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REVIEW ARTICLE

Bromatological, analytical and chemometric assessment of animal and plant foods based on mineral composition

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Abstract

There are several examples of numerous applications of analytical and multivariate techniques useful in investigations of varied assortment of food products. The successful use of chemometrics in study of food such as meat and its products, fish, seafood, milk and dairy products, honey, cereal products, oils, oilseeds and nuts, vegetables, fruits, mushrooms, tea, coffee, confectionary products, mineral waters and alcoholic beverages deserves attention. RDA indicated exceeded its normative values for Se, Cu, Mn, Fe and Cr in some groups of animal food and Cr, Mn, P and Fe in some assortment of plant food. Based on PTWI values for Pb, Cd and Hg, there is no threat to human health resulting from the consumption of the investigated food products. It is concluded that the proper use of analytical and chemometric tools is useful for assessing nutritive and health quality of animal and plant foods. They play an important role in quality control, and their classification in view of geographical origin, confection and degree of environmental pollution. Both, instrumental and multivariate techniques would be useable in differentiating unprocessed and technologically processed food as well as detecting fraud to preserve the brand name of the original product. The aim of this study is to give an overview of the crucial issues associated with the implementation of chemometrics in food research and development.

Keywords: assessment of food quality · analytics · chemometrics · bromatology

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In order to perform adequate analytical and chemometric assessment of original data it is important to use skillfully modern both analytical and computational tools following strictly the rules and research criteria. In recent times dynamic progress of analytical and chemometric techniques has been observed owing to new and advanced informative technologies. They make it possible to reliably obtain useful information from an experimental data set. Therefore, multivariate techniques appeared to be the key statistical and mathematical approach to explore extensive data base being highly helpful in simple and quick explorations as well as identification of similarity between samples (objects) and measured parameters (variables). The aim of this study is to give an overview of the crucial issues associated with the implementation of chemometrics in food research and development.

Material and methods

The Scopus, ScienceDirect, Medline and Web of Science databases were searched for literature published from 1989 to 2021 using the following keywords: Chemometric evaluation; Analytical evaluation; Food authenticity; Food adulteration; Meat; Fish flesh; Seafood; Milk and dairy products; Honey; Grain products, Olive oils and oilseeds; Vegetables and legume seeds; Mushrooms; Fruit and its products; Tea and its infusion; Coffee and its infusion; Cocoa and its products; Sweets; Mineral and drinking water; Alcoholic beverages. The main inclusion criterion was whether the article contained evaluation of data obtained by using combination of more advanced analytical and chemometric (mainly multivariate) methods/techniques. The exclusion criteria were: small number of the samples studied, lack of sufficiently advanced analytical and chemometric methods or techniques.

Results

The search retreived 1478 articles of which 341 were included in the review.

Analytical and chemometric methods

The following analytical methods have been routinely applied: Atomic Absorption Spectrometry with four techniques, i.e. flame technique (FAAS), electrothermal (ET-AAS), cold vapor (CV-AAS), hydrogen generation (HG-AAS) as well as Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). Reliability and correctness of concentration data were checked under the quality assurance test by the use of appropriate certificate reference materials (CRMs) with declared, known concentration of analytes [1-2]. The validated analytical data were then processed chemometrically by means of univariate, bivariate and other multivariate techniques, e.g. bar charts, histograms, one-way ANOVA, correlation and regression analysis and other, advanced and frequently applied techniques such as Principal Component Analysis (PCA) or Factor Analysis (FA) and Cluster Analysis (CA) or Hierarchical Cluster Analysis (HCA) [3-12]. Among the different criteria for determining the number of components/factors, the Kaiser criterion was selected and therefore factors greater than 1 were exclusively considered and interpreted. The aim of multivariate data analysis is to divide data matrix into its components to reduce relatively numerous variables to a smaller number of orthogonal factors. Such approach guarantees achieving a high degree of generalization of registered tendencies or statistical relationships, and what more, at a high level of statistical significance [2-3, 13].

Meat

Bromatological, analytical and chemometric assessment of foods of animal origin based often on stable chemical elements has attracted a special attention of environmentalists as well as scientists specializing in food. Such investigations resulted in recognition of environmental parameters differentiating geographical distribution and diverse assortment of defatted mutton samples [14], pork belly [15], poultry breast meet and dried beef samples [16-17], labeling lamb meat [18], bovine muscles [19-22], liver, kidney and muscle of sheep [23], beef steak [24-25], pork [26], pork, beef and chicken [27-28] and others.

