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REVIEW

Authentication of Vinegars with Targeted and Non-targeted Methods

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ABSTRACT
There has been a growing interest in vinegar, especially after the increasing reports about its beneficial health effects. Bioactive compounds of vinegar are associated with its antimicrobial, antioxidant, antidiabetic, antitumor, and anti-obesity types of activities. Quality of vinegar is related with the authenticity of the product besides the amounts of bioactive compounds in its composition. Addition of cheaper substitutes to higher quality vinegars and false labeling are some common authentication problems for this product. There are various examples of the use of targeted and untargeted methods in authentication studies for vinegars. Specific constituents and properties of vinegars such as molecular isotope ratios and individual volatile compounds were used to detect adulteration with targeted methods. On the other hand, untargeted methods, mostly in the form of the application of spectroscopic techniques, such as infrared and fluorescence spectroscopy in combination with chemometrics, provide an overall measurement. This review mainly focuses on adulteration types and elaborates on different targeted and non-targeted methods used to authenticate vinegars.

KEYWORDS
Vinegar; authentication; adulteration; spectroscopic methods; chemometrics

Introduction

Vinegar is defined as "a liquid fit for human consumption, produced from a suitable raw material of agricultural origin, containing starch, sugars or starch and sugars such as fruit, berries, cereal grains, malted barley, whey, honey; by the process of double fermentation, alcoholic and acetous, and contains a specified amount of acetic acid" by Joint FAO/WHO Food Standards Programme.[1] There are some variations in regulations regarding vinegar depending on the legal entity. Codex[1] specifies that vinegar shall not contain more than 0.5% alcohol and less than 50 g/L acetic acid. According to Food and Drug Administration (FDA), the final vinegar at the end of processing should contain "4 g acetic acid per 100 mL". European Union (EU) recognizes that "acetic acid when diluted with water (4–30% by volume) could be used as a food or food ingredient in the same manner as vinegars from agricultural origin (Commission Regulation 2016/23)". However, "in some Member States only vinegars obtained from the fermentation of agricultural products are allowed to be named vinegars", according to the same regulation.

Vinegar is consumed as a seasoning, preservation agent, and one of the main ingredients in salad dressings, ketchup and other sauces.[12] Vinegars can be classified into five groups: cereal, wine and grape, traditional balsamic (TBV), Jerez, and cider vinegars.[3] However, this classification does not include types of vinegars such as spirit vinegars produced by acetic oxidation of ethanol derived from the distillation of fermented mashes or petrochemical ethanol. Codex also provides definitions for the following vinegar groups: 1. wine, fruit vinegar, berry vinegar, cider vinegar, 2. Spirit vinegar, 3. Grain vinegar, 4. Malt vinegar, 5. Distilled malt vinegar, 6. Whey vinegar, 7. Honey vinegar. Vinegar may

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contain some optional ingredients such as plants, particularly herbs, spices and fruits, whey, concentrated or fresh fruit juices, sugars, honey and food-grade salts, according to Codex again.

History of vinegar has been evolved from its production as a by-product of wine processing to the production of a wide spectrum of vinegars, including cheap to quite expensive products. With increasing number of researches on its beneficial effects on health, this product is getting even more consumer attention. However, this increased attention makes product, especially certain economically valuable traditional ones, more prone to counterfeiting. There are various reports about mixing different types of vinegars with different adulterants to obtain extra profit. Since vinegar could be a very complex liquid depending on its type, it can be quite challenging to determine its adulteration. There are examples of the use of both targeted and non-targeted approaches in authentication studies that could be found in the literature. Targeted methods identify specific constituents of vinegars such as certain phenolic compounds or volatiles, while non-targeted methods are based on overall measurement of the sample as in spectroscopic analyses. It is aimed to provide a literature review about the use of targeted and non-targeted techniques for vinegar authentication. However, it is important to understand the characteristics of the product itself to better evaluate these frauds. Therefore, a brief information about the types, production, composition and functional properties of the vinegar will be provided first.

Vinegar types

Diversity of the vinegars is due to not only by raw materials but also processes used in the production. Various raw materials including grape, apple, cereals, and other starch and sugar-containing foods, such as pomegranate, lemon, artichoke, tomato, onion, bamboo, ginseng, are used in the production of vinegar. Production and aging steps could also specify the characteristics of vinegar. As an example, balsamic and sherry vinegars are differentiated from the others by their production through traditional processes. In this part, some significant vinegar types will be described.

