Indonesian Journal of Chemometrics and Pharmaceutical Analysis

Review Article

A Chemometric Approach to Chromatography for Authentication Milk Product

Mitsalina Fildzah Arifah[1] and Abdul Rohman[2]*

[1]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Universitas Gadjah Mada, Yogyakarta, Indonesia

[2]Center of Excellence, Institute for Halal Industry and System, Universitas Gadjah Mada, Yogyakarta, Indonesia

*Corresponding author: Abdul Rohman | Email:abdulkimfar@gmail.com

Received: 22 August 2021; Revised: 3 October 2021; Accepted: 4 December 2021; Published: 19 December 2021 2021

Abstrak: Milk is the most common adulterated food product in the world. Currently, trend milk-based beverages provide easy distribution and add the desirable bioactive compound, such as fermented or heat treatment milk products. Milk authenticity is the critical parameter for assuring quality food to distinguish the various new products compare to raw milk. This review concerns the development of the chromatography-based method (gas chromatography or liquid chromatography) coupled with chemometrics for authentication milk products based on geographical origin, treatments for differentiated quality categorization, and adulteration milk. Several chemometric approaches can be chosen for classification and quantification analysis such as discriminant analysis, cluster analysis, principal component analysis, etc. The combination of chromatography and chemometrics as a powerful tool for authenticity milk is reviewed here.

Keywords: Milk, chromatography, chemometric, adulteration, authenticity

1. INTRODUCTION

Food authenticity is an important role for scientists, producers, retailers until regulatory authorities at all levels of the manufacturing process. Quality of milk needs to guarantee from raw milk to the final product [1]. Milk authenticity can be validated by several indicators, according to the unique element of geographic origin, metabolic profiles, sensory profiles, and microbial fingerprinting [2]. Geographical origin and metabolite profile are the main focuses for the authenticity of dairy products in Europe. Eisenstecken et al. reported that dairy products could be distinguished from six geographical areas in Europe and their fat profiles [3].

The several common adulterants of dairy products were the addition or substitution of the cheaper price milk, foreign fat, thickener, or preservatives [4]. The cheaper price of milk is added to the higher price's milk to raise economic profits. Addition thickener or water purpose to increase volume in milk fraud, which these excipients are starch, sodium chloride, and sucrose [5]. The addition of foreign fats is animal fat from cow tallow and pork lard and vegetable oils, such as palm, sunflower, coconut, groundnut, soybean, and peanut oil [1], [6]. The purpose of adding preservatives such as formaldehyde and hydrogen peroxide may be to increase the shelf life of dairy products against microbial growth [5].

Some analytical methods controlled the quality of milk such as chromatography, vibrational spectroscopy, electrophoresis, and immunoassay [7]. Nowadays combining vibrational spectroscopy

and chemometrics approach are used for the authentication of milk products [8]. The chromatography-based method is most chosen to determine different milk products from humans, cows, goats, horses, and mammals. The FTIR spectra for discrimination of dairy food are rapid, more practical, and less expensive than the fatty acid (FA) profiling of gas chromatography (GC) technique. In contrast, FA profiling of milk samples is more validated than FTIR spectra to discriminate the different farming systems [9]. The application of chromatographic method coupled chemometrics on fats, oils, milk, and dairy products could characterize and predict the triacylglycerol composition in a few categories, including species, varieties, geographical origin, treatments for differentiated quality categorization, or adulterant detection [10]. The LC/MS-based metabolomics identified 37 different metabolites in human, cow, goat, and horse milk [11]. The gas chromatography fingerprinting and chemometrics also verified dairy products based on their chemical composition, geographical origin, specified botanical sources, and adulterations from foreign fats [1], [6]. This article aims to provide the current issues related to the development of chromatography-based method combined chemometrics to authenticity milk products.

2. MATERIALS AND METHODS

Several databases were used to conduct a comprehensive search on related topics, such as Science Direct, Scopus, Research Gate, Journal of Dairy Science, and Google Scholar. This narrative review selected relevant and current papers between 2005-2021, while the keywords included milk, chemometrics, or multivariate analysis, chromatography, food authenticity or milk authenticity, and adulteration or fraud.

3. DISCUSSION

3.1. Trend Milk Beverages

Milk is a good source of vitamin D and calcium for human development. The chemical properties of milk are the complex colloidal aqueous suspension that contains caseins, lactose, fatty acid, whey proteins, minerals, and other compounds [12]. Whole fresh cow's milk was the main source of global milk production, approximately 715 million tons in 2019 of total milk production in the world according to FAO [13]. In several studies, researchers are interested in milk authenticity about 6% over the last four years (on Figure 1) and are still continuing with the rapidly growing global food industry due to the adulteration of dairy products [2].