Fish and other seafood

Interesting information is also available on the application of chemometrics in assessment of world-wide populations of fish; such investigations were performed by many researchers, e.g. Julshamn and Grahl-Nielsen [29], Szefer et al. [30], Molkentin et al. [31], Ye et al. [32], Yamashita et al. [33], Li et al. [34], Ahmed et al. [35], Rahman et al. [36] and Marpaung et al. [37]. Chemometric processing of mineral composition related to vendace caviar has been performed by Rodushkin et al. [38]. Edible mussels were also analysed and assessed chemometrically, e.g. by Struck et al. [39], Favretto et al. [40], Bechmann et al. [41], Julshamn and Grahl-Nielsen [29], Szefer and Wołowicz [42], Szefer et al. [4-5, 42-45], Mesa et al. [46], Bartolomé et al. [47], Przytarska et al. [48], Chen et al. [49] and Bennion et al. [50, 51]. Among marine organisms also edible crustaceans were investigated by Li et al. [52-55]

and Nędzarek et al. [56-58]. Kwoczek et al. [59] analysed different assortment of seafood available in Poland exported from different geographical regions.

Milk and dairy products

Milk and its products from different geographical regions were analysed for mineral component composition to assess their authenticity in the view of chemometric evaluation, among others milk [18, 60-67], commercial skim milk powders sweet whey and different milk-based infant formulae [68-79], cheeses [80-85], butter, margarine, and peanut butter [37] and eggs [86-89].

Honey

Honey samples were also chemometrically classified relative to their type and origin based on the content of chemical elements [7, 90-114].

Cereal products

Application of the chemometric techniques in evaluation of cereal products in view of their mineral composition was performed by many researchers, e.g. wheat samples [115-117], rice [118-125], wheat, barley and faba bean [126], buckwheat [127-128] and sorghum [129-130]. Different kinds of grain products (bread, cereals, rice, flour, pasta) purchased from the local market in Poland originated from 14 different countries were analysed and evaluated chemometrically by Grembecka [8] and Grembecka et al. [131].

Oils, oilseeds and nuts

Mineral components of edible oils [132-137] as well as oilseeds and nuts [138-145] were analysed and evaluated chemometrically. Six different kinds of oilseeds purchased from the local market in Poland originated from 6 different countries were investigated and assessed by Grembecka [8].

Vegetables and fruits

Different types of vegetables originated from various geographical regions were studied in accordance of chemometric evaluation of chemical elements concentration, namely potato [146-152], tomato [153-155], cabbage [156-157], broccoli [158], caper [159, 160], carrot [161, 162], onion [163-169], garlic [170-172], beetroot [173], pea, bean, faba bean [164, 174-175], lentil [176], parsley, carrot, onion, carrot, cabbage, lettuce, cucumber, green bean [177], parsley [178], paprika [179], chili pepper [180], Sechium edule fruits [181], Caigua [182], Taro [183] and sea cucumber [184]. Twenty five different kinds of commercially available fresh and processed vegetables and 5 kinds of leguminous vegetables purchased from the local market in Poland originated from 4 different countries and other EU countries were investigated and assessed by Grembecka [8] and Grembecka et al. [185].

The following assortment of fruits was assayed and estimated: pear [186], apple [187], lemon pulps samples [188], orange [189], pomelo [190], kaki fruit [191] and fruit juice, i.e. lemon juice [192, 193], grape juice [194, 195] and orange juice [196]. Twenty four different kinds of commercially available fresh fruits purchased from the local market in Poland originated from different countries were analysed and assessed by Grembecka and Szefer [9].

Tea and coffee

Different kinds of tea originated from various countries were analysed and chemometrically classified in view of chemical elements composition by Marcos et al. [197], Wong et al. [198], Fernández-Cáceres et al. [199], Herrador and González [200], Moreda-Piñeiro et al. [201, 202], Fernández et al. [203], Chen et al. [204], McKenzie et al. [205], Mbaye et al. [206], Marcelo et al. [207], Paz-Rodríguez et al. [208], Brzezicha-Cirocka et al. [11, 209-211], Ma et al. [212], Milani et al. [213], Ye et al. [214], Lou et al. [215], Zhao et al. [216-219], Malinowska et al. [220], Zhang et al. [221], Idrees et al. [222], Liu et al. [223-226] and Motta et al. [227].

There are also numerous available literature data on application of the chemometric techniques in analytical evaluation of coffee in view of their mineral composition. Differentiation and classification of coffee samples have been achieved by Krivan et al. [228], Martin et al. [229-231], dos Santos et al. [232], Anderson and Smith [233], Fernandes et al. [234], Filho et al. [235], Grembecka et al. [236], Akamine et al. [237], Muñiz-Valencia et al. [238], Valentin et al. [239], Barbosa et al. [240], Liu et al. [241], Oliveira et al. [242], Szymczycha-Madeja et al. [243], Habte et al. [244], Mehari et al. [245], Pohl et al. [246], Zhang et al. [247], Al-Jaf and Saydam [248], Cloete et al. [249], Worku et al. [250], Endaye et al. [251], Voica et al. [252] and Bitter et al. [253].