Wine vinegar

Wine vinegar is made from red or white wine and is the most commonly used vinegar in the households of the Mediterranean countries and Central Europe. Wine vinegars are mostly produced using the semi-continuous submerged process.[2] The acetic acid content of wine vinegar is set as at least 6% (w/v), and the maximum allowed ethanol concentration is specified as 1.5% (v/v) by European Union Regulation (EC) 1493/1999. Phenolic acids and aldehydes are indicated as useful quality parameters of wine vinegars besides their major components.[4]

Balsamic vinegar

Production of balsamic vinegar was first originated from Italy and there are two types of balsamic vinegar: "balsamic vinegar of Modena" (BVM) and "traditional balsamic vinegar of Modena" (TBVM). The first one is a flavored wine vinegar obtained by blending cooked must and wine vinegar and, in some cases, by adding a small amount of caramel. TBVM is produced in Modena and Reggio Emilia with cooked grape must, through a three-step process: conversion of sugars to ethanol by yeasts; oxidation of ethanol to acetic acid by acetic acid bacteria; and, finally, at least 12 years of aging. The final product is a highly dense, dark-brown aged vinegar, having a sweet and sour taste, fruity and complex in flavor.[3] Grapes, from the northern region of Italy near Modena, which are used in vinegar production are left on the vine for as long as possible to increase the sugar level, as ripened grapes contain higher sugar levels. TBV may age up to 25 years.[5] The commercial version of balsamic vinegar is designated as Aceto Balsamico di Modena (BVM) and must be aged for a minimum of two months and up to three years to meet the minimum requirements to claim protected geographical indication.[6]

Sherry vinegar

Sherry vinegar, considered as a traditional food product, has been commonly used as a seasoning and a condiment.[7] As for balsamic type, this vinegar is also a high-quality product with fame all over the world.[8] It can be produced by both traditional methods and submerged culture acetification followed by aging in wood (dynamic or static system). Special type of traditional methods, the "solera" system and the static method, are used in its production. According to aging time in barrels, Sherry vinegar is defined as "Vinagre de Jerez", "Reserva", and "Gran Reserva".[9] These vinegars from Spain have also Protected Designated of Origin (PDO) status, which shows that the product quality is attributed to the region of production.

Cider vinegar

Processed apple products, apple juice, or fermented apple cider can be used as raw materials in the production of cider vinegar through a double fermentation: alcoholic and acetic.[3] Most natural raw materials do not require the addition of extra nutrients, but apple cider is usually low in nitrogenous materials; for this reason, addition of extra nitrogen in the form of ammonium phosphate and thiamin is a common practice.[10]

Cereal vinegar

Malt and rice vinegars are the most widely produced cereal vinegars. Malt vinegar is an aged and filtered product made by alcoholic and subsequent acetous fermentation, without distillation, of an infusion of barley malt with or without the addition of other cereals.[10] Malt has a distinctive flavor that contributes to the flavor of the deriving vinegar. Malt vinegar is popular for pickling, especially walnut pickles. It is the most famous one as a condiment for fish and chips.[11] Rice vinegar is a traditional seasoning that has long been used in China, Japan, and Korea.[12] Rice vinegar is produced from fermented polished and unpolished rice and there are amber, red and black colored rice vinegars having different acidity values and usages.[3]

Production

Production of vinegar is a two-stage fermentation process: conversion of fermentable sugars to ethanol by yeasts, usually *Saccharomyces* species, at acidic pH and the oxidation of ethanol by bacteria, usually *Acetobacter* species.[13] Acetic acid fermentation occurs in two steps, first ethanol is oxidized to acetaldehyde, then further oxidation yields acetic acid. These reactions are catalyzed by cytoplasmic enzymes, alcohol dehydrogenase, and aldehyde dehydrogenase. During alcohol fermentation, anaerobic conditions prevail and after the consumption of sugars by yeasts aerobic conditions develop at the surface with further progress of the process. Factors including starter culture, ethanol concentration at the start of fermentation, fermentation temperature, oxygen flow rate, method of maturation, storage conditions, bottling, and pasteurization influence the quality of the product.[13] After acetification of mash, vinegar can be maturated or aged. Currently, oak is the most commonly used wood in enology for aging wines, spirits, and vinegars.[14]

The traditional process is one of the main methods of vinegar production and it is based on surface culture fermentation, where the acetic acid bacteria is placed on the air–liquid interface in direct contact with atmospheric air. The presence of the bacteria is limited to the surface of the acidifying liquid and hence, it is also considered as a static method.[2] This method includes gradual filling of the barrel with slime or "mother of vinegar" and the rate of reaction is slow with low efficiency.[15] Traditional vinegar production taking place in wood barrels is known as Orleans process and is especially used in the production of high-quality table vinegars.

Submerged culture system is the other common method of vinegar production. In this type of system, must is spread through a large area with a slow flow rate and acetic acid fermentation takes place with the inoculation of acetic acid bacteria. *Acetobacter xylinum, Acetobacter pasteurianus, Acetobacter aceti, Acetobacter hansenii, Acetobacter lovaniensis, Acetobacter liquefaciens* are commonly used cultures for this purpose. Fermentation occurs with the activity of bacteria which are homogeneously spread in the must. In this type of production, fermentation takes place on the whole media by the airing of reactor. High production capacity is obtained with fast conversion to acetic acid. Because of the faster processing and the higher productivity, commercial vinegar production is mostly done with this method.[13] The Frings Acetator is the most widely used equipment for the production of all kinds of vinegar.[10] The rotor is installed on the shaft of a motor mounted under the fermenter, connected to an air suction pipe, and surrