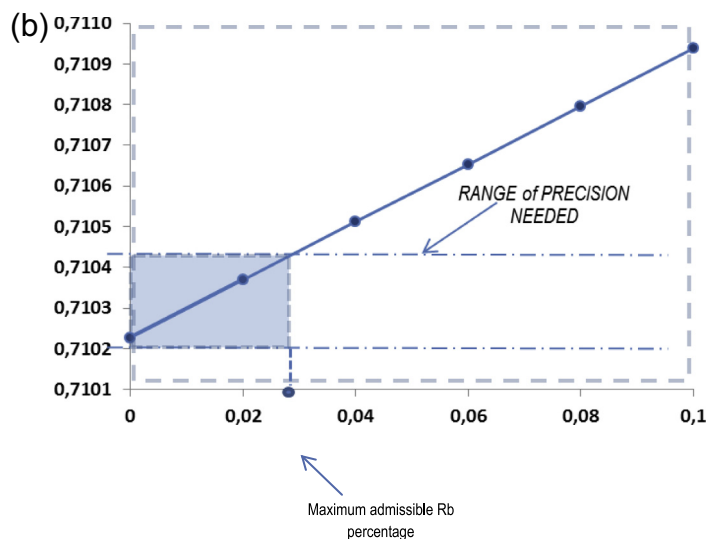
**Fig. 2b.** The smallest dark area shows the precision range required and the relative maximum allowable percentage of Rb according to the precision needed.
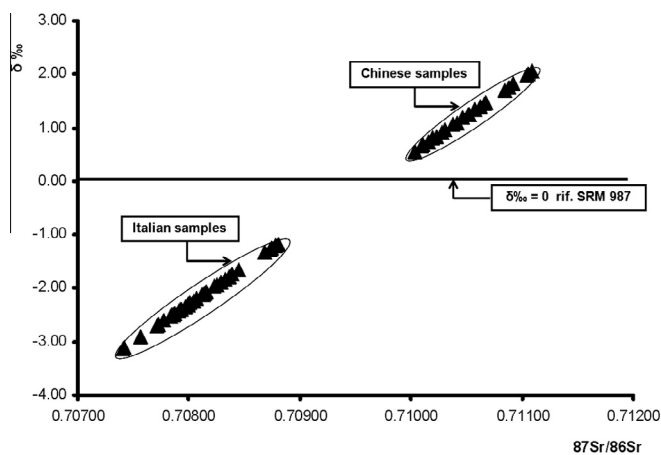


**Fig. 3.** Data concerning the $^{87}$Sr/$^{86}$Sr ratio and $\delta$‰ in tomato samples from Italy and China; $\delta$‰ = 0 is for the SRM 987 standard certified sample.

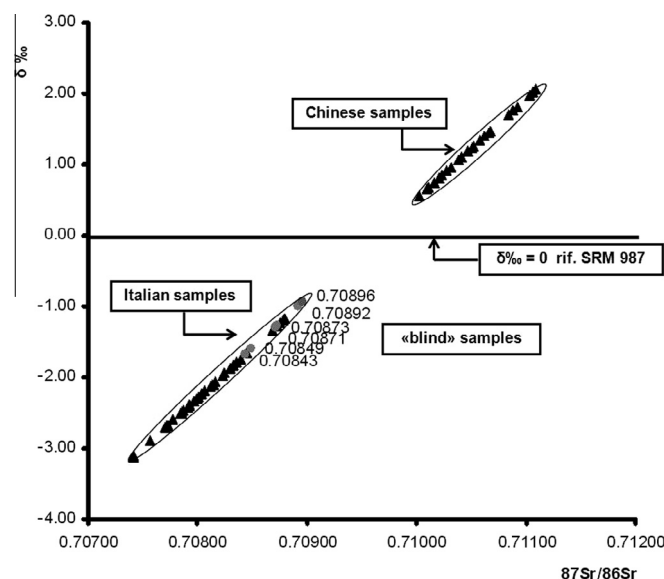standard deviation (RISD) $\leqslant$ 40 ppm and of the accuracy, the relative external standard deviation (RESD), about 20 ppm. All samples were analysed in duplicate and the results gave a value of reproducibility <40 ppm. The $\delta$‰ of the isotopic ratio $^{87}$Sr/$^{86}$Sr was calculated by the algorithm:

$$\delta^{87}\mathrm{Sr}(‰) = \left(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{analysed}}/^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{standard}} - 1\right) \times 1000 \qquad (1)$$

where SRM 987 is the reference standard.