Confectionary products

Different beet and cane sugar products (cane sugar plants, maple syrup, crude and syrup juices, molasses, the end products of consumer sugar) have been investigated and assessed chemometrically in aspect of the mineral composition by several authors, e.g. Awadallah et al. [254], Nunes et al. [255], Rodushkin et al. [256], Grembecka and Szefer [257], Barbosa et al. [258], Andrade et al. [259] and Guedes and Pereira [260]. Different ingredients such as sugarcane, soy, citrus, coffee, maize, eucalyptus, mango, bean, banana, lettuce, brachiaria, pearl millet, grape, rubber tree and tomato were analysed by de Carvalho et al. [261]. Chemometric estimation of both the confectionary and geographical provenance of cocoa and chocolate was performed by some authors, e.g. Pedro et al. [262], Grembecka and Szefer [257], Bertoldi et al. [263], Junior et al. [264], Kruszewski and Obiedziński [265] and Vanderschueren et al. [266].

Mushrooms

Chemometric techniques have been used to explore the elemental data for different species of mushrooms coming from various geographical areas, e.g. by Malinowska et al. [10], Cocchi et al. [267], Chudzyński et al. [268, 269], Falandysz et al. [270-273], Pająk et al. [274], Drewnowska and Falandysz [275], Kojta et al. [276-277], Mleczek et al. [278], Niedzielski et al. [279], Brzezicha-Cirocka et al. [280], Wang et al. [281], Zsigmond et al. [282], Buruleanu et al. [283] and Nowakowski et al. [284].

Mineral water

Application of the chemometric techniques in analytical evaluation of mineral water in view of their elemental composition has been performed by Misund et al. [285], Versari et al. [286], Kraic et al. [287], Bityukova and Petersell [288], Birke et al. [289-291], Cicchella et al. [292], Demetriades et al. [293], Fugedi et al. [294], Dinelli et al. [295-297], Grošelj et al. [298], Kermanshahi et al. [299], Peh et al. [300], Avino et al. [301], Bertoldi et al. [302], Cidu et al. [303], Souza et al. [304], Banks et al. [305], Flem et al. [306], Pantić et al. [307], Khan et al. [308] and Bodor et al. [309].

Alcoholic beverages

Different investigators have processed chemometrically the concentration of chemical elements in different kinds of red and white wines, including must, e.g. Latorre et al. [310], Barbaste et al. [311], Pérez Trujillo et al. [312], Marengo et al. [313], Coetzee et al., [314], Gonzálvez et al. [315], Rodríguez et al. [316], Aceto et al. [317], Durante et al. [318], Catarino et al. [319], Pořízka et al. [320], Cruz et al. [321], Dembroszky et al. [322], Shimizu et al. [323] and Grembecka et al. [324]. Chemometric evaluation of mineral composition of beers appeared to be useful in the classification of different features of this alcoholic beverage as has been proved by Bellido-Milla et al. [325], Alcázar et al. [326], Wyrzykowska et al. [327], Mahmood et al. [328], Carter et al. [329], Voica et al. [330], Rodrigo et al. [331], Styburski et al. [332] and Redan et al. [333]. Ciders were also studied and chemometricaly considered relative to their mineral composition [334-335] as well as to different kinds of Scotch whisky [336], sherry brandy, whisky [337-338] and traditional Galician orujo alcoholic distillates with and without a certified brand of origin (CBO) [339].

Differentiation of geographical origin

For instance, a clear discrimination between soft tissue of Mytilide originated from different coastal regions of subarctic, temperate, subtropical and tropical marine ecosystems was achieved owing to use of FA technique [45]. Object samples are separately distributed along F1 axis (relative to F1 score values) corresponding to edible mollusks inhabited coastal regions of marine ecosystems including also intertidal zones of Atlantic, Pacific and Indian Ocean (Table 1).

