Food Chemistry 246 (2018) 313–322

Contents lists available at ScienceDirect

Food Chemistry

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

$^{87}Sr/^{86}Sr$ isotope ratio and multielemental signatures as indicators of origin of European cured hams: The role of salt

Ekaterina N. Epova[a,b,*], Sylvain Bérail[a], Tea Zuliani[c], Julien Malherbe[a], Laurence Sarthou[b], Manuel Valiente[d], Olivier F.X. Donard[a]

[a] LCABIE, UMR UPPA-CNRS 5254 IPREM, Hélioparc, 2 avenue President P. Angot, 64053 Pau, France
[b] Laboratoires des Pyrénées et des Landes, rue des Écoles, 64150 Lagor, France
[c] Jozef Štefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[d] The Autonomous University of Barcelona, Chemistry department, Centre GTS, Campus de la UAB, Edifici CN, 08193 Bellaterra, Barcelona, Spain

ARTICLE INFO

Keywords:
$^{87}Sr/^{86}Sr$ isotope ratio
Dry-cured ham
Multielemental analysis
Salt
Geographic origin
Multi-collector ICP-MS

ABSTRACT

We have examined the potential of discriminant inorganic constituents (trace-, ultra-trace elements and Sr isotope ratios) to assess the origin of world famous brands of European dry-cured hams. The variation of the multielemental composition with principal component analysis allowed to discriminate the origin of Bayonne hams. Determined ratio $^{87}Sr/^{86}Sr$ was recognized as a strong additional distinctive parameter. The ratio $^{87}Sr/^{86}Sr$ allowed to better separate all the different categories of hams in addition to the multi-elemental detection. The major contribution of the value $^{87}Sr/^{86}Sr$ for the Bayonne ham is directly related to its curing due to the salt used in process coming from the nearby salt mine Salies-de-Béarn. Since the salt represents around 4% of the final product, it will therefore strongly influence the elemental and isotopic composition of hams. The overall discrimination potential of strontium isotope ratio is evidenced in the final statistical discrimination of the origin of hams.

1. Introduction

Dry-cured ham is a traditional meat product originating from southern European countries. Today the production is mainly carried out in Spain, France and Italy. Different types of dry-cured ham can be found depending on the origin of raw material and techniques of curing. All these dry-cured hams bring a significant economic importance for the national meat industries and potentially can become an object of forgery or mislabeling. European Union schemes of geographical indications, known as Protected Designation of Origin (PDO) and Protected Geographical Indications (PGI), distinguished them on the basis of their genotypes, regional origins and the features of curing processes, and hence have the motivation to guarantee the authenticity and quality of products. The requirements of various regulatory authorities for chemical analysis applied in food control domain are becoming more sophisticated every day (De La Guardia & Gonzálvez, 2013). Various analytical methods, such as spectroscopy, genetic analysis, metabolomics- and proteomics technologies, are widely applied to determinate the geographical origin and authenticity of meat products (Franke, Gremaud, Hadorn, & Kreuzer, 2005). Among them, inductively coupled plasma mass-spectrometry (ICP-MS) implies a quadrupole-based mass analyzer system (Q-ICP-MS) is the fastest growing multi-element trace element analysis technique, while the multicollection ICP-MS (MC-ICP-MS) allows the determination of isotopic composition of elements with exceptional precision. Both techniques are widely used in last decade in studies of geographical origin determination (De La Guardia & Gonzálvez, 2013).

Multielemental fingerprinting achieves a certain success in geographical provenance determination of meat. It reflects the mineral composition of surrounding environment (soil, water, and litter) but also includes the incoming contribution of elements associated with the feeding and supplementation of animals, and finally the anthropogenic pollutions (Franke et al., 2005). Recent studies evidenced the relevance of use the multi-elemental composition for the geographic authentication of pork (Kim et al., 2017; Kreitals & Watling, 2014) and its potential to differentiate between conventional and organic pork (Zhao, Wang, & Yang, 2016). However, some of agricultural practices, such as controlled feeding and intensive rearing, can minimize the chemical variation and will then interfere with geographic origin determination based on multi-discriminant statistics (Kreitals et al., 2014). The