The statistical analysis was performed with the IBM SPSS© vers.19.0 software package. All data were tested firstly for normality (Shapiro & Wilk, 1965), then underwent both the Levene's test for equality of variances (Levene, 1960) and the ANOVA 1-way and the $t$-test of independent samples (Clewer & Scarisbrick, 2001).

## 4. Results and discussion

In preliminary trials a series of 40 tomato samples (berries, double and triple concentrate) from the Province of Piacenza (north Italy) were analysed in order to set up the method in terms of the optimisation of the conditions for the analysis (amount, contact time, reading time, etc.). Subsequently a series of 30 selected samples (berries and "passata") from north Italy and 30 samples
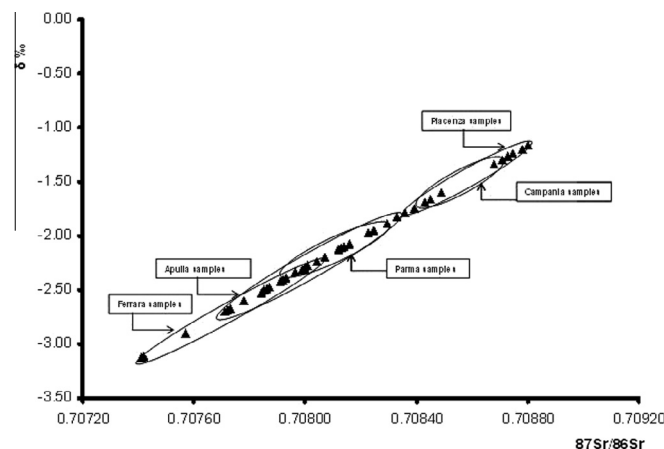


**Fig. 4.** Position of values of $^{87}$Sr/$^{86}$Sr and $\delta$‰ "blind" tomato samples respect to Italian and Chinese samples.



**Fig. 5.** Italian sample distribution according to different areas of production: $\delta$‰ vs $^{87}$Sr/$^{86}$Sr ratio.

**Table 1**
Mean values of the $^{87}Sr/^{86}Sr$ ratio and $\delta\text{‰}$ in tomato samples; statistical results ($t$-test of the independent samples) for mean comparisons.

| Provenance of samples | $^{87}Sr/^{86}Sr$ | $\delta\text{‰}$ | Statistical comparisons | | |
|---|---|---|---|---|---|
| North-Italy | 0.70817 ± 0.00039 | −2.06 ± 0.548 | n.s. | ** | |
| South-Italy | 0.70793 ± 0.00022 | −2.39 ± 0.303 | n.s. | | ** |
| China | 0.71051 ± 0.00033 | +1.24 ± 0460 | | ** | ** |
| "Blind" samples | 0.70871 ± 0.00022 | −1.30 ± 0.303 | n.s. | ** | |
| Italy | 0.70810 ± 0.00036 | −2.15 ± 0.303 | n.s. | | ** |
| China | 0.71051 ± 0.00033 | +1.24 ± 0460 | | ** | ** |

n.s. = not significantly different.
** Statistical significance ($t$ independent test) with $P < 0.01$.

(sauces, double and triple concentrated tomato paste) from China (Xingiang and Hubei Provinces) were analysed, together with the certified standard SRM 987, in order to verify a real discriminant capacity of the proposed technique. The $^{87}Sr/^{86}Sr$ ratio mean values were 0.70817 ± 0.00039 for the samples from north Italy and 0.71051 ± 0.00033 for the samples from China; $\delta\text{‰}$ mean values were −2.06 ± 0.548 for the northern Italian samples and 1.24 ± 0.460 for the Chinese samples. The $t$-test of the independent samples highlighted significant differences ($P < 0.01$) between mean values of samples from the two populations (north Italy and China).