Table 1. Application of the chemometric techniques in analytical evaluation of animal food in view of its mineral composition

Kind of animal food, no of samples, country of origin	Chemical elements as descriptors	Analytical technique	Chemometric /statistical technique	Reference
81 samples of perch (muscle and liver) from Pomeranian Bay and Szczecin Lagoon (n = 162) Southern Baltic	Hg, Cd, Pb, Cu, Zn	FAAS, ET-AAS, Hg analyser	Correlation and regression analysis, One and two-way ANOVA, FA	[30]
Cockle *Cerastoderma glaucum* from the Bay of Gdańsk (Baltic Sea), Marennes-Oleron and Arcachon Bay (French Atlantic coast), Embiez Islands (Mediterranean Sea) (n = 50 pooled samples) Poland, France	Cd, Cu, Fe, Mn, Ni, Zn	AAS	PCA	[42]

Kind of animal food, no of samples, country of origin	**Chemical elements as descriptors**	**Analytical technique**	**Chemometric /statistical technique**	**Refe-rence**
800 specimens of *Mytella strigata* (soft tissues and byssus), and 200 specimens of *Chione subrugosa* and the associated sediments from 4 sampling sites in a tropical mangrove lagoon (n = 1000 specimens) Mexico	Cd, Pb, Zn, Cu, Ag, Cr, Co, Ni, Mn, Fe	FAAS	Correlation and regression analysis	[44]
Samples of cockle from 6 sites along the Mediterranean Lagoon Etang de Thau (n = 12 pooled samples) France	Ag, Cd, Co, Cr, Cu, Ni, Pb, Zn, Mn, Hg	FAAS, CV-AAS	Correlation and regression analysis	[5]
About 4200 specimens of Blue mussel from 23 sites from in 3 sectors of the southern Baltic Sea; i.e. pooled samples of soft tissues (ca. 350), shells (ca. 200) and byssus (26) (n ≅ 580) Poland	Ag, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn, Hg	FAAS, CV-AAS	Correlation and regression analysis, FA	[4]
3600 specimens of *M. galloprovincialis* from 7 sampling sites in Masan Bay and Ulsan Bay, i.e. pooled samples of soft tissue (119), byssus (30); moreover water (24) and suspended matter (26) (n ≅ 2 00) South Korea	Cd, Co, Cu, Cr, Fe, Hg, Mn, Ni, Pb, Sn, Ti, Zn	ICP-MS, AFS, HRICP-MS, AAS	Correlation and regression analysis, two-way ANOVA, DFA	[6]
About 5000 specimens of Mytilids (101 soft tissue samples and 48 byssus samples) from different geographical coastal regions all over the world, i.e. North Sea, Mediterranean Sea, Atlantic coast, Southern Baltic, Northern Baltic, White Sea, Arabian Sea, East Sea, Indian Ocean coast, Pacific coast (n = 150) France, Holland, Poland, Sweden, Russia, Spain, Yemen, South Korea, Japan, Mexico, Brazil	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	FAAS	FA	[45]
Pooled samples of edible parts of shellfish products (shrimps, surimi products, octopus, mussels, squids, octopuses, crabs, lobsters) from 8 countries (n = 88) Great Britain, Norway, Spain, India, Philippines, Thailand, Canada, New Zealand	Cu, Zn, Fe, Mn, Co, Ni, Cr, Mg, Na, K, Ca, Cd, Pb, Se, Hg	FAAS, GF-AAS, HG-AAS, CV-AAS	FA, correlation analysis	[59]

Kind of animal food, no of samples, country of origin	Chemical elements as descriptors	Analytical technique	Chemometric /statistical technique	Refe- rence
Approximately 1000 specimens of blue mussel *M. edulis* from east coast of Kyushu Island (n = 46 pooled samples) Japan	Cd, Pb, Zn, Cu, Ag, Cr, Co, Ni, Mn, Fe	FAAS	Correlation and regression analysis	[43]
260 specimens of *Perna perna* from 3 locations of Gulf of Aden (n = 8 pooled samples) Yemen	Cd, Pb, Zn, Cu, Mn, Fe	FAAS	Correlation and regression analysis	[340]
Samples of 4 bivalve species (800 specimens) and associated sediments from 7 locations of Gulf of Aden (n = 94) Yemen	Cd, Pb, Zn, Cu, Ni, Co, Cr, Mn, Fe	FAAS	ANOVA, FA, correlation and regression analysis	[341]
Several brands of commercially available honeys and bee products of different botanical origins from 3 different countries and other EU countries (n = 66) Poland, Italy, Hungary, EU	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn	FAAS, spectro- photometric method	CA. FA, ANOVA	[7]

Interesting results were obtained in investigations of cockle (C. edule) from the Bay of Gdansk (Southern Baltic), Marennes-Oleron Bay, Arcachon Bay (French Atlantic coast) and Embez Islands (Mediterranean Sea). The PCA data displayed that Mn and Fe are responsible for discrimination between individuals originated from Marennes-Oleron Bay and Arcachon Bay whilst Zn, Cd and partly Ni have a main contribution in separation of the Bay of Gdansk from the others [42].

It was also stated that FA technique is helpful in discrimination of the Korean Peninsula mussel *M. galloprovincialis* with respective to its geographical origin, i.e. from the Masan Bay and the Ulsan Bay, i.e. more and less polluted regions with heavy metals, respectively [6].

Another exemplar concerns application of CA technique in processing of concentration data obtained for *Boletus edulis* mushroom and the adjacent soil as substratum from 12 different forest regions of Poland (Table 2). There is a significant grouping of samples collected in the Tricity Landscape Park, adjacent to the Tricity agglomeration and Pb is a main descriptor responsible for separation of this region from other 11 Polish forest sampling sites as protected areas, deprived of industrial and urban influences [10]. Based on obtained concentration data corresponding to 22 different species of mushrooms collected from different forest regions of Poland it is found that *C. cibarius*, *B. edulis* and *L. scabrum* were diversified relative to their geographical provenance [280].

Interesting results were reported for tea samples imported from Asiatic countries which allow differentiation of object scores corresponding to Japan, India and China as well as it was possible to identify particular varieties of the green tea studied (Sencha, Kokeicha, Bancha, Darjeeling, Gunpowder, Chun Me and Yunnan) [11]. Two multivariate techniques, i.e. FA and CA were applied to differentiate black tea samples and their infusions in view of their geographical origin. These chemometric tools proved to be able to discriminate samples according to their provenance as well as plantation within the common regions [12].

CA technique allowed differentiation of teas relative to the country of origin, i.e., China, India, Ceylon and Kenya as well as it was useful in distinguishing of teas originated from various plantations within a single country. Thus, chemometrics proved to be effective tool to discriminate these samples in view of their provenance as well as plantation within the common region. Moreover, FA technique appeared to be useful in differentiating of various wine varieties in aspect of their geographical origin [324].

Table 2. Application of the chemometric techniques in analytical evaluation of plant food in view of its mineral composition

Kind of animal food, no of samples, country of origin	Chemical elements as descriptors	Analytical technique	Chemometric /statistical technique	Refe-rence
Different kinds of grain products (bread, cereals, rice, flour, pasta) purchased from a local market in Poland, originated from 14 different countries (n = 146) Poland, Germany, Italy, Spain, India, Pakistan, Singapore, Thailand, China, Vietnam, Japan, Borneo, Guyana, USA	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn	FAAS, spectro-photometric method	CA. FA, ANOVA	[8, 131]
25 different kinds of commercially available vegetables (fresh and processed) and 5 kinds of leguminous vegetables purchased from the local market in Poland originated from several EU countries and Canada (n = 129) Poland, Spain, France, Italy, EU	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn	FAAS, spectro-photometric method	CA, FA, ANOVA	[8, 185]
Samples of instant and ground coffee (dry coffee and infusions) (n = 120) South America, Africa, Asia	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Na, P, Pb, Zn	FAAS	Correlation coefficients, ANOVA, CA, FA	[236]
25 different kinds of commercially available fresh fruits purchased from the local market in Poland originated from different countries (n = 98) Poland, Europe, Asia, Africa, America	Mg, Ca, K, Na, P, Zn, Cu, Fe, Cr, Co, Ni, Mn	FAAS, spectro-photometric method in the form of phospho-molybdate	ANOVA, FA, CA	[9]
Several types of green tea including their infusions from 3 countries (n = 41) China, India, Japan	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb Zn	FAAS, spectro-photometric method	Kruskal-Wallis test, FA, CA	[11]
Black tea samples including their infusions from different areas of 4 countries (n = 118) China, India, Ceylon, Kenya	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb Zn	FAAS, UV-Vis spectrometry	Spearman rank correlation analysis, Kruskal-Wallis test, FA, CA	[12]
Samples of dark (Pu-erh) and fruit tea leaves including their infusions from one country of declared origin (n = 32) China	Mg, Ca, K, Na, Mn, Cu, Fe, Zn, Cr, Ni, Co, Cd, Pb	FAAS, spectro-photometric method in the form of phospho-molybdate	Spearman rank correlation analysis, Kruskal-Wallis test, FA, CA	[210]

Kind of animal food, no of samples, country of origin	Chemical elements as descriptors	Analytical technique	Chemometric /statistical technique	Reference
Samples of teas (black, dark and green) from 3 different countries of declared origin (n = 30) China, India, Sri Lanka	Oxalate, Mg, Ca	Mangano-metric method, FAAS	Spearman rank correlation analysis, Kruskal-Wallis test, CA	[209]
Infusions of commercially available teas (black, green, oolong, Pu-erh and white), herbal infusions, instant tea and ready-to-drink tea beverages from 13 different countries in Eurasia, Asia, Southeast Asia and Oceania, Africa, South America (n = 64) China, India, Sri Lanka, Nepal, Vietnam, Taiwan, Japan, Java, Kenya, Georgia, Brazil, Argentina, South Africa	F-	Ion-selective electrode	CA	[220]
Samples of cocoa and chocolates (dark and milk) (n = 33) Poland, USA	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn	FAAS	ANOVA, CA, FA	[257]
Samples of sugar (from beet and cane), molasses, maple syrup (n = 15) Poland, India, Republic of Mauritius, Hawaii, Argentina, Canada	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn	FAAS	ANOVA, CA, FA	[8, 257]
166 samples of fruiting bodies (caps and stalks) of *Xerocomus badius* and 31 soil samples from 12 different 12 regions (n = 197) Poland	Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Na, K, Ca, Mg	FAAS	Correlation analysis, HCA, FA	[10]
Samples of 22 different species of mushrooms collected from different forest regions (n = 1500) Poland, Sweden	Ca, Na, K, Mg, Zn, Fe, Mn, Cu, Cr, Cd, Ag, Ni, Pb, Al, Ba, Sr	FAAS, ICP-AES	Non-parametric R-Spearman test, ANOVA Kruskal-Wallis test, post-hoc Dunns test, FA	[280]
6 different kinds of oilseeds purchased from the local market in Poland originated from 6 different countries (n = 14) Poland, Czech Republic, Hungary, Belgium, India, China	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Zn	FAAS, spectro-photometric method	CA, FA, ANOVA	[8]
Different types of red wines dry, semi-dry, sweet and semi-sweet wine) obtained at retail (n = 32) Austria, France, Chile, Hungary, Italy, USA, Portugal, Spain, Bulgaria, Germany, Poland, Moldavia	Mg, Ca, Na, K, Zn, Cu, Fe, Mn, Co, Cr, Ni, Cd, Pb, P	FAAS, spectro-photometric method with phospho-molybdate	ANOVA, Kruskal-Wallis test, FA	[324]

Differentiation of varietal origin

As shown in Table 1, the FA technique appeared to be helpful research tool in analysis of diverse assortment of seafood (oysters, mussels, prawns, surimi products, octopus, squids, octopuses, crabs, lobsters) originated from various over-worlds waters bordering 8 countries, i.e. Norway, England, Spain, India, Thailand, Canada, Philippines and New Zealand. Obtained data documented significant discrimination between factorial distribution of scores with respect to a degree of technological processing (described by F1 values) and taxonomic features of seafood [59].

Based on the FA technique, it is found that samples of artificial honey are separated from samples of natural honey. Moreover, natural honeys indicated a clear differentiation relative to their botanical origin. CA technique resulted in the dendrogram consisted of two main clusters, i.e. representing dark and light color honeys. The dark color honeys cluster contains generally samples corresponding to honeydew, buckwheat and heather honeys, while the second cluster is consisted of acacia, lime, rape and multifloral honeys. The FA technique appeared to be effective chemometric tool to separate the data concerning artificial honey samples (described by the highest levels of Ca and Na) whilst natural honeys and those with natural additives were characterized by K, P, Cu, Mn and Mg. Moreover, F2 achieved the lowest values for natural and syrup-feed honeys identified by high levels of Fe and Zn [7].

The analytical data obtained for different kinds of grain products (bread, cereals, rice, flour, pasta) purchased from the local market in Poland were also processed chemometrically (Table 2). FA appeared to be helpful technique in differentiating these products according to their type, especially in case of flour and rice [8, 131].

It was possible to discriminate numerous types of vegetables and fruits relative to their botanical type. Vegetables, legumes and oilseeds were characterized by the most effective discrimination by means of FA technique [8, 185]. There is differentiation of fruits in view of their belonging to botanical type (accessory, berry, pip and stone fruits) and family, i.e. Grossulariaceae (GR), Actinidiaceae (AC), Musaceae (MU), Bromeliaceae (BR), Cucurbitaceae (CU), Caricaceae (CA), Anacardiaceae (AN), Rosaceae (RO), Rutaceae (RU), Lauraceae (LA), Vitaceae (VI) and Ericaceae (ER) [9].

Chemometric analysis (ANOVA Kruskal Wallis test, Dunn's test, R-Spearman correlation, FA) of 6 species of mushrooms from 2 forest regions of Poland indicated that Ca, Na, K, Mg, Zn, Fe, Mn, Cu and Cd are effective descriptors of interspecies differentiation [280].