Trend milk-based beverages are fermented milk, pasteurized, and ultra-high temperature (UHT) milk because of easy distribution from producer to consumer and incorporate the desirable bioactive compound of milk product [14]. UHT and pasteurized milk are raw milk that is heated high and quickly, therefore they are preferred over raw milk on the market with their long shelf life [15]. Yogurt and fermented dairy products are fermented by lactic acid bacteria, for example, *Lactobacillus bulgaricus* and *Streptococcus thermophilus*. Microbial growth and fermentation temperature impacted yogurt quality[16]. Koumiss is fermented from mare's milk, while this product is used to treat cardiovascular diseases, pneumonitis, tuberculosis, asthma and increase weight gain [14], [17].

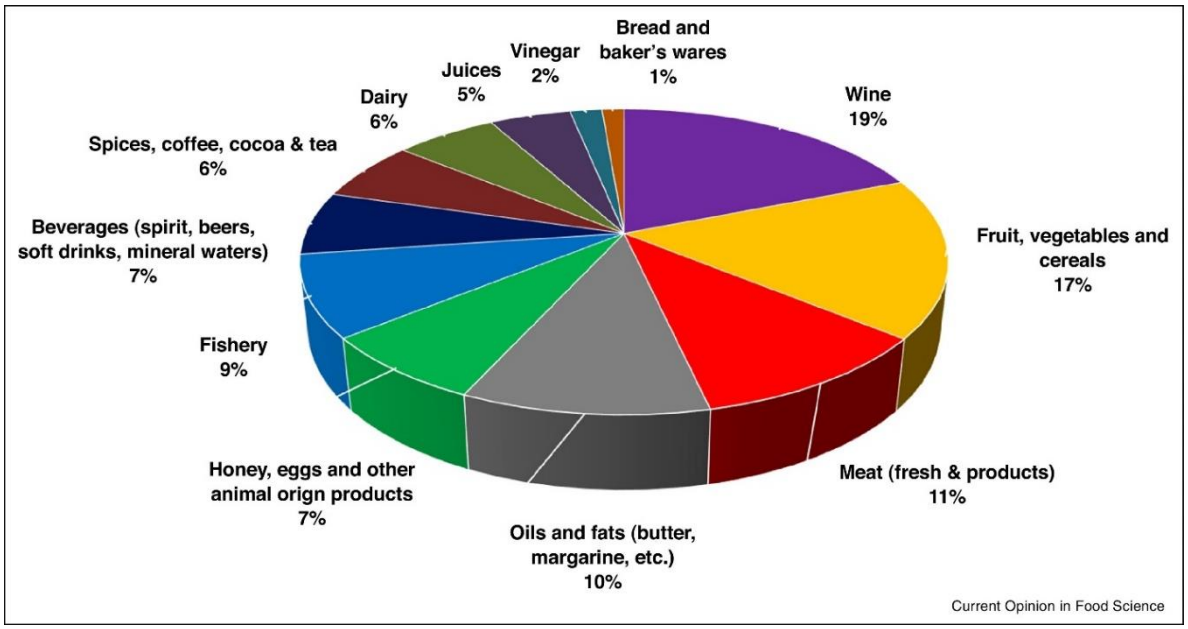

Figure 1. Food Authentication Publication [2]

3.2. Chemometrics

3.2.1 Linear discriminant analysis (LDA)

The linear discriminant analysis (LDA) is one of the supervised pattern recognition models to predict and classify which item belongs to their class. This method aims to use these objects to find a rule for allocating a new object from an unknown group to the correct group [18]. LDA combined fatty acid profiles and FTIR spectra estimated dairy products from the various farm system, which the data set were divided randomly into the data training set used for calibration and the remaining data for cross-validation [9].

3.2.2. Principal component analysis (PCA)

The principal component analysis (PCA) is to reduce the number of predictor variables using their first principal component (PCs) from original variables. The PCA technique identifies the most important variables in the data and explores the clustering of samples based on spectral differences. The idea behind PCA is to find principal components Z1, Z2, ..., Zn, which are linear combinations of the original variables describing each specimen, X1, X2, ..., Xn, i.e.

$$Z1 = a11X1 + a12X2 + a13X3 + \cdots a1nXn$$

$$Z2 = a21X1 + a22X2 + a23X3 + \cdots a2nXn$$

The coefficients such as a11, a12, ...a1n are selected as the new variables and aren't correlated with the original variables. The first principal component (PC1), Z1 accounts are most of the variation in the data set, and the second (PC2), Z2 accounts are the next largest variation. The number of useful PCs is much less than the number of original variables if a significant correlation occurs. The PCA was used to classify the metal content of milk to investigate the different geographic origins [19]. The

PCA also visualized fatty acid profiles from the dairy products using the R statistical environment (Figure 2).