* Corresponding author at: LCABIE, UMR UPPA-CNRS 5254 IPREM, Hélioparc, 2 avenue President P. Angot, 64053 Pau, France.
E-mail addresses: ekaterina.epova@univ-pau.fr (E.N. Epova), sylvain.berail@univ-pau.fr (S. Bérail), tea.zuliani@ijs.si (T. Zuliani), julien.malherbe@univ-pau.fr (J. Malherbe), l.sarthou@labopl.com (L. Sarthou), Manuel.Valiente@uab.cat (M. Valiente), olivier.donard@univ-pau.fr (O.F.X. Donard).

https://doi.org/10.1016/j.foodchem.2017.10.143
Received 16 August 2017; Received in revised form 24 October 2017; Accepted 29 October 2017
Available online 31 October 2017
0308-8146/

application of the precise and accurate specification of isotopic compositions of elements can reinforce the discrimination potential (Balcaen, Moens, & Vanhaecke, 2010; Camin, Bontempo, Perini, & Piasentier, 2016; Franke et al., 2005; Zhao et al., 2014). Stable isotope ratio determination is one of the robust and most discriminant methods with traditional approach based on ratios of light bio elements such as hydrogen, nitrogen, oxygen, carbon and sulfur, determined often by methods isotope ratio mass spectrometry (IRMS) and nuclear magnetic resonance (NMR). The ratios of $^{2}H/^{1}H$, and $^{18}O/^{16}O$ are strongly latitude dependent, while local agricultural practices and animal diet will rather affect the ratios $^{15}N/^{14}N$, and $^{13}C/^{12}C$, respectively. Stable isotope ratios of light elements have been recently successfully applied to identify authenticity of food of animal origin (Camin et al., 2016), and, especially, for the dry-cured ham differentiation (Perini, Camin, Sánchez Del Pulgar, & Piasentier, 2013). The recent instrumental development of MC-ICP-MS have expanded the potential of isotope analysis by adding the so-called “non-traditional” elements – strontium, lead (Balcaen et al., 2010). This innovation has improved the information related with the provenance studies due to the outstanding precision and accuracy of simultaneous multi-isotopes detection.

Dealing with non-traditional isotopes, Sr isotope ratios are routinely used in geosciences for dating and origin determination of minerals and for tracing the temporal changes in the hydrologic and sedimentary cycles. Over the last decade there has been an increasing interest in the Sr isotopes application as a sensitive geochemical tracer in paleontology, archeology and food sciences (Balcaen et al., 2010; Coelho, Castanheira, Bordado, Donard, & Silva, 2017). The geochemical basis for application of Sr isotope ratio to food’s geographical origin has been recently reviewed (Baffi & Trincherini, 2016). In summary, the ratio $^{87}Sr/^{86}Sr$ is a long-term stable parameter, which does not significantly depend on human activity, climate or season of production, but is regulated by local geological environment. The ratio $^{87}Sr/^{86}Sr$ appears to be an encouraging provenance tracer and has already demonstrated its great discriminating potential for geographical origin differentiation of various types of food matrices (e.g. Zhao et al., 2014).

Food of animal origin is of special concern. Animals continuously consume a large variety of foods with associated elements and compounds that do not only originate from their natural surroundings. Supplementary nutrition can be industrially produced or brought from geographically distant sources. When animals are mainly feed by local produced feeds, the values of the ratio $^{87}Sr/^{86}Sr$ in their tissues will then reflect the local geological settings and could be used as a tracer for geographical origin. This was demonstrated on various types of meats and poultry (Baroni et al., 2011; Franke et al., 2008; Rees et al., 2016; Rummel et al., 2012). For processed food, different preparation steps can alter the original $^{87}Sr/^{86}Sr$ ratio of the raw material. Despite of these limitations, the discriminating potential of the $^{87}Sr/^{86}Sr$ ratio was confirmed on different types of prepared food matrices, such cheese (Bontempo et al., 2011; Fortunato et al., 2004; Pillonel et al., 2003) and butter (Rossmann et al., 2000).

Raw meat used in dry-cured ham production varies largely by the mode of farming. While black Iberian pigs are free-range-reared race, the white genotypes used for Parma, San Daniele, and Bayonne hams are intensively reared (Ordóñez & De La Noz, 2007). The main ingredient generally added during production is salt (Jiménez-Colmenero, Ventanas, & Toldrá, 2010). This addition will modify the taste of cured ham and will add the presence of trace elements associated in the salt matrix.