Authenticity of confectionery products was assessed based on CA data which distinguished samples of varied types in view of their botanical origin. According to [257], hierarchical dendrogram distinguishes two main clusters corresponding to the analyzed chocolate samples. The first cluster of scores represents dark chocolates, while the second one grouping milk chocolates. Dark chocolates are adjacent to subclusters representing cocoa products with content > 70% (C2–C4, C13) and others. However, dark chocolates, with declared cocoa content at least 45% (C7, C11), are ascribed to the grouping of milk chocolates (C15-C21), which means that these products contain less of cocoa than was stated on the label by the producer. Therefore, CA technique appeared to be effective tool in fraud detection [257].

As for coffee analysis (Table 2), chemometric assessment was performed in aim of categorization of samples in view of varieties characteristics. Based on FA data, classification of object samples and variables (loadings) relative to numerous coffee samples was achieved [236]. Analysis of their different technological forms (ground, instant coffee and coffee infusions) resulted in clear discrimination of the particular varieties of this assortment. Interesting results were obtained based on FA data which makes possible to distinguish arabica from robusta coffees. Higher values of F1 corresponded to 100% coffee of one bean type. Expensive brand coffee samples are generally situated near arabica coffee scores whilst less expensive brands are corresponded to robusta ones. It is pointed out that Mn is the best descriptor for identification of arabica samples whilst P identifies robusta ones [236].

Chemometric assessment was also helpful in classification of different types of teas based on their mineral composition (Table 2). For instance, CA technique was successfully used to identify several varieties of tea, e.g., Earl Grey, Assam, Ceylon and English Breakfast. Moreover, based on content of oxalates, Ca and Mg, it was possible to differentiate three types of tea according to their degree of technological processing (fermentation), i.e. black, green and Pu-erh tea [209].

Promising results were obtained for different assortment of wines (Table 2). A statistically significant correlation was found between the type of wine and the content of alcohol, K, P, Co and Pb concentrations. Moreover, FA technique allowed differentiation of individual types of wine based on its elemental composition. Macroelements such as Ca, K and P were responsible for distinguishing the group of dry wines and semi-dry wines corresponded to Pb, Cr, Co and Mg, while sweet wines contained the highest levels of Zn and Ni [324].

Differentiation of degree of pollution and other parameters

Bearing in mind the need to guarantee the quality of food, several multivariate techniques have been applied in identification of the sources of chemical pollutants in food. For instance, PCA data concerning heavy metals in molluscs of the Bay of Gdansk, French Atlantic coast and the Mediterranean Sea (Table 1) allowed for identification of the population of zoobenthos exposed to Zn, Cd and partly Ni in the

Gulf of Gdansk. It means that anthropogenic sources could be responsible for higher levels of these three elements in contrast to specimens inhabited the French aquatic regions. Moreover, besides the inter-regional differentiation also seasonal factors have an important influence on the heavy metals content in the cockles [42]. Seasonal variations were also observed in case of mussel *M. galloprovincialis* from the southern part of the Korean Peninsula [6]. ANOVA data indicated that seasonal variations in the both regions, i.e. the Ulsan Bay and the Masan Bay are statistically significant for mussel content of Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Ti, Pb, Sn and Zn. Moreover, based on FA data, the Masan Bay and partly of the Ulsan Bay samples were identified by the lowest values of F1, whilst most mussel samples originated from the Ulsan Bay situated near heavily industrialized area were described by the highest values of F1 [6].

For instance, concentration data for perch from southern Baltic was processed by chemometric techniques (Table 1). It is concluded that Hg in muscle and Cd, Pb and Cu in liver are descriptors for factorial differentiation of age groups of the fish investigated. The positive relationship between muscle Hg and age (weight-length) seems to be associated with the specific bioaffinity of CH_3Hg with a high biological half-life. Moreover, FA technique supported seasonal differences in muscle and especially hepatic samples; specifically, summer muscles were clearly separated from winter ones [30].

RDA and PTWI

The concentration data obtained for food have been frequently applied for an assessment of the hypothetical percentage realization of the recommended dietary intakes (RDA) for the essential elements in question and of provisional tolerable weekly intakes (PTWI) of toxic elements from the consumption of 100 g food product. For instance, Cd and Pb levels in muscle of perch are significantly lower than the PTWI and do not constitute any threat to man [30].

RDA and PTWI values of 15 elements were assessed for edible parts of 8 types of shellfish products. As for the former one, higher percentages of Ca (38. 8), Mg (17.2-22.5), Zn (88.2-121), Cu (88.2) and Se (155) were generally achieved for crabs. High values were also observed for lobsters, i.e. Ca (18.2), Mg (8.1-11.9), Zn (38.8-53.4), Cu (204) and Se (120). It should be emphasized that high RDA was also obtained for Mn (174-222) and Fe (52.6-118) in great scallop and mussels in shell, respectively. In view of the PTWI assessed for seafood products characterized by the highest levels of Hg, Cd and Pb, no health hazard is posed by exposure to these toxic heavy metals through seafood consumption [59].

