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Geographical origin authentication of pork using multi-element and multivariate data analyses

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ABSTRACT

In the recent years, consumers have become increasingly concerned about the authenticity and labeling claims associated with meat and meat based products. In this study, investigating geographical origin authenticity of pork, 323 samples of pork belly were collected from Korea, USA, Germany, Austria, Netherlands and Belgium. These were analyzed for twenty-nine macro and trace elements using inductively coupled plasma-optical emission spectroscopy (ICP-OES), and ICP-mass spectrometry (MS). The applied analytical techniques were validated by quality assurance parameters in which the values of correlation coefficient, limits of detection and quantification, precision, and spiking recovery confirmed that the methods were well efficient and in accordance to the criteria set by the Association of Official Analytical Chemists (AOAC) for metals analysis. From the results of multivariate analyses, it was found that the trace elements are promising constituents which could be used to accurately determine the inter-continental provenance of pork.

1. Introduction

Pork is recognized as an important source of fatty acids, protein and minerals. Today's consumers are concerned about the information on the origin and accurate labeling of meat they consume, raising concerns of nagging the problem of adulteration or fraud of cheaper or inferior quality (Franke, Gremaud, Hadorn, & Kreuzer, 2005; Zhao, Wang, & Yang, 2016). Due to the price difference between domestic and imported products, it has also become the public's interest and demand to provide them complete and transparent information on the type and origin of meat they purchase (Martinez et al., 2003). This demand has driven the researchers' attention to develop and standardize robust analytical methods which can rapidly confirm the information given by the label, prevent food fraud, ensure adherence to regulations and safety, and verify the provenance of meat (Heaton, Kelly, Hoogewerff, & Woolfe, 2008). For this, different approaches to determine authenticity of meat, including its geographical origin, have been developed. The analytical methods such as polymerase chain reaction, chromatography, microscopy, electronic spin resonance, enzymatic assays, and mass spectrometry and spectroscopy for the identification of sex, feed intake, processing treatment, and elemental analysis for nutritional assessment and origin authentication, were used from time to time around the world (Ashoor, Monte, & Stiles, 1988; Hartwig, Hartmann, & Steinhart, 1997; Draisci, Palleschi, Ferretti, Lucentini, & Cammarata, 2000; Calvo, Rodellar, Zaragoza, & Osta, 2002; Chou et al., 2007; Franke et al., 2008; Haunshi et al., 2009; von Bargen, Brockmeyer, & Humpf, 2014; Zhao et al., 2016). Multi-element analysis is one of the valuable and rapid methods used for the authentication of meat and meat products (Arvanitoyannis & Van Houwelingen-Koukaliaroglou, 2003). Previous studies indicate that trace elements are the promising meat constituents which could accurately determine the geographical origin. The contents of trace elements in animals depend on various factors such as feed intake, drinking water, pollution, and soil composition, which all in turn depend on the geographical origin (Franke et al., 2005). For example, the selenium concentration in American soil is known to be higher than that of Europe which was also reflected in the study carried out by Haldimann, Dufossé, Mompart, and Zimmerli (1999), reporting that selenium contents were approximately twice higher in a beef from North America than that of Switzerland. Furthermore, Hintze, Lardy, Marchello, and Finley (2001) also reported close correlations of selenium concentration in soil to grass and beef. Similarly, herbivores of the naturally different soils (granite and gneiss weathering) were found to store 37 and 33% more Rb in the liver than carnivores and omnivores, respectively (Anke & Angelow, 1995). Furthermore, in the study about Cd, Pb and Zn contents in the muscles of sheep from

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Table 1
Summary of information on collection of pork belly samples analyzed in the current study.

Domestic		Imported	
Origin country	No. of samples	Origin country	No. of samples
Korea	227	Netherlands	14
		USA	36
		Belgium	19
		Austria	15
		Germany	12
	227		96
Total			323

polluted and unpolluted areas of southwest Sardinia did not show significant differences in their concentrations (Chessa, Calaresu, Ledda, Testa, & Orrù, 2000). The effect of altitude on the elements composition of lambs, reindeer and grass was also reported in literature, showing comparatively high Cs and lower K contents in the samples of high altitude (Andersson, Lönsjö, & Rosén, 2001; Åhman, Wright, & Howard, 2001; Gastberger, Steinhäusler, Gerzabek, Lettner, & Hubmer, 2000). As K is known to be the competitor of Cs during absorption in the digestive tract, thus Cs concentration might be a suitable indicator for authentication of origins of meat samples. Hence, the use of multi-element analyses, specifically trace elements, to provide information on the provenance of foods is considered more reliable. Inductively coupled plasma mass spectroscopy (ICP-MS) was used for the determination of trace elements in chicken, pork and beef from Brazil for the authentication of their geographical origins (Batista, Grotto, Carneiro, & Barbosa, 2012). Similarly, using ICP-MS and linear discriminant analysis (LDA), Franke et al. (2008) analyzed fifty elements, and authenticated the origins of dried beef from France, Germany, Hungary and Switzerland. Recent developments in chemometric techniques such as use of the statistical tests; principal component analysis (PCA) and linear discriminant analysis (LDA) are of great use in the authentication of geographical origins of food/food products (Guo et al., 2016).

