ORIGINAL PAPER

Indications for the applicability of element signature analysis for the determination of the geographic origin of dried beef and poultry meat

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Abstract In order to determine the geographic origin of poultry and dried beef, concentrations of a total of 72 different elements (occasionally represented with several isotopes) were analyzed by inductively coupled plasma high resolution mass spectrometry (ICP-HRMS). Additionally, gross chemical composition (GCC) was analyzed. The 25 poultry breast filets samples originated from Switzerland, France, Germany, Hungary, Brazil, and Thailand, and the 23 dried beef samples, made from *M. biceps femoris* and *M. semitendinosus*, were produced in Switzerland, Austria, Australia, United States, and Canada out of raw meat originating either from these or from other countries. A total of 66 and 46 of the elements and isotopes followed were detected in beef and poultry, respectively. For statistical analyses, only the most abundant isotopes per element were used. For both poultry meat and dried beef, a differentiation of the origins was possible using those elements, which were significantly different across countries (As, Na, Rb, and Tl in poultry; B, Ca, Cd, Cu, Dy, Eu, Ga, Li, Ni, Pd, Rb, Sr, Te, Tl, Tm, V, Yb, and Zn in beef). No sufficient differentiation between origins was possible with GCC. Further studies have to confirm the suitability of this approach for meat authentication with more samples.

Keywords Cattle · Broiler · Meat · Trace elements · Gross chemical composition · Authentication · Traceability

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Introduction

The globalized food market produces an increasingly blurred image of the food chain and makes traceability of foods important for consumer purchase as recent evaluations in Sweden and Switzerland have demonstrated [1, 2]. Traceability requires not only a flawlessly documented record, e.g., in the form of certificates of origin but also appropriate analytical methods to be able to control the validity of such certificates. Elements, including trace elements and minerals essential and non-essential to man and animal, are a promising way to determine the geographic origin of different foods [3–5]. Certain regions have specific 'fingerprints' of elements and a conclusion about the origin can be drawn [6, 7] by analyzing these fingerprints. Various studies so far concentrated on selenium (Se). The average Se concentrations (mg/kg dry matter) in Swiss organic (0.15) and conventional beef (0.26) were found to be clearly lower than those observed in beef originating from North America (0.43) [8], being in line with corresponding differences in Se concentrations of European and American soil [9]. Similarly, Swiss poultry meat was found to be lower in Se (0.58) than Brazilian poultry (0.73) [8]. Hintze et al. [10] described close correlations between Se concentrations of soil, grass, and beef skeletal muscle, allowing to clearly distinguish between the beef originating

from areas with low and high soil Se concentrations [10]. The indicative value of Se and several other elements is, however, seriously limited by the common practice to supplement livestock diets with these elements. This is done differently by individual farmers using mineral mixtures either offered separately at *ad libitum* access or as a fixed component of the concentrate or the complete feed [11–13]. Trace elements most frequently supplemented to poultry feed are Zn, Cu, Mn, and Se [14], either in an inorganic form or linked to organic substances such as amino acids, while beef get furthermore elements like Ca, P, Mg, Na, I, and Co [15]. Additionally, for regions with a known deficiency in feed and soil, which is particularly true for Se, it is strongly recommended (also for animal welfare reasons) to cover such a deficit or counteract an imbalance by strategic supplementation, thus reducing the indicative value of such elements. However, many more elements could be indicative for specific regions, which are not specifically recommended to be supplemented, but this potential so far remained unexplored for authentication of meat.

The objective of this preliminary study, different from previous approaches, was therefore to analyze the concentration of as many elements as possible and to look at both individual elements and combinations of them with respect to their suitability to trace the geographic origin of meat. As commodities, raw poultry breast meat and dried beef with known origin from different countries were selected. These samples were also analyzed for their gross chemical composition (GCC) as, especially in the beef, different processing procedures might yield a useful signature of production origin, too.

Material and methods

Sample selection and preparation

The poultry samples were obtained from six different countries: Thailand ($n = 3$ independent samples), France ($n = 2$), Germany ($n = 3$), Hungary ($n = 6$), Brazil ($n = 4$), and Switzerland ($n = 7$). The Swiss poultry originated from conventional, free-range, and organic production fattened for either short or normal periods. All other samples were from conventionally housed broilers. The authenticity of all samples had been certified with valid custom documents which also specified slaughter place and date. Each sample consisted of four breast filets without skin (approximately 450 g meat in total) being kept frozen at $-25\ °C$. The filets were homogenized (Büchi Mixer B 400, Büchi AG, Flawil, CH) using ceramic knives in order to avoid any metallic contamination. Sub-samples of the homogenate were shrink-wrapped and frozen again.