A second series of 12 mini-tins of tomato samples from southern Italy, subsequently analysed, gave mean values of 0.70793 ± 0.00022 for $^{87}Sr/^{86}Sr$ ratio and of −2.39 ± 0.303 for $\delta\text{‰}$. The $t$-test of the independent samples confirmed the presence of significant differences ($P < 0.01$) between mean values of samples from south Italy and China and no difference between southern a northern Italian tomato samples.

Fig. 4 shows data of the $^{87}Sr/^{86}Sr$ ratio and the $\delta\text{‰}$ values for Italian and Chinese tomato samples. The former constitutes a unique homogeneous population with mean values of 0.70810 ± 0.00036 for the $^{87}Sr/^{86}Sr$ ratio and of −2.15 ± 0.303 for $\delta\text{‰}$, below the zero line $\delta\text{‰} = 0$ of certified standard SRM 987. Mean values for the $^{87}Sr/^{86}Sr$ ratio and $\delta\text{‰}$ of the two populations resulted significantly ($P < 0.01$) different with the $t$-independent test.

Lastly 6 "blind" samples were analysed; the results gave mean values of 0.70871 ± 0.00022 for the $^{87}Sr/^{86}Sr$ ratio and of −1.30 ± 0.303 for $\delta\text{‰}$. Fig. 5 shows the positions they occupy in the plot $\delta\text{‰}$ vs $^{87}Sr/^{86}Sr$ ratio, with respect to the Italian and Chinese samples. The $t$ test highlighted that they were significantly ($P < 0.01$) different from the Chinese samples but did not differ from the Italian samples (see Table 1). The firm which supplied the "blind" samples afterwards told us their provenance: southern Italy (three from the Apulia Region and three from the Campania Region).

A series of ten samples, five Italian and five Chinese, was analysed later in time, in order to investigate the total *reproducibility* of the method, including both the sample preparation and the mass-spectrometric measurement. For nine samples the reproducibility was ⩽60 ppm and for one sample was equal to 91 ppm; these values guarantee the boundaries of the relative clusters and, according to this, the certain discrimination between the two geographical origins. A one-way ANOVA carried out on all of the Italian samples revealed significant differences ($P < 0.01$) concerning the mean values of the $^{87}Sr/^{86}Sr$ ratio and $\delta\text{‰}$ values, with lower values observed for samples from organic hydromorphic soils of the youngest geological age, intermediate values for samples from poorly evolved soils of intermediate geological age and higher values for samples from more ancient soils developed on older rocks (see Fig. 5). In literature there is little research on the correlation between the Sr isotope ratio and soil geographical

origin, compared to the numerous studies on mineral waters (Voerkelius et al., 2010).

There are rare cases where only the measurement of the isotopic ratio $^{87}Sr/^{86}Sr$ is not sufficient to discriminate two geographical areas showing similar geological features; consequently, it is necessary to add at least one other technique, for example the multielemental analysis (Bong et al. 2012). Here the main aim was to supply a sure method to discriminate two distant geographical origins (Italy and China), which could be used for anti-fraud purposes.

For this aim our study has taken into account more than one hundred of tomato samples of different types and the results unambiguously prove that this aim was achieved. The precision and accuracy of the employed method were able to differentiate, within Italian tomato samples, those coming from soils with different geological ages.

## 5. Conclusions

For the aim of this work TIMS proved to be a "robust" analytical technique, in that it allowed a precise geographical discrimination of the origin of tomato products, both fresh and processed, coming from Italy and China. Within the Italian samples due to the high precision and accuracy of this technique, the method was able to discriminate tomato products from soils of different geological ages.

This method could be used as a profitable tool to authenticate tomato origin of both fresh and processed samples coming from Italy and China, because it is independent from the industrial treatment that tomatoes undergo and depends only on the cultivation soil age. As a consequence the two distinct "clusters" of population built up in this study could be useful for identifying the certain geographical origin of tomato products in case of doubt concerning trade declaration about the provenance. This could be important to contrast the growing illegal imports of tomato products from countries where the strict EU legislation is not in force. If, on the one hand, this method fights trade frauds, on the other hand, its importance is particularly relevant for the defence of certified foods (PGI and PDO) and for the protection and safety of consumer health. A further development could consist in an increase of the database through the introduction of new samples both from selected areas and, later on, from geographical areas with few food frauds.