In South Korea, greatest volume of pork imports originates from USA, Germany, Austria, Netherlands and Belgium. So far, there has been no published research focusing on the provenance establishment of the domestic and imported pork consumed in South Korea, by using multi-element analysis, with the exception of stable isotope studies of beef carried out by Horacek and Min (2010), and Bong et al. (2010). Therefore, the present study aimed to determine the concentrations of twenty-nine elements in 323 pork belly samples including 227 domestic (from Suncheon, Naju, Chungju, Gangjin and Yongin cities of South Korea), and 96 samples imported from USA, Germany, Austria, Netherlands and Belgium. The macro elements including aluminium (Al), boron (B), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), phosphorus (P), sulphur (S), and zinc (Zn) were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). For trace elements including barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), cesium (Cs), gallium (Ga), lithium (Li), manganese (Mn), nickel (Ni), lead (Pb), rubidium (Rb), selenium (Se), strontium (Sr), uranium (U) and vanadium (V), an ICP-MS was used. The applied analytical techniques for multi-element analyses were also validated by the appropriate quality assurance parameters of linearity, precision, and spike recovery. For provenance authenticity, the multivariate data analyses of PCA and LDA were applied to the elements content for the analyzed samples.

2. Materials and methods

2.1. Reagents and instrumentation

All the reagents used in this study were purchased from Sigma and Fisher Scientific (USA). Analytical reagent grade concentrated HNO_3 (70%) and H_2O_2 (30%) were obtained from Dong Woo Fine Chem Co. Ltd. Iksan, Korea. Ultrapure deionized water (resistivity >18 MΩ·cm) was obtained from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA). The working solutions for calibration curves were prepared from multi-element standard solution containing all the analyte elements (10 μg/g, Perkin Elmer, CT, USA) by diluting in 24.5% HNO_3, the same percentage of acid present in the digested samples. The plastic/glass ware were soaked in 10% v/v HNO_3 overnight and rinsed with Milli-Q water thoroughly during use. For digestion of samples, a microwave reaction system, Anton Paar Multiwave 3000 (Graz, Austria) programmable for time and power between 600 and 1400 W and equipped with 20 high pressure polytetrafluoroethylene vessels (MF 100) was used. For elemental analyses, ICP-OES (730-ES simultaneous CCD, Varian, USA) and ICP-MS (Elan 6100 DRC II, Perkin-Elmer Sciex, and Norwalk, CT, USA) were used.

2.2. Samples collection, preparation and microwave digestion

In this study, a total of 323 pork belly samples consisting of 227 domestic (Suncheon, Naju, Chungju, Gangjin and Yongin cities of Korea) provided by Korea Institute for Animal Products, Quality Evaluation, and 96 imported samples from USA, Germany, Austria, Netherlands and Belgium given by Korea Meat Import Association, were analyzed. Detailed information on samples collection, location and number is given in Table 1. The fresh pork belly samples were ground to homogenous particle size in a blender (MR 350 CA, Braun, Spain) and subjected to microwave assisted nitric acid digestion. In microwave digestion, a slightly modified procedure of Khan et al. (2014) was followed. Briefly, 0.5 g of each sample was accurately weighed directly into PTFE digestion vessel in triplicate followed by addition of 7 mL concentrated HNO_3 (70%) and 1.0 mL H_2O_2 (30%). The combustion procedure is

Table 2
Method validation parameters (sensitivity, linearity, precision, and spiking recovery) data of ICP-OES and ICP-MS for quantification of elements.

Element	Limits of detection (ng/g)	Limits of quantification (ng/g)	Correlation coefficient (R^2)	Coefficient of variance (CV%)	Spiking recovery (%)
Macro elements (ICP-OES)					
Al[a]	0.269	0.8877	0.9996	2.33	102.2
B	0.514	1.6962	0.9990	2.84	91.54
Ca	0.288	0.9504	0.9999	1.29	98.2
Fe[a]	0.092	0.3036	0.9999	1.38	95.6
K	0.511	1.6863	0.9990	2.69	97.9
Mg	0.314	1.0362	0.9998	2.42	101.8
Na[a]	0.209	0.6897	0.9995	2.37	94.2
P	0.471	1.5543	0.9991	2.55	95.0
S	0.134	0.4422	0.9997	1.71	96.6
Zn	0.341	1.1253	0.9991	2.67	94.22
Trace elements (ICP-MS)					
As	0.009	0.024	0.9999	1.01	103.0
Ba	2.975	11.32	0.9990	2.89	94.2
Be	0.040	0.096	0.9998	1.38	96.0
Bi	0.029	0.067	0.9998	2.97	95.4
Cd	0.017	0.036	0.9998	2.83	98.9
Co	0.008	0.016	1.0000	1.95	96.8
Cr	0.941	3.025	0.9992	2.11	91.4
Cs	0.004	0.008	0.9996	2.90	91.0
Cu	0.120	0.387	0.9999	2.81	95.8
Ga	0.007	0.015	0.9999	1.49	88.6
Li[b]	0.029	0.059	0.9997	2.87	89.6
Mn	0.051	0.101	0.9999	2.22	98.1
Ni	0.142	0.393	0.9995	2.63	93.4
Pb	0.019	0.062	0.9998	2.98	97.3
Rb	0.010	0.023	0.9996	1.38	97.0
Se	0.899	3.262	0.9995	2.55	104.3
Sr	0.207	0.711	1.0000	2.19	105.3
U	0.008	0.012	0.9999	1.54	102.0
V	0.081	0.114	0.9999	1.68	92.5

[a] Elements spiked at 1000 μg/g, other macro elements were spiked at 100 μg/g.
[b] Elements spiked at 1000 ng/g, other trace elements were spiked at 100 ng/g.