The dried beef samples produced in Switzerland were directly collected at the site of production ($n = 7$, raw Swiss

beef; $n = 4$, raw Brazilian beef). The foreign samples were purchased directly from producers in Austria ($n = 2$, using raw Brazilian beef), Canada ($n = 2$, raw Canadian beef), United States ($n = 2$, raw meat from United States), and Australia ($n = 4$, Australian raw meat). Two Bresaola samples from Switzerland (made from raw Swiss or Brazilian beef) were produced by curing and drying but without pressing, while all others underwent a sequence of pressing and drying after curing. All samples were produced either from *M. biceps femoris* or from *M. semitendinosus*. Dried beef samples were shrink-wrapped and stored in a cooling room at 2.5 °C. Aliquots for analyses were taken from the center of the whole piece of dried beef by using a ceramic knife and were homogenized (Büchi Mixer B 400, Büchi AG, Flawil, CH, equipped with ceramic knives) before being analyzed. In both meat types, sample sizes for analyzing elements and GCC were 0.5–1 and 100 g, respectively.

Element analysis

In order to determine the concentration of various elements and isotopes of the same element, the homogenized samples were subjected to microwave-assisted pressure digestion with nitric acid. For that, 0.3 g of reference material (bovine muscle, BCR-CRM 184, Community Bureau of Reference, Geel, Belgium; NIST-RM 8414 National Institute of Standards & Technology, Gaithersburg, USA) and either 0.5 g of dried beef or 1 g of poultry meat were placed in a Teflon tube together with 4 ml nitric acid (650 g/kg). This tube was put in a larger Teflon vessel, surrounded by a safety shield, containing 5 ml of ultra pure water (>18 MΩ) and 2 ml hydrogen peroxide (300 g/kg). The samples were digested under pressure using a microwave oven (MLS ETHOS plus, MLS GmbH, Leutkirch, Germany). The temperature was increased from ambient temperature up to 100 °C within 5 min and maintained for another 5 min. Afterwards, the temperature was increased up to 200 °C within 17 min and maintained for further 10 min, then cooled down below 30 °C before opening the vessels. A maximum of 10 samples could be digested at once, including at least one certified reference sample. The digested solution was diluted to approximately 15 g with ultra pure water (>18 MΩ) and stored in plastic tubes (15 ml, PP, Sarstedt, Sevelen, CH) until analysis was performed. Shortly before measurement, 1 ml of this solution was diluted with 1 ml ultra pure water (>18 MΩ). The measurements were carried out using a sector field ICP-MS (Element 2, Finnigan MAT, Bremen, Germany). Each sample was digested and analyzed once, since initial determinations revealed that outliers were unlikely. Radio frequency power was 1250 W. Plasma, auxiliary, and nebulizer (Sea Spray; Glass Expansion, Melbourne, Australia) argon flow rates were 16, 0.9, and 1.0 ml/min, respectively, and the sample uptake rate was 0.3 ml/min.

The acquisition mode was E-scan with eight scans performed and 1.2 s of acquisition time per nuclide. Take-up and washing time were 2 and 5 min, respectively. CertiPUR® Rhodium ICP Standard (Merck, Darmstadt, Germany), diluted to 1 μg/kg, was used as internal standard. The solutions contained in the multi-element standard for calibration were 1 ml ICP multi-element standard solution VI (Merck, Darmstadt, Germany), 0.01 ml spectrascan (Catalog no. 028315, Teknolab, Norway), 0.01 ml CertiPUR® Hafnium ICP Standard (Merck), 0.01 ml CertiPUR® Phosphorus ICP Standard (Merck), 0.01 ml CertiPUR® Palladium ICP Standard (Merck), and 0.01 ml CertiPUR® Mercury ICP Standard (Merck). This mixture was diluted with 26 g/kg nitric acid to complete 1 l of multi-element standard solution. Two different calibration solutions (0.5 and 1 μg/l) were prepared from the multi-element standard and subsequently the internal Rhodium standard was added.