## References

Arvanitoyannis, I. S., & Vaitsi, O. B. (2007). A review on tomato authenticity: Quality control methods in conjunction with multivariate analysis (Chemometrics). *Critical Reviews in Food Science and Nutrition, 47,* 675–699.

Barbaste, M., Robinson, K., Guilfoyle, S., Medina, B., & Lobinski, R. (2002). Precise determination of the strontium isotope ratios in wine by inductively coupled plasma sector field multicollector mass spectrometry (ICP-SF-MC-MS). *Journal of Analytical Atomic Spectrometry, 17,* 135–137.

Beard, B. L., & Johnson, C. M. (2000). Strontium isotope composition of skeletal material can determine the birth place and geographic mobility of humans and animals. *Journal of Forensic Sciences, 45*(5), 1049–1061.

Bong, Y. S., Shin, W. J., Gautam, M. K., Jeong, Y. J., Lee, A. R., Jang, C. S., et al. (2012). Determining the geographical origin of Chinese cabbages using multielement composition and strontium isotope ratio analyses. *Food Chemistry, 135,* 2666–2674.

Capo, R. C., Stewart, B. W., & Chadwick, O. A. (1998). Strontium isotopes as tracers of ecosystem processes: Theory and methods. *Geoderma, 82,* 197–225.

Chaudhuri, S. (1978). Strontium isotopic composition of several oilfield brines from Kansas and Colorado. *Geochimica et Cosmochimica Acta, 42,* 329–331.

Clewer, A. G., & Scarisbrick, D. H. (2001). *Practical statistics and experimental design for plant and crop science*. Chichester, UK: John Wiley and Sons Inc.. 332 pp..

Commission Regulation (EC) No. 1898/2006 of 14 December 2006 laying down detailed rules of implementation of Council Regulation (EC) No. 510/2006 on the protection of geographical indications and designations of origin for agricultural products and foodstuffs (OJ L369; 23.12.2006).

Consonni, R., Cagliani, L. R., Stocchero, M., & Porretta, S. (2009). Triple concentrated tomato paste: Discrimination between Italian and Chinese products. *Journal of Agricultural and Food Chemistry, 57,* 4506–4513.

Consonni, R., Cagliani, L. R., Stocchero, M., & Porretta, S. (2010). Evaluation of the production year in Italian and Chinese tomato paste for geographical determination using O2PLS models. *Journal of Agricultural and Food Chemistry, 58,* 7520–7525.

Council Regulation (EC) No. 509/2006 of 20 March 2006 on agricultural products and foodstuffs as traditional specialities guaranteed (OJ L 93; 31.3.2006).

Council Regulation (EC) No. 510/2006 of 20 March 2006 on the protection of geographical origin (OJ L 93; 31.3. 2006).

Dickin, A. P. (1995). In A. P. Dickin (Ed.), *Radiogenic isotope geology*. Cambridge University Press.

Eichrom. <http://www.eichrom.com/products/info/sr-resin.aspx>.

Evans, J. A., Chenery, C. A., & Montgomery, J. (2012). A summary of strontium and oxygen isotope variation in archaeological human tooth enamel excavated from Britain. *Journal of Analytical Atomic Spectrometry, 27*(5), 754–764.

Faure, G. (1986). *Principles of isotope geology* 2nd ed.. New York: John Wiley.

Fortunato, G., Mumic, K., Wunderli, S., Pillonel, L., Bosset, J. O., & Gremaud, G. (2004). Application of strontium isotope ratios measured by MC-ICP-MS for food authentication. *Journal of Analytical Atomic Spectrometry, 19,* 227–233.

Horn, P., Schaaf, P., Holbach, B., Holzi, S., & Eschnauer, H. (1993). [87]Sr/[86]Sr from rock and soil into vine and wine. *Zeitschrift für Lebensmittel–Untersuchung und – Forschung, 196,* 407–409.

Horwitz, E. P., Chiarizia, R., & Dietz, M. L. (1992). *Solvent Extraction and Ion Exchange, 10*(2), 313–336.

Huchon, P., Taylor, B., & Klaus, A. (2001). In P. Huchon, B. Taylor, & A. Klaus (Eds.), *Proceedings of the ocean drilling program – Scientific results* (pp. 1–36). College Station, TX: Ocean Drilling Program. Leg 180.