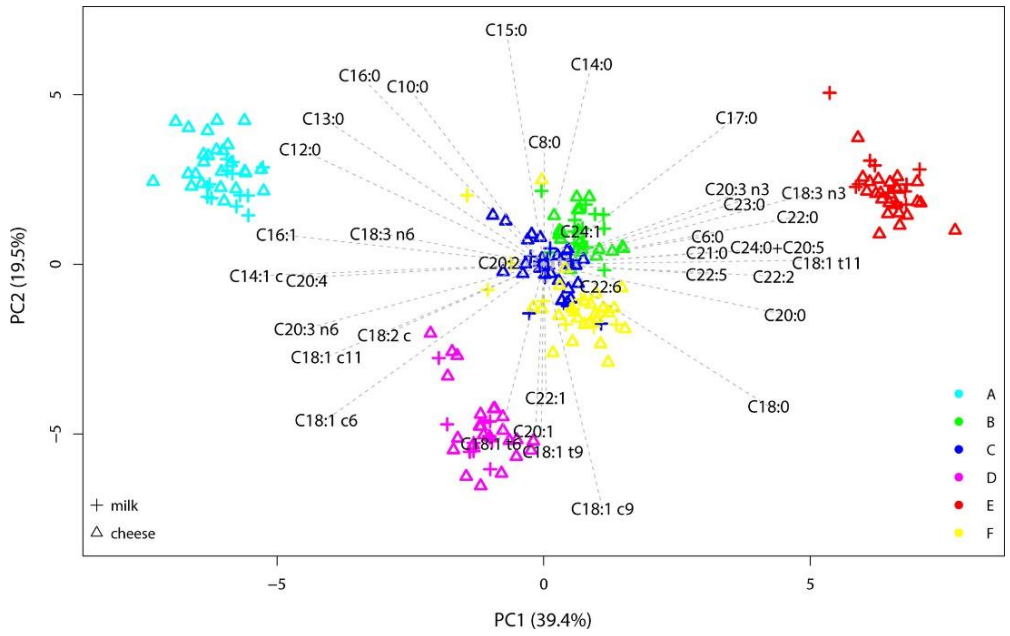

Figure 2. PCA Biplot of Fatty Acid Profiles on Milk (+) and Cheese (Δ) samples, (A= Slovakia, B= Italy, C= Germany, D= Netherlands, E= Austria, F= France) [3]

3.2.3. Partial Least Squares (PLS)

Partial least squares (PLS) is a regression method used to construct a relationship data matrix X to matrix Y into a linear model. The X matrix comprises fingerprinting spectroscopy or chromatographic data, where Y as independent prediction contains quantitative values. This model can predict the properties of the new sample from the original independent variable. Partial least square-discriminant analysis (PLS-DA) was one of the main discriminant techniques for classification and quantitative analysis [1]. PLS-DA was used to determine the fatty acid profiles in different countries using an untargeted GC-MS approach on Figure 3 [3].

3.2.4. Hierarchical Cluster Analysis (HCA)

The hierarchical cluster analysis (HCA) is described that once an object has been assigned to a group the process cannot be reversed [18]. The model is useful for calculating the same characters in metabolites based on Euclidean or Malahobis or Manhattan distance [8]. The different metabolite between milk and koumiss was γ-linolenic acid by the pattern of HCA. The γ-linolenic acid of koumiss was more decreased than mare's milk [17]. HCA also evaluated five clusters of milk and cheese products for the effect of ripening time and milk extraction technology based on the squared Euclidean distance and average linkage method on Figure 4 [20].

3.3. Application Chromatography-based Coupled Chemometric

3.3.1. Cow's Milk

a. Geographical Origin of Milk

The element of geographic origin is divided into macro-elements (like Na, Ca, K), trace-elements (Se, Zn, Fe, etc), rare elements (Ce, Sm, La, etc) dan ultra-trace elements (platinum or

gold). ICP-MS combined chemometrics authenticated cow's milk by geographical origin clustering. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) determined trace elemental composition using ICP-MS from the Malaysian dairy product in comparison to selected countries such as Australia, Europe, America, and Middle East Asia. The metal elements of milk products were discriminated from Mg, Na, Ca, K, Ba, Cu, Fe, Zn, Se, Mo, and Mn [21]. The chromatography-based and chemometric discriminated the fatty acid profiles of cow's milk and cheese from six geographic regions in Europe, including Austria, France, Germany, Italy, Netherlands, and Slovakia. Fatty acid classes were reported as biomarkers to track regional differences in dairy products, such as odd-chain and branched-chain FA, long-chain PUFA, and MUFA [3]. The other studies, Graviera cheese from the six different geographical origins in Greece characterized and identified using fatty acid and volatile profiling with chemometric[22].