Samples were analyzed for a total of 72 different elements, respectively isotopes of the same element, at three different resolution settings. ^{7}Li, ^{9}Be, ^{10}B, ^{45}Sc, ^{53}Cr, ^{59}Co, ^{63}Cu, ^{67}Zn, ^{75}As, ^{82}Se, ^{85}Rb, ^{86}Sr, ^{88}Sr, ^{89}Y, ^{95}Mo, ^{104}Pd, ^{105}Pd, ^{109}Ag, ^{111}Cd, ^{113}Cd, ^{126}Te, ^{128}Te, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{142}Nd, ^{147}Sm, ^{149}Sm, ^{151}Eu, ^{153}Eu, ^{155}Gd, ^{157}Gd, ^{159}Tb, ^{161}Dy, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{167}Er, ^{169}Tm, ^{171}Yb, ^{172}Yb, ^{175}Lu, ^{177}Hf, ^{178}Hf, ^{202}Hg, ^{203}Tl, ^{205}Tl, ^{207}Pb, ^{208}Pb, ^{209}Bi, ^{232}Th, and ^{238}U were measured with the resolution setting 300. Setting 4000 was applied for ^{23}Na, ^{24}Mg, ^{27}Al, ^{42}Ca, ^{44}Ca, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{60}Ni, ^{63}Cu, ^{68}Zn, and ^{69}Ga and setting 10,000 for ^{39}K, ^{75}As, ^{76}Se, ^{77}Se, ^{78}Se, and ^{80}Se. The accuracy of the measurements was verified using bovine muscle reference materials. This verification showed that all signals except those for Se were within the given range of the certified materials. The signals for Se were overstated, most likely due to signal enhancement caused by residual carbon compounds as the digestion method had not been optimized for Se. As a control for specific interference patterns, different isotopes were measured for certain elements. For ^{104}Pd, this revealed the likely presence of several interferences (e.g., ^{208}Pb^{++}, ^{207}Pb^{++}, ^{64}Zn^{40}Ar, ^{88}Sr^{16}O, and ^{209}Bi^{++}), making the measured concentrations in meat not quite reliable. Due to apparently invalid calibrations, also the values of Ba and K for poultry and of Mg and K for dried beef samples were excluded from further analysis. Detection limits were defined as the determined means of the peak intensity of all blanks, taken during measurement, plus three times the standard deviation of these blank peak intensities.

Due to the consecutive measurement of the isotopes in this type of ICP-MS apparatus, the accuracy of these ratios is not satisfactory enough to get reliable deviations of the natural abundance, which for some elements are often discussed to be promising indicators of meat authenticity [compiled by 5].

Gross chemical composition analysis

The analyses of the contents of water (method 5.4.1), protein (methods 5.5.1 and 5.5.2), fat (method 5.5.6), carbohydrates (method 5.5.8), and Cl (method 5.6.1, Sher-Indicator, Büchi, Flawil, Switzerland) were carried out as outlined in the Swiss Food Manual [16]. In order to determine the contents of nitrate and nitrite, 1 g of dried beef and 3 g of poultry were homogenized with 10 ml distilled water and centrifuged at $300 \times g$ (Labofuge A, Heraeus Sepatech, Osterode, Germany). After membrane filtration (0.2 μm, regenerated cellulose, BGB, Adliswil, Switzerland), the meat juice was analyzed for its contents of nitrate and nitrite using HPLC (HP 1090, Hewlett Packard, Santa Barbara, CA, USA) complete with a PV5 solvent delivery system, a diode array detector, and an auto-injector. Column (YMC ODS A S 3 μm, 50 × 3 mm; YMC, Kyoto, Japan) temperature was adjusted to 45 °C and a volume of 25 μl of the meat juice was injected. 1-Octylamine (20 mmol/l in ultra pure water; pH 6.5, 25 °C) and acetonitrile supragradient (HPLC grade; AC0331, Scharlau Chemie, Barcelona, Spain) were used as eluents (mobile phase). During the analysis, the flux was adjusted at 0.7 ml/min during the first 7 min and afterwards was increased to 1.0 ml/min for another 7 min. The content of acetonitrile was increased from 50 to 500 g/kg after 6 min and was kept at 800 g/kg from 8 min onward. The equilibration time was 5 min. The UV-detection was carried out at 214 nm (SBW 4 nm, reference 300 nm, SBW reference 60 nm) after a retention time of 4.8 min for nitrite and 5.3 min for nitrate. The detection limit was 0.03 mg/l for both nitrate and nitrite.