For this study, we have selected some of the most representative European cured hams: Iberian Ham (Jamón ibérico, Spain, Portugal), Bayonne Ham (Jambon de Bayonne, France), Parma (Prosciutto di Parme, Italy), San Daniele Ham (Prosciutto san Daniele, Italy). The objective of this study was to investigate their elemental and Sr isotopic compositions and use them to address the potential discriminant power of combination of multi-elemental, isotopic and statistical analysis to discriminate the ham’s geographical origin.

2. Material and method

2.1. Samples

Eleven Iberian hams originating from various provenances were collected from local producers from southwestern regions of the Iberian Peninsula, which are the principal production areas of Iberian ham, including Huelva, Seville, Avila, Badajoz and Estremadura in Spain, and Alentejo in Portugal. Two sample of Parma and San Daniele ham were purchased in local Spanish markets. Finally, three samples of Bayonne ham from different producers were purchased on local French supermarkets. From each packet a slice of ham without visible fat was taken, lyophilized, homogenized and kept frozen until analysis.

In order to assess the role of salt in the process of discrimination several of natural salts have been purchased on local supermarkets and specialized bio-stores. The different salts used in this study were coming from seawater production plants from the French Atlantic coast (“Noirmoutier”, “Guérande”, “Île de Ré”), the Mediterranean Sea (“Camargue”, Cypriot “Pyramid salt”), and from the Pacific Ocean (Hawaiian “Alaea salt”). Other type of salt originated from salts mines were from France (Saline “Salies-de-Béarn”), Pakistan (mine Khewra, “Himalayan pink salt“), Poland (mine “Wieliczka”), Austria (Salzkammergut, table salt “Alpine”), Iran (“Persian blue salt”), and finally Spain (“Andalusia”). Table S1, Supplementary material presents the list of hams and salt samples, detailed information about its origin, source of provenance, preparation and conditioning.

2.2. Instrumentation

Two ICP-MS instruments have been used in this study. At first, a quadrupole NexION 300X ICP-MS fitted with a Meinhard® nebulizer and a cyclonic spray chamber in standard mode, and with collision cell filled with Helium (Perkin-Elmer, Shelton, CT, USA) has been used for multi-elemental analysis. For precise isotopic ratios, a high resolution multi-collector MC-ICP-MS Nu Plasma HR (Nu Instruments Ltd., Wrexham, UK) with cinnabar cyclonic spray chamber and micro-concentric nebulizer and Nickel plasma cones (Type A) was used. The ICP-MS measurement conditions were daily optimized to provide the highest intensity using standard built-in software procedures. Operating conditions for both instruments and determined elements/isotopes are given in Tables S2 and S3, Supplementary material.

Sample preparation was accomplished after freeze drying of the samples based on the meat with a low fat content (Lyophilisateur Freeze Dryer Alpha 1–4 LSC (Martin Christ Gefriertrocknungsanlagen GmbH). Digestion for multi-elemental analysis was performed on a DigiPREP Block Digestion Systems (SCP Science, Canada). The digestions for further isotopic ratios measurements were performed in closed vessel microwave Mars 5 (CEM Corporation, USA).

2.3. Reagents and supplies

All polyethylene and Teflon vessels used in preparation and measurement processes were cleaned with HNO_3 (10% v/v) and rinsed with ultrapure water before use. Sample digestion was performed with the following reagents: nitric acid HNO_3 (69.0–70.0%, Instra Analysed Reagent, J.T.Baker®, Fisher Scientific, France) and hydrogen peroxide H_2O_2 (30%, ULTREX® II Ultrapure Reagent, J.T.Baker®, Fisher Scientific, France). All subsequent dilution steps involved in standard, sample and reagent preparation were performed with HNO_3 (2% v/v), made of ultrapure water obtain by Milli-Q system (Millipore, Molsheim, France) and HNO_3 (67–70%, ULTREX® II Ultrapure Reagent, J.T.Baker, Fisher Scientific, France).

For elemental analysis, a series of multielemental standards was prepared out of two commercially available multi-element standards CCS-4 and CCS-6 (Multi Analyte Custom Grade Solution, Inorganic Ventures, USA). To assess the quality of the measurements, the certified