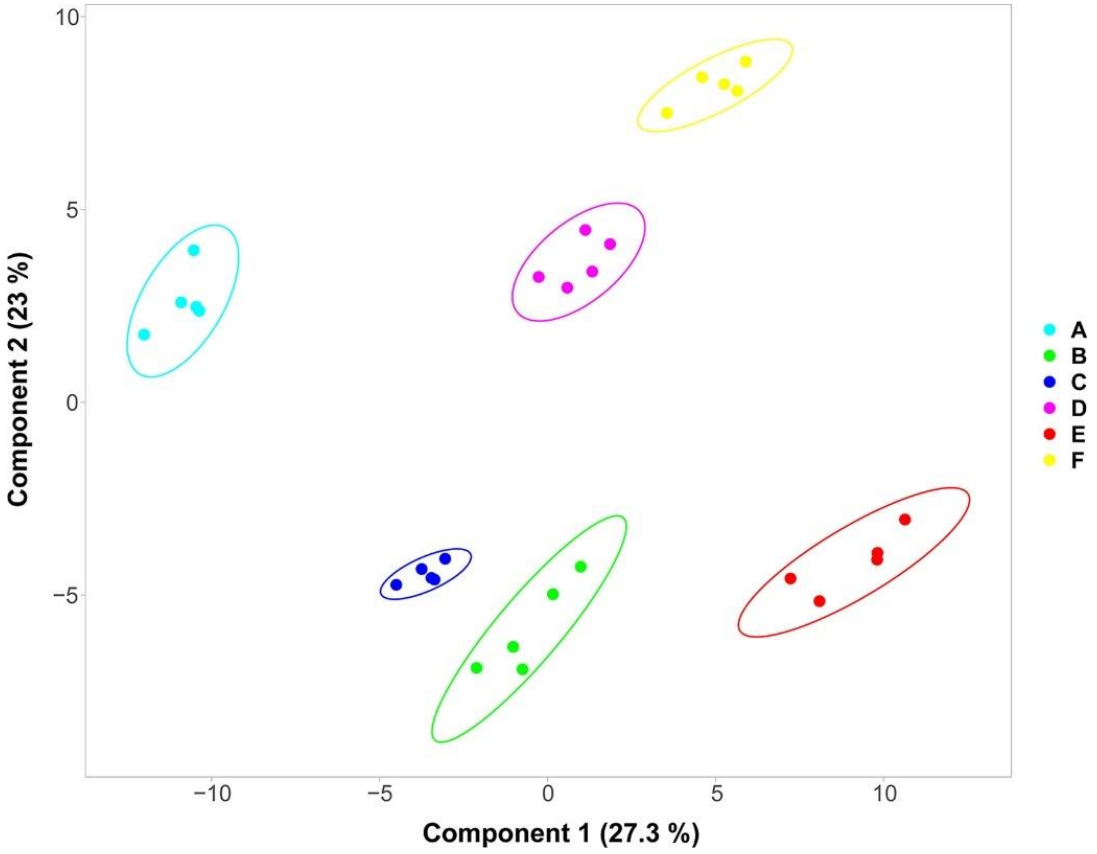

Figure 3. Scores plot of raw milk by GC-MS coupled PCA Model (A = Slovakia, B = Italy, C = Germany, D = Netherlands, E = Austria, F = France) [3]

b. Treatments for Differentiated Quality Categorization

The different treatment method on raw milk using heat process means to increase shelf life and reduce spoilage microorganisms in long term. The heat treatment is divided into specified temperatures and times, such as pasteurization and ultra-high temperature (UHT). Continuous heat treatment can remove approximately 5%-20% of water-soluble vitamins after heat treatment compared to raw milk [15]. The ultra-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UPLC-QTOF-MS) identified metabolite on raw,

pasteurized, and UHT milk. Different heat treatment of milk composition was distinguished into 8 potential metabolites with UPLC-QTOF-MS coupled chemometrics, such as a phospholipid and seven oxy-lipids (9-hydroxydecanoic acid, 12-hydroxydodecanoic acid, 2-hydroxymyristic acid, 3-hydroxytetradecanoic acid, 5-hydroxyeicosatetraenoic acid, 3-hydroxyhexadecanoic acid, and 10-hydroxyocta- decanoic acid) [23]. RP-HPLC with diode array detection (HPLC-DAD) combined chemometrics identified different fermented food based the short-chain organic acids. Short-chain organic acids were malic, oxalic, formic, lactic, acetic, citric, pyruvic, succinic, tartaric, propionic, and α-cetoglutaric [24].