Statistical analysis

Before statistical evaluation, all elements with concentrations below their detection limits were eliminated. In cases, where several isotopes of one element were determined, the consistency of the differences between contents of isotopes in the samples was checked. Per element, only the most abundant isotope was used for statistical analysis, thus reducing the amount of data. The statistical analysis of each constituent (element, GCC) for significance of country of origin was performed using analysis of variance (ANOVA). For beef, analyses were performed separately for country of origin of raw meat (to account for region effects on raw meat) and country of processing (to account for effects of processing procedures). Some, but not all, elements appeared in both lists of significant variables. When the factor origin was significant in ANOVA, Bonferroni adjusted pairwise comparisons among means were performed in order to determine significant differences between individual countries of origin. For poultry meat, a combination of all datasets was, after standardizing, analyzed using linear discriminant

analysis (LDA) with stepwise backward elimination (probability to enter/to remove 0.15). As this resulted in over-fitting for dried beef, a principal component analysis (PCA) was performed with this commodity to reduce the dimensions. The principal components (PC) were subsequently used for LDA and so PCs with discriminating influence were determined. Finally, the elements with high influence on these PCs were identified by checking the loadings of the respective PCs (considered as important when loadings were ≥ 0.7 respectively ≤ -0.7) [17–19]. All analyses were performed by Systat (version 11, Systat Software Inc., Richmond, California, USA).

Results and discussion

Gross chemical composition

Table 1 gives the average GCC of fresh poultry meat and dried beef across all samples. The values were comparable with those given in literature [20, 21]. As expected, there were clear differences in water content between commodities and, associated with that, in protein and fat contents. Dried beef, as dry-cured product, was also massively enriched in Cl and nitrate compared to poultry meat. In none of the GCC variables, significant country of origin differences were found, which is why the corresponding data are not given individually in the tables. Also, nitrite contents (not presented in Table 1) were not significantly different among origins in beef and could not be detected in poultry meat anyway. Consistent and repeatable regional origin-determined differences were not expected in nutrient contents, as these are either highly genetically determined (protein content) or varied by feeding intensity (fat content), which is not really country specific. Nevertheless, some studies were able to differentiate between poultry meat for label and conventional origin using fat content or profile, but in that case, clear differences in realized fattening intensity were likely as a consequence of prescribed label conditions [22–25]. Expectations were higher for dried beef where producers might have ap-

plied different processing recipes, e.g., the addition of herbs and sodium chloride, etc. However, the only variable with discriminating power was water content ($p < 0.001$), since the two 'Bresaola' type samples had been deliberately produced for different final water contents than the other dried beef products.

Concentrations of characteristic elements in meat

Poultry meat

In poultry meat, out of the 72 elements/isotopes analyzed, 46 were found, while concentrations of ^{7}Li, ^{9}Be, ^{10}B, ^{59}Co, ^{76}Se, ^{80}Se, ^{89}Y, ^{109}Ag, ^{126}Te, ^{128}Te, ^{141}Pr, ^{149}Sm, ^{151}Eu, ^{159}Tb, ^{157}Gd, ^{161}Dy, ^{165}Ho, ^{169}Tm, ^{175}Lu, ^{177}Hf, ^{178}Hf, ^{202}Hg, ^{207}Pb, ^{208}Pb, ^{209}Bi, and ^{232}Th remained below the detection limit. The mean country-specific concentrations of the four elements significantly differing between countries of origin of poultry meat are listed alphabetically in Table 2.

Based on the arsenic (As) contents, Thai samples could clearly be separated from the other origins. Drinking water in some regions of Thailand, besides other countries, was found to have As contents higher than the official WHO threshold for arsenic contamination of 0.01 mg/l [26]. This might explain why also the poultry meat is enriched in As. However, there are other sources of As to be accumulated in poultry tissue, namely the use of organic arsenic compounds as feed additives [27] and diets containing fish meal because marine fish has high As concentrations [27]. In a coastal country like Thailand, fish meal is a frequent component of livestock diets, while the feeding of fish meal to poultry is uncommon, e.g., in Switzerland and is even prohibited as a feed for cattle in the EU (2000/766/EG) and in Switzerland (FMBV Art. 2). Two samples came from regions close to the sea (near Bangkok and in the east of the country), one sample came from a region more centrally located, but all were rich in As.

There were also some differences among countries in sodium (Na) content, with particularly low contents in the Thai samples. These differences may have resulted from different salt supplementation practices but, in essential electrolytes, the body typically controls its blood and tissue level and prevents the development of excessive concentrations. This would mean that the Thai poultry meat would have originated from production systems more or less omitting salt supplementation.

Rubidium (Rb) concentrations were high in Brazilian samples, allowing a differentiation between the samples originating from Switzerland and Germany. Rb is an indicator for the kind of soil and its geological underground [28]. Accordingly, granite and gneiss have high contents of Rb [29].