Latkoczy, C., Prohaska, T., Watkins, M., Stingeder, G., & Teschler Nicola, M. (2001). Strontium isotope ratio determination after on-line matrix separation by coupling ion chromatography (HPIC) to an inductively coupled plasma sector field mass spectrometer (SF-ICP-MS). *Journal of Analytical Atomic Spectrometry, 16,* 806–811.

Levene, H. (1960). Robust tests for equality of variances. In I. Olkin & H. Hotelling, et al. (Eds.), *Contribution to probability and statistics* (pp. 278–292). New York: Stanford University Press.

Lo Feudo, G., Naccarato, A., Sindona, G., & Tagarelli, A. (2010). Investigating the origin of tomatoes and triple concentrated tomato pastes through multielement determination by inductively coupled plasma mass spectrometry and statistical analysis. *Journal of Agricultural and Food Chemistry, 58,* 3801–3807.

Luykx, D. M. A. M., & van Ruth, S. M. (2008). An overview of analytical methods for determining the geographical origin of food products. *Food Chemistry, 107,* 897–911.

Mout, L. (2004). *Geographical indicated products in The Netherlands.* PhD thesis, Wageningen, The Netherlands.

Regulation (EC) No. 178/2002 of the European Parliament and of the Council of 28 January 2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety (OJ L31; 1.2.2002).

Regulation (EC) No. 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules (OJ L165; 30.4.2004).

Rosner, M. (2010). Geochemical and instrumental fundamentals for accurate and precise strontium isotope data of food samples: Comment on "Determination of the strontium isotope ratio by ICP-MS ginseng as a tracer of regional origin" (Choi et al., 2008). *Food Chemistry, 121,* 918–921.

Rossmann, A., Haberhauer, G., Holzl, G., Horn, P., Pichlmayer, F., & Voerkelius, S. (2000). The potential of multielement stable isotope analysis for regional origin assignment of butter. *European Food Research and Technology, 211*(1), 32–40.

Rummel, S., Dekant, C. H., Hoelzl, S., Kelly, S. D., Baxter, M., Marighito, N., et al. (2012). Sr isotope measurements in beef – Analytical challenge and first results. *Analytical and Bioanalytical Chemistry, 402,* 2837–2848.

Rummel, S., Hoelzl, S., & Horn, P. (2007). *Biologische spurenkunde, Band I: Kriminalbiologie.* Berlin, Heidelberg: Springer. 381–407.

Sequi, P., Dell' Abate, M. T., & Valentini, M. (2007). Identification of cherry tomatoes growth origin by means of magnetic resonance imaging. *Journal of the Science of Food and Agriculture, 87,* 127–132.

Shapiro, S. S., & Wilk, M. B. (1965). Analysis of variance tests for normality (complete sample). *Biometrika, 52,* 591–611.

Stewart, B. W., Capo, R. C., & Chadwich, O. A. (1998). Quantitative strontium isotope models for weathering, pedogenesis and biogeochemical cycling. *Geoderma, 82,* 173–195.

Swoboda, S., Brunner, M., Boulyga, S. F., Galler, P., Horacek, M., & Prohaska, T. (2008). Identification of Marchfeld asparagus using Sr isotope ratio measurements by MC-ICP-MS. *Analytical and Bioanalytical Chemistry, 390*(2), 487–494.

Trincherini, P. R., Serra, F., Pivato, M., Tanet, G., Van Haecke, F., Raniero, F. and Guillou, C. (2003). The characterization of the geographical origin of green coffee: A multi-isotopic approach. In: *ISI: 2nd international symposium on isotopomers,* Stresa, Italy.

Voerkelius, S., Lorenz, G. D., Rummel, S., Quétel, C. R., Heiss, G., Baxter, M., et al. (2010). Strontium isotopic signatures of natural mineral waters, the reference to a simple geological map and its potential for authentication of food. *Food Chemistry, 118*(4), 933–940.

WPTC. (2012). *ANICAV (Associazione Nazionale Industriali Conserve Alimentari Vegetali), Stime mondiali di prodotto trasformato.* Newsletter 184/2012, Napoli, Italy.

## Website

http://www.zipmec.eu/en/Vegetables-production-and-processing-trade/tomatoes-history-production-trade.html.