The different farming systems were evaluated cow's milk to milk ripped cheese using GC and FTIR combined SAS logistic regression. The third combination method increased discrimination ability than individual FTIR spectra or individual fatty acid profiles for validation and calibration. Although fatty acid of milk samples was more validated than FTIR spectra (77,3%, 73,5%), FTIR spectra gave correct classification greater than fatty acid (97,4%, 81,1%) by GC method [9].

The ripening time of dairy products impacted physical, chemical, and enzymatic modifications their component involves casein, fat, and other soluble components. The extraction process can affect the compactness and size of fat globules and the occurrence of coalescence and aggregation in milk products. The headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS) coupled to chemometric classified dairy products milk and cheese according to similarity Euclidean distance values. Based on the dendrogram, ripening time and extraction ability were the main factors to create 5 clusters of irradiated dairy products on Figure 4 [20].

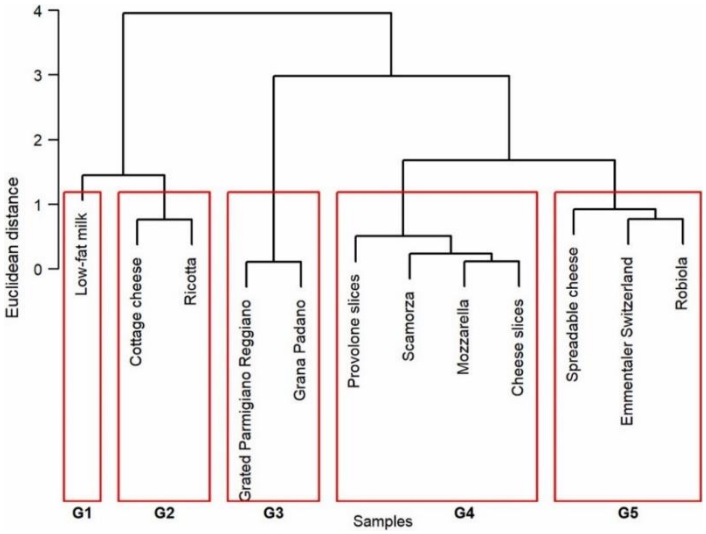

Figure 4. A dendrogram of 12 irradiated dairy products was grouped into G1-G5 using the HCA model at 0.5, 1.0, 3.0, and 5.0 kGy [20].

c. Adulteration Milk

Milk products are often counterfeited in the market to increase profit in proportion to the high demand and higher prices, which causes food quality problems. Various detection methods can detect adulteration milk with markers including fatty acids (FAs) by chromatography or elements by inductively coupled plasma (ICP). OPLS-DA model was constructed using 35 fatty acids (FAs) as the variables to differentiate organic milk (OM) from conventional milk (CM). Linolenic acid (ALA) was the critical parameter of fatty acid profiling to assess OM and CM [25]. Type milk protein determined different milk protein to soybean protein in the mixture binary using chromatographic profiles coupled to principal component analysis (PCA) and cluster analysis (CA). The result of PCA selected 14 PCs in 83% of the total variability. The cluster analysis characterized 11 peaks based on Euclidean distance similarity [26].

3.3.2. Horse's Milk

Horse milk is distinctive and luxurious milk than other milk. The female horse's milk is called mare's milk, which is lactated seasonally from early June until mid-October. The lactation period of mare's milk occurs at 6-9 months a year without human interference [12], [17]. Cow's milk produced 40 L in the morning and evening, compared with 3L a day for mare's milk [17] The horse's milk reported less fat and casein than cow's milk [12].

Several studies reported composition horse milk to other milk or dairy product using the chromatography method. The composition of whey and casein from mare's milk is similar to human milk[12]. The comparison of horse milk and human milk evaluated 17 different metabolites using LC-MS, such as 12 upregulated (cis-octadecanoic acid-9 oleic acid, oleic acid, linoleic acid, inositol, d-Glucose, arachidonic acid, lactic acid, 2-Oxobutanoate, d-Glucosamine, docosapentaenoic acid, 8,11,14-Eicosatrienoic acid, and docosahexaenoic acid) and five downregulated metabolites [11].