The element thallium (Tl) turned out to be characteristic for poultry meat of French origin (significantly higher com-

Table 1 Average gross chemical composition (mean ± SD) of poultry breast meat and dried beef

	Poultry meat (n = 26)		Dried beef (n = 23)	
Water (g/kg)	744.0	8.4	463.6	51.5
Protein (g/kg)	240.8	5.2	429.7	56.4
Fat (g/kg)	4.5	2.7	6.6	4.8
Carbohydrates (g/kg)	1.2	0.4	3.0	2.8
Cl (g/kg)	1.5	0.4	29.7	4.7
Nitrate (mg/kg)	3.6	1.0	23.2	7.2

SD, standard deviation

Table 2 Differences in country of origin in trace element contents[a] of poultry breast meat

	p^b	Brazil ($n=4$)		Switzerland ($n=7$)		Germany ($n=3$)		France ($n=2$)		Hungary ($n=6$)		Thailand ($n=3$)	
^{75}As (μg/kg)	***	26.68 b	1.49	28.27 b	2.16	26.05 b	3.90	27.28 b	1.13	52.7 b	36.44	141.36 a	42.46
^{23}Na (mg/kg)	*	72.08 ab	11.49	89.04 a	17.41	89.29 ab	6.90	79.28 ab	4.03	73.07 ab	12.98	49.92 b	19.81
^{85}Rb (mg/kg)	**	17.05 a	3.12	8.09 b	4.52	5.68 b	1.42	7.20 ab	1.80	10.91 ab	2.08	12.66 ab	4.62
^{205}Tl (μg/kg)	***	2.72 b	0.84	2.00 b	1.06	5.59 ab	0.85	10.33 a	5.63	2.46 b	0.75	3.39 b	1.24

[a]Only elements with significant country effects included; means from different countries of origin without common letter are significantly different ($p<0.05$). Note: The discrimination power among countries depends on numbers of observation. The values are mean $\pm$ standard deviation.
[b]Effect of country of origin: *$p<0.05$, **$p<0.01$, ***$p<0.001$.

pared to poultry meat from Brazil, Switzerland, Hungary, and Thailand). This may be related to the fact that some French soils exhibit relatively high contents of Tl from pedogeo-chemical origin [30]. However, concentrations of Tl might also be influenced by industries such as cement factories [31], metallurgy, or coal combustion [30], but the world-wide industrial production and use of Tl is low [32]. In another study, it was shown that rape, which is frequently incorporated in broiler diets, tends to accumulate Tl [33]. Different from soybean products, feeds made from rape are more regionally used and exported to a lesser degree, and therefore might be important mediators to allow such geographic differences as Tl soil concentrations be reflected in meat.

Dried beef

Sixty-six out of 72 elements/isotopes (all except ^{9}Be, ^{149}Sm, ^{165}Ho, ^{172}Yb, ^{202}Hg, and ^{209}Bi) were found in dried beef. There were 15 elements in which statistically significant differences were found in between-country raw meat (Table 3), and 16 elements in which contents were significantly different according to site of processing (Table 4). From these elements, concentrations of those five listed in the major food table used in the German-speaking area of Europe [21] were widely in the range reported for raw beef. It has to be emphasized that variations between countries were high and processing might have led to increases of these elements in some cases, while reductions compared to raw beef are less likely.

Calcium (Ca) was found to be highest in Austrian samples, and concentrations significantly differed from samples originating from Australia, Switzerland, and the United States when compared according to its place of processing (Table 4). Ca is given via supplements to most cattle diets. However, Ca was lower also in those Swiss samples (113.7 ± 21.7 μg/kg) which were prepared from Brazilian raw beef different from the Austrian samples. Furthermore, excessive dietary Ca contents are not likely to increase meat Ca further due to homeostatic control of this important element for muscle function. This suggests that Ca salts might have been added (in higher amounts) in the Austrian dried beef manufacturing.

High cadmium (Cd) levels were found in United States and Australian dried beef compared to the other countries of origin (Tables 3 and 4). This seems to be a raw beef effect rather than a processing effect. Uraniferous black shale was described to be rich in Cd, which can be accumulated in rice [28] and potatoes [3]. Sager [34] mentioned phosphates fed as supplements as a possible sources of Cd.

Copper (Cu) concentrations separated Austria from Switzerland as processing countries (Table 4). High Cu levels were found in samples processed in Switzerland and Canada, while samples from Austria and United States showed lower levels. Cu concentrations (μg/kg) of the samples prepared from Brazilian raw meat differed also between Austria (0.66 ± 0.19) and Switzerland (1.53 ± 0.16), while there was no such difference between the origins of the raw meat (Swiss, 1.60 ± 0.44; Brazilian, 1.53 ± 0.16). This strongly suggests that the Cu concentration of the dried beef was mainly determined by processing. Possible sources might be curing salts or herbs used in processing. Cu as well as Pb and Zn can be bound to sulfide ore, which could release its minerals through weathering. The minerals could then accumulate in soil [35] and, consequently, in herbs.