Assessed RDA values for bee honey and syrup-feed honeys ranged from 0.35% (Na) to 5.84-23.4% (Cr) and from 0.20% (Na) to 3.85-15.4% (Cr), respectively. Consumption of bee products supplies human organism with the lowest and the highest percentages of RDA, i.e. from 1.21% (Na) to 68.5--103% (Mn) and 119-478% (Cr) [7].

It is reported that consumption of 100 g different kinds of grain products provides daily human organism with bioelements within a range of 0.33% (Na) to 321 (Cr) and 353--530% (Mn). It means that the highest average percentages of RDA were observed for Cr and Mn in bran and germs [8]. Assessment of PTWI for Pb and Cd in different cereal products (bread, cereals, rice, flour, pasta) allowed to conclude that consumption of 100 g of these products did not exceed allowed daily intake of both toxic heavy metals.

RDA values of 11 essential elements ranged from 1.65 to 2.07% (Cu) for fresh vegetables, 1.26-1.58% (Cu) to 40.8% (Na) for processed vegetables and 18.3% (Na) to 211-269% (Fe), 149-224% (Mn) and 72.7-291% (Cr) for dried vegetables. The latter three elements exceeded recommended dietary intakes resulting from daily consumption of 100 g different vegetables. As for RDA for legumes, minimum values achieved for Na (0.25%), whilst maximum values for P (94.7%). In case of oilseeds they oscillated between 2.29% (Na) and from 168% (P) to 173% (Mn) [8]. Referring to PTWI it is found that daily consumption of 100 g fresh, processed or dried vegetables poses no health hazard relative to Pb and Cd of food origin.

It is shown that RDA reached the highest values for K, Mg and Cu in 22 species of mushrooms. Based on PTWI it was concluded that the consumption of mushrooms collected from different forest regions of Poland poses no risk to human health [280].

Confectionary products (beet and cane sugar, molasses, maple syrup, cocoa, dark and milk chocolates) were also categorized according to hypothetical percentage realization of the recommended dietary intakes (RDA) for the essential elements in question. RDA values obtained for 11 elements in beet and cane sugar and its products such as molasses and maple syrup varied from 0.37% (Zn) to 8.19-32.8% (Cr) and from 2.28% (Ca) to 78.6-118% (Mn), respectively. Among all the analyzed confectionary products, cocoa was characterized by the highest RDA values, i.e. 41.6-51.9% (Na), 61.1% (K), 97.7-147% (Mn), 129% (P), 149-186% (Cu), 262-333% (Fe) and 215-862% (Cr). Dark and milk chocolates contained accordingly less essential elements than cacao. Relatively high RDA values were obtained for dark chocolate, i.e. 15.8-22.1% (Zn), 16.5% (P), 20.6% (K), 34.4-43.0% (Mg), 44.5-66.8% (Mn), 60.2-241% (Cr), 63.2-80.4% (Fe) and 67.1-83.9% (Cu). RDA values for milk chocolate were appropriately lower as compared with those obtained for dark chocolate [257]. Based on PTWI values for Pb and Cd, there is no threat to human health resulting from the consumption of honey [7] and confectionary products [257].

Concerning RDA estimated for essential elements, it is concluded that consumption of instant coffee supplies human organism with the highest average percentages of realization of this index for adult [236]. Based on assessed PTWI for Cd and Pb corresponding to their content in 2 cups of coffee, it is shown that daily consumption of coffee did not exceed the tolerance limit (0.21% for Pb and 0.22% for Cd) [236].

Bearing in mind that the RDA of Mn approximately amounted to 15 % and 28.3% for black tea and green tea, respectively, it seems that black and green teas could be a good source of Mn. However, its bioavailability to the human body needs to be considered [11-12]. It is reported that one cup of black tea or green tea provided very low levels of Pb and Cd suggesting that consumption of both tea varieties does not exceed the PTWI recommendation for these toxic heavy metals.

Conclusions

Instrumental methods, e.g. spectroscopy combined with multivariate analysis techniques, appear to be helpful in quantitative food authentication, identification of adulterants/mislabeling and determination of food safety. The proper use of analytical and chemometric tools for assessing nutritive and health quality of animal and plant foods plays an important role in quality control, their classification in view of geographical origin, confection and degree of environmental pollution. Both these techniques would be useful in differentiating unprocessed and technologically processed food as well as detecting fraud to preserve the brand name of the original product. Application of chemometric tools leads to a deeper understanding of the distribution of mineral components in foods, what is especially important feature in the bromatological and ecotoxicological aspect.

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Conflicts of interest

None.

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