The chromatography method coupled chemometric evaluated metabolite of different dairy products. Differential analyses of horses' milk and koumiss were classified and identified their metabolites using UPLC-Q-TOF-MS/Ms coupled to PCA and PLS-DA model. The OPLS-DA model was more consistent than the PCA model, so this model was chosen to distinguish horse's milk from koumiss. The OPLS-DA model described the values of R2 (0, 0.862) and Q2 (0,-0.848) [7].

3.3.3. Goat's Milk

Goat's milk (*Capra hircus*) contains a small amount of α-casein which affects the poor coagulation ability of this milk. Goat's milk has 59 fatty acids with a high amount of short and medium-chain fatty acids (C4:0-C12:0). The fatty acids profiles of goat's milk may reduce the risk of hypertension, dyslipidemia, and glucose intolerance. The specific amino acids of goat's milk versus cow's milk contain threonine, lysine, isoleucine, cysteine, tyrosine, and valine [11][27]. The combined gas chromatography-mass spectrometry (GC-MS) and chemometric determined their polar metabolite profiles as milk typologies from goat's milk and cow's milk as adulterants. The OPLS model obtained R2 (Y) = 0.996 and Q2 = 0.879 and the root mean square error (RMSE) of 5% for the cross-validation value. Specific metabolites of goat's milk are valine and glycine, while cow's milk shared talose and malic acid, and pasteurized milk was known to be hydroxyglutaric acid [28].

3.3.4. Camel's Milk

Camel milk is a high-value protein source with commercial products such as raw camel milk (RCM), high-temperature processed liquid camel milk (PLCM), and camel milk powder (CMP). Camel milk contains high levels of butyric acid (12.2 ± 0.09 g/100 g) compared to other milk[11]. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) combined KEGG analysis identified and quantified proteins of camel's milk product due to heat treatment. PLCM and CMP changed protein profiles by 246 and 170 proteins of the total protein (807 proteins) [27]. The GC-MS explored the differences of fatty acid profiles on camel's milk and ghee with the chemometric model. The result also confirmed the relation between different fatty acids with similar physiological and molecular characteristics [30].

Table 1. Application chromatography-based coupled chemometric on Milk Product

Compound	Chromatography	Chemometric	Sample	Ref
Fatty acid	GC-FID, GC-MS	PCA, PLS-DA using R statistical environment	Cow's Milk and Cheese	[3]
Fatty acid	GC-FID	DA, logistic regression, SAS Logistic	Cow's Milk and Ripened Cheese	[9]
Metabolites (7 oxylipid and 1 phospolipid)	UPLC–QTOF MS	PCA	Raw, pasteurized, and UHT Milk	[23]
Fatty acid and volatile compounds	GC-FID, SPME GC-MS	DA	Graviera cheese	[22]
2-dodecylcyclobutanone (2-DCB) and 2-tetradecylcyclobutanone (2-TCB) as	HS-SPME-GC-MS	HCA	Milk and dairy samples	[20]
α-Linolenic acid (ALA)	GC-FID	OPLS-DA	Organic milk and conventional milk	[25]
Short-chain organic acids	HPLC-DAD	PARAFAC and U-PLS/RBL	Yogurt, fermented milk, and cheese	[24]
Free Peptide	RP-HPLC	PCA and Cluster Analysis	Cow's milk protein and soybean protein	[26]
Metabolites	UPLC- Q- TOF-MS	PCA, OPLS-DA, Hierarchical cluster analysis	Fermented mare milk & Koumiss	[17]
Metabolites	GC-MS	PCA, PLS, PLS-DA, OPLS-DA	Goat's milk and cow's milk	[28]
Protein	LC-MS/MS	KEGG analysis	Raw camel milk, high-temperature processed	[29]

			liquid camel milk, and camel milk powder	
Fatty acid	GC-MS	Correlation network	Ghee from camel milk	[30]

*Abbreviation: GC-FID: Gas chromatography-flame ionization detector; GC-MS: Gas chromatography-mass spectrometer; HS-SPME-GC-MS: The headspace-solid phase microextraction-gas chromatography-mass spectrometry; HPLC-DAD: High-performance liquid chromatography-diode array detection; UPLC- Q- TOF-MS: ultra-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry; LC-MS/MS: LC-Tandem mass spectroscopy.

4. CONCLUSION

This review discussed the combination of chromatography and chemometric for authentication of several milk products from cow's milk, goat's milk, horse's milk, and camel's milk. Milk authenticity could be investigated based on geographical origin, treatments for differentiated quality categorization, or adulteration milk. This interesting topic studied the authenticity of commercial milk beverages to improve the quality of these products from milk fraud that might occur.

5. Conflict of interest

The authors declare no conflict of interest.

6. Acknowledgements

The authors thanks to the Ministry of Education, Culture, Research, and Higher Education for financial support through the PDUPT 2021 scheme. The authors also acknowledge Universitas Gadjah Mada for the scheme of Post-Doctoral Research 2021.

References

1. M. Esteki, Z. Shahsavari, and J. Simal-Gandara, "Gas Chromatographic Fingerprinting Coupled to Chemometrics for Food Authentication," *Food Reviews International*, vol. 36, no. 4, pp. 384–427, 2020, doi: 10.1080/87559129.2019.1649691.
2. G. P. Danezis, A. S. Tsagkaris, V. Brusic, and C. A. Georgiou, "Food authentication: state of the art and prospects," *Current Opinion in Food Science*, vol. 10, pp. 22–31, 2016, doi: 10.1016/j.cofs.2016.07.003.
3. D. Eisenstecken, J. Stanstrup, P. Robatscher, C. W. Huck, and M. Oberhuber, "Fatty acid profiling of bovine milk and cheese from six European areas by GC-FID and GC-MS," *International Journal of Dairy Technology*, vol. 74, no. 1, pp. 215–224, Feb. 2021, doi: 10.1111/1471-0307.12749.
4. "(7) (PDF) Quantitative Detection of Cow Milk in Goat Milk by Chemometrics Analysis Based on Mid Infrared Spectroscopy." Available on: https://www.researchgate.net/publication/341384525_Quantitative_Detection_of_Cow_Milk_i

n_Goat_Milk_by_Chemometrics_Analysis_Based_on_Mid_Infrared_Spectroscopy (accessed Dec. 21, 2021).

5. C. de S. Gondim, R. G. Junqueira, S. V. C. de Souza, I. Ruisánchez, and M. P. Callao, "Detection of several common adulterants in raw milk by MID-infrared spectroscopy and one-class and multi-class multivariate strategies," *Food Chemistry*, vol. 230, pp. 68–75, Sep. 2017, doi: 10.1016/j.foodchem.2017.03.022.
6. D. Trbović, R. Petronijević, and V. Dordević, "Chromatography methods and chemometrics for determination of milk fat adulterants," *IOP Conference Series: Earth and Environmental Science*, vol. 85, no. 1, 2017, doi: 10.1088/1755-1315/85/1/012025.
7. A. Poonia, A. Jha, R. Sharma, H. B. Singh, A. K. Rai, and N. Sharma, "Detection of adulteration in milk: A review," *International Journal of Dairy Technology*, vol. 70, no. 1, pp. 23–42, 2017, doi: 10.1111/1471-0307.12274.
8. A. Windarsih, A. Rohman, Irnawati, and S. Riyanto, "The Combination of Vibrational Spectroscopy and Chemometrics for Analysis of Milk Products Adulteration," *International Journal of Food Science*, vol. 2021, 2021, doi: 10.1155/2021/8853358.
9. M. Bergamaschi, C. Cipolat-Gotet, A. Cecchinato, S. Schiavon, and G. Bittante, "Chemometric authentication of farming systems of origin of food (milk and ripened cheese) using infrared spectra, fatty acid profiles, flavor fingerprints, and sensory descriptions," *Food Chemistry*, vol. 305, Feb. 2020, doi: 10.1016/j.foodchem.2019.125480.
10. J. M. Bosque-Sendra, L. Cuadros-Rodríguez, C. Ruiz-Samblás, and A. P. de la Mata, "Combining chromatography and chemometrics for the characterization and authentication of fats and oils from triacylglycerol compositional data-A review," *Analytica Chimica Acta*, vol. 724, pp. 1–11, 2012, doi: 10.1016/j.aca.2012.02.041.
11. R. Wu, J. Chen, L. Zhang, X. Wang, Y. Yang, and X. Ren, "LC/MS-based metabolomics to evaluate the milk composition of human, horse, goat and cow from China," *European Food Research and Technology*, vol. 247, no. 3, pp. 663–675, Mar. 2021, doi: 10.1007/s00217-020-03654-1.
12. J. Sharifi Rad, M. Hoseini Alfatemi, and M. Sharifi Rad, " Horse Milk; the Composition, Equine Milk Proteins, Milk Allergy and Homology between Mammal Species with Horse," *British Biomedical Bulletin*, no. September, 2013.
13. "FAOSTAT." https://www.fao.org/faostat/en/#data/QCL (accessed Dec. 17, 2021).
14. P. Tallapragada and B. Rayavarapu, *Recent trends and developments in milk-based beverages*. Elsevier Inc., 2019. doi: 10.1016/B978-0-12-815504-2.00005-0.
15. S. Cole, A. Goetze, and L. Meunier-Goddik, "Pasteurized Milk," *Encyclopedia of Dairy Sciences*, pp. 444–450, Jan. 2022, doi: 10.1016/B978-0-12-818766-1.00142-2.
16. Y. Gao *et al.*, "Metabolomics approaches for the comprehensive evaluation of fermented foods: A review," *Foods*, vol. 10, no. 10, pp. 1–18, 2021, doi: 10.3390/foods10102294.

17. Y. Xia, J. Yu, W. Miao, and Q. Shuang, "A UPLC-Q-TOF-MS-based metabolomics approach for the evaluation of fermented mare's milk to koumiss," *Food Chemistry*, vol. 320, no. November 2019, p. 126619, 2020, doi: 10.1016/j.foodchem.2020.126619.
18. Miller, *Chemometrics for Analytical*. 2005.
19. S. M. Zain, S. Behkami, S. Bakirdere, and I. B. Koki, "Milk authentication and discrimination via metal content clustering - A case of comparing milk from Malaysia and selected countries of the world," *Food Control*, vol. 66, pp. 306–314, 2016, doi: 10.1016/j.foodcont.2016.02.015.
20. R. Zianni *et al.*, "An investigation using a validated method based on HS-SPME-GC-MS detection for the determination of 2-dodecylcyclobutanone and 2-tetradecylcyclobutanone in X-ray irradiated dairy products," *LWT*, vol. 153, Jan. 2022, doi: 10.1016/j.lwt.2021.112466.
21. S. M. Zain, S. Behkami, S. Bakirdere, and I. B. Koki, "Milk authentication and discrimination via metal content clustering e A case of comparing milk from Malaysia and selected countries of the world," 2016, doi: 10.1016/j.foodcont.2016.02.015.
22. K. Vatavali, I. Kosma, A. Louppis, I. Gatzias, A. v. Badeka, and M. G. Kontominas, "Characterisation and differentiation of geographical origin of Graviera cheeses produced in Greece based on physico-chemical, chromatographic and spectroscopic analyses, in combination with chemometrics," *International Dairy Journal*, vol. 110, p. 104799, Nov. 2020, doi: 10.1016/J.IDAIRYJ.2020.104799.
23. Y. D. Zhang *et al.*, "A metabolomics approach to characterize raw, pasteurized, and ultra-high temperature milk using ultra-performance liquid chromatography–quadrupole time-of-flight mass spectrometry and multivariate data analysis," *Journal of Dairy Science*, vol. 101, no. 11, pp. 9630–9636, 2018, doi: 10.3168/jds.2018-14441.
24. P. Mortera, F. A. Zuljan, C. Magni, S. A. Bortolato, and S. H. Alarcón, "Multivariate analysis of organic acids in fermented food from reversed-phase high-performance liquid chromatography data," *Talanta*, vol. 178, no. July 2017, pp. 15–23, 2018, doi: 10.1016/j.talanta.2017.09.005.
25. S. Xu *et al.*, "Multivariate analysis for organic milk authentication," *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, vol. 1186, no. May, 2021, doi: 10.1016/j.jchromb.2021.123029.
26. J. Dziuba, D. Nałęcz, P. Minkiewicz, and B. Dziuba, "Identification and determination of milk and soybean protein preparations using enzymatic hydrolysis followed by chromatography and chemometrical data analysis," *Analytica Chimica Acta*, vol. 521, no. 1, pp. 17–24, Sep. 2004, doi: 10.1016/J.ACA.2004.05.071.
27. C. S. Ranadheera *et al.*, "Probiotics in Goat Milk Products: Delivery Capacity and Ability to Improve Sensory Attributes," *Comprehensive Reviews in Food Science and Food Safety*, vol. 18, no. 4, pp. 867–882, Jul. 2019, doi: 10.1111/1541-4337.12447.

28. P. Scano, A. Murgia, F. M. Pirisi, and P. Caboni, "A gas chromatography-mass spectrometry-based metabolomic approach for the characterization of goat milk compared with cow milk," *Journal of Dairy Science*, vol. 97, no. 10, pp. 6057–6066, 2014, doi: 10.3168/jds.2014-8247.
29. R. R. Li *et al.*, "Protein profile of whole camel milk resulting from commercial thermal treatment," *Lwt*, vol. 134, no. May, p. 110256, 2020, doi: 10.1016/j.lwt.2020.110256.
30. G. K. Deshwal, R. Singh, A. K. Singh, D. Kumar, and H. Sharma, "Comparative characterisation of ghee from Indian camel breeds using GC-MS and FTIR techniques," *International Journal of Dairy Technology*, 2021, doi: 10.1111/1471-0307.12826.