Gallium (Ga) was found to be high in samples from Australia, where one of the largest world production is estimated [36], as well as from United States, where large natural deposits are reported [37] and a large Ga recycling industry has been established [36] (Tables 3 and 4).

High nickel (Ni) concentrations were detected in meat from Canada, Brazil (especially in meat processed in Austria), and Switzerland, while Australia and United States showed lower levels (Tables 3 and 4). Abundant deposits of Ni ore are found in Australia, Canada, and Russia [38]. Common stainless steel, as used for food processing machines and meat cutting knives, contains Ni and vanadium (V) beside other elements. Accordingly, the ranking of the processing origin of the dried beef samples was quite similar for Ni and V. A contamination of the meat by abrasions from these tools during de-boning or carving is therefore possible. However, a release of high amounts is still quite unlikely. Ni was also found to be high in soils from serpentine, which is

Table 3 Differences in country of raw meat origin in trace element contents[a] of dried beef

	p[b]	Australia[c] ($n = 4$) Australia[d]		Brazil[c] ($n = 7$) Austria/Switzerland[d]		Canada[c] ($n = 2$) Canada[d]		Switzerland[c] ($n = 8$) Switzerland[d]		USA[c] ($n = 2$) USA[d]	
[10]B (mg/kg)	***	17.61 a	1.14	0.47 b	0.19	0.56 b	0.06	0.59 b	0.21	22.68 a	1.33
[111]Cd (µg/kg)	***	4.73 a	2.33	1.24 b	0.67	1.30 bc	0.02	1.51 bc	0.81	4.27 ac	0.17
[161]Dy (µg/kg)	*	3.65 a	0.69	3.23 ab	0.27	3.38 ab	0.02	3.61 a	0.46	2.36 b	0.03
[151]Eu (µg/kg)	***	3.07 a	0.52	2.90 a	0.26	3.07 a	0.02	3.13 a	0.12	1.69 b	0.02
[69]Ga (µg/kg)	***	3.24 a	2.00	0.76 c	0.35	0.84 bc	0.07	0.69 c	0.16	3.15 ab	0.03
[7]Li (µg/kg)	**	12.47 bc	3.30	12.28 c	3.80	23.00 ab	3.13	13.25 bc	2.73	26.69 a	10.88
[60]Ni (µg/kg)	*	65.2 b	91.5	250.8 a	96.7	218.0 ab	6.4	194.3 ab	65.0	72.6 ab	68.9
[104]Pd (µg/kg)	***	189.6 a	137.1	17.5 b	12.7	22.0 b	14.0	16.8 b	9.8	154.3 ab	1.5
[85]Rb (mg/kg)	***	8.30 ac	3.32	16.24 a	3.26	17.33 ab	15.49	5.17 c	1.39	3.60 bc	0.44
[128]Te (µg/kg)	**	3.46 a	1.28	1.94 b	0.21	2.02 ab	0.05	2.19 b	0.41	1.67 b	0.02
[203]Tl (µg/kg)	*	3.04 a	1.15	1.78 b	0.23	2.61 ab	1.14	1.90 b	0.23	2.02 ab	0.05
[169]Tm (µg/kg)	**	3.14 a	1.04	1.73 b	0.17	1.84 b	0.02	1.88 b	0.07	2.31 ab	0.03
[51]V (µg/kg)	**	4.32 ab	2.76	3.52 b	2.04	1.14 b	0.11	2.10 b	1.11	8.80 a	3.87
[171]Yb (µg/kg)	***	2.65 b	0.69	3.28 ab	0.30	3.47 ab	0.03	3.56 a	0.15	0.87 c	0.01
[68]Zn (mg/kg)	**	59.7 b	11.2	85.8 ab	15.4	129.9 a	35.0	107.2 a	31.0	43.3 b	3.3

[a]Only elements with significant country effects included; means from different countries of origin without common letter are significantly different ($p < 0.05$). Note: the discrimination power among countries depends on numbers of observation. The values are mean ± standard deviation.

[b]Effect of country of origin: *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$.

[c]Country of origin.

[d]Country of processing.

Table 4 Differences in country of processing in trace element contents[a] of dried beef

	p[b]	Austria[c] ($n = 2$) Brazil[d]		Australia[c] ($n = 4$) Australia[d]		Canada[c] ($n = 2$) Canada[d]		Switzerland[c] ($n = 13$) Switzerland/Brazil[d]		USA[c] ($n = 2$) USA[d]	
[10]B (mg/kg)	***	0.62 b	0.32	17.62 a	11.41	0.56 b	0.06	0.53 b	0.20	22.68 a	1.33
[44]Ca (mg/kg)	*	312.7 a	278.4	75.8 b	27.4	142.7 ab	16.9	115.2 b	24.9	78.9 b	3.9
[111]Cd (µg/kg)	***	1.22 b c	0.00	4.73 a	2.33	1.30 bc	0.02	1.41 c	0.79	4.27 ab	0.17
[63]Cu (mg/kg)	**	0.66 b	0.19	1.24 ab	0.36	1.51 ab	0.29	1.56 a	0.35	0.84 ab	0.23
[151]Eu (µg/kg)	***	3.04 b	0.14	3.07 b	0.52	3.07 b	0.02	3.02 b	0.24	1.69 a	0.02
[69]Ga (µg/kg)	***	1.02 ac	0.56	3.24 a	2.00	0.84 bc	0.07	0.68 c	0.19	3.15 ab	0.03
[7]Li (µg/kg)	***	16.67 ac	0.51	12.47 b c	3.30	23.00 ab	3.13	12.21 c	2.99	26.69 a	10.88
[60]Ni (µg/kg)	**	340.8 a	181.7	65.2 c	91.5	218.0 abc	6.4	202.2 ab	51.0	72.6 bc	68.9
[104]Pd (µg/kg)	***	35.4 ac	8.1	189.6 a	137.1	22.0 bc	14.0	14.4 c	8.2	154.3 ab	1.5
[88]Sr (mg/kg)	***	1.59 a	0.43	0.34 b	0.14	0.29 b	0.10	0.23 b	0.08	0.18 b	0.05
[128]Te (µg/kg)	**	2.04 ab	0.02	3.46 a	1.28	2.02 ab	0.05	2.08 b	0.37	1.67 b	0.02
[203]Tl (µg/kg)	*	2.01 ab	0.10	3.04 a	1.15	2.61 ab	1.14	1.82 b	0.24	2.02 ab	0.05
[169]Tm (µg/kg)	**	1.81 b	0.09	3.14 a	1.04	1.84 b	0.02	1.81 b	0.15	2.31 ab	0.03
[51]V (µg/kg)	**	4.46 ab	0.08	4.32 ab	2.76	1.14 b	0.11	2.50 b	1.70	8.80 a	3.87
[171]Yb (µg/kg)	***	3.42 ab	0.16	2.65 b	0.69	3.47 ab	0.03	3.43 a	0.28	0.87 c	0.01
[68]Zn (mg/kg)	**	76.5 ab	3.3	59.7 b	11.4	129.9 a	35.0	100.4 ab	27.2	43.3 b	3.3

[a]Only elements with significant country effects included; means from different countries of origin without common letter are significantly different ($p < 0.05$). Note: the discrimination power among countries depends on numbers of observation. The values are mean ± standard deviation.

[b]Effect of country of origin: * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

[c]Country of processing.

[d]Country of origin.

Table 5 Jackknifed matrix for classification of poultry breast meat[a]

	Estimated origin						
Actual origin	Brazil	Germany	France	Switzerland	Thailand	Hungary	% correct
Brazil	4	0	0	0	0	0	100
Germany	0	3	0	0	0	0	100
France	0	2	0	0	0	0	0
Switzerland	1	0	0	6	0	0	86
Thailand	0	0	0	0	3	0	100
Hungary	0	0	0	0	0	6	100
Overall	5	5	0	6	3	6	88

[a]Figures represent sample numbers.

plant available [35], as well as in aquatic plants, but not in fish [38].

Palladium (Pd) was found to show higher level in Australian and US samples (Tables 3 and 4). Sources of Pd are known to exist in Russia, South Africa, Canada, and United States [39].

Brazilian and Canadian samples showed higher amounts of Rb than other raw-meat origins (Table 3). For the Brazilian origin, this is in line with the high contents found in poultry meat from Brazil compared to the other countries of origin (see earlier discussion).

The Austrian samples had high levels of Sr compared to all others places of processing (Table 4). This was likely to have been a processing effect, since there was a clear difference in Sr concentration (ng/kg) in dried beef made from Brazilian raw meat in Austria (1587 ± 429) and Switzerland (289 ± 50).

Similar to poultry, there were significant differences in Tl concentration, which was highest in the beef samples from Australia (Tables 3 and 4). Possible reasons are most likely to be sought in regional differences in soil and plant accumulations (see discussion on poultry meat).

Zinc (Zn) concentrations in Australian and US samples were lower than those in the other origins (Tables 3 and

4). Zn is used as component of many mineral supplements for beef which could influence the Zn levels found in the analyzed meat. Also interactions with other elements have an influence. For instance, feeding of high Ca levels along with plant protein containing phytate caused Zn deficiencies through reducing its bioavaility [40]. Other than with the rare and typically unsupplemented elements, interpretation of the relation of Zn concentrations in meat to its geographic origin is therefore quite difficult.

Boron (B), dysprosium (Dy), lithium (Li), tellur (Te), europium (Eu), thulium (Tm), and ytterbium (Yb) showed significant origin-specific differences as well (Tables 3 and 4), but no information about these elements in relation to feeding, processing, and meat was obvious from the literature.

Multivariate element signature of meat

Stepwise backwards discriminant analysis of all elements and isotopes analyzed in poultry meat allowed to establish a classification matrix using the elements As, Cd, Na, Rb, and Tl. In Jackknife cross-validation (leave-one-out procedure), all samples, except those from Swiss and French origin, could be classified correctly (Table 5). Both French samples were

Table 6 Jackknifed matrix for classification of dried beef according to country of origin of raw meat and country of processing[a]

	Estimated origin					
Actual origin	Australia	Brazil/Austria[b]	Canada	Switzerland	USA	% correct
Country of origin of raw meat						
Australia	3	1	0	0	0	75
Brazil	0	5	0	2	0	71
Canada	0	0	0	2	0	0
Switzerland	0	0	1	7	0	88
USA	0	0	0	0	2	100
Overall	3	6	1	11	2	74
Country of processing						
Austria	0	1	1	0	0	50
Australia	3	0	1	1	0	75
Canada	0	0	0	2	0	0
Switzerland	0	0	1	12	0	92
USA	0	0	0	0	2	100
Overall	3	1	2	15	2	78

[a]Figures represent sample numbers.

[b]Country of origin of raw meat/country of processing.

misclassified as German, one Swiss samples was estimated to be of Brazilian origin. Extending the database with further representative samples is necessary to improve the statistical representation of the origins, thus providing more reliable classification functions and probably lower error rates also for the authentication of Swiss and French poultry meat.

In dried beef, LDA with stepwise backward elimination (probability to enter/to remove: 0.15) carried out with the PC from PCA showed that PC 1, 2, 3, and 4 were useful to separate both the different countries of origins of raw meat and the places of processing. The following elements were found to have an important influence on the different PCs (loadings ≥ 0.7 respectively ≤ -0.7): B, Cd, Ga, Ni, Pd, Te, Tl, and Tm on PC 1 and Dy, Eu, U, and Yb on PC2. For PC 3 and 4, the loadings for all elements were between 0.7 and -0.7, indicating that all elements had an equal separation influence in these PCs. The classification matrices (Table 6) show that, according to the origin of raw meat, both Canadian and US origins could be correctly identified, while one Brazilian and three Swiss samples were incorrectly identified as Canadian samples. Concerning the place of processing a completely correct identification was only possible for US samples. Overall, this suggests that the discriminative power of the element signature is quite good.

Conclusion

Elements, especially As, Na, Rb, and Tl for poultry meat and B, Ca, Cd, Cu, Dy Eu, Ga, Li, Ni, Pd, Rb, Sr, Te, Tl, Tm, V, Yb, and Zn for dried beef, turned out to be useful to differentiate for the geographic origin respectively the place of processing of the meat, while GCC obviously does not have the potential to assist in tracing the origin of these meat types. A multi-element (signature, fingerprinting) approach is more promising, since, when looking at single characteristic elements, it remains uncertain whether the element concentration is really characteristic for an entire country or only for a relatively small production region where the correspondingly enriched soils are present. Therefore, and due to the small number of samples, the present results can only give an indication, and the results obtained on the discriminating power of the promising elements await confirmation by a larger sample set.

There are also differences in the interpretation of the results between the two commodities investigated. Although more elements seem to characteristically differ in dried beef, clarification of the origin of certain elements is also more demanding than in poultry meat. In addition to the elements accumulated in the raw meat from the environment or from feed additives, the processing steps (seasoning, curing, drying) add or, less likely, remove further elements, thus changing the specific element signature of the raw meat. If these factors can be separated, this would give a link for the place of origin of meat and the place of processing. However, further clarification is required. The advantage of the multi-element analysis over single indicative elements, especially those included in the list of elements sometimes or often supplemented to livestock diets could be that most of these rare elements are not influenced by this supplementation and, more important, are not likely to get subject to response or even fraud once the method is adopted as standard technique for meat authentication with respect to geographic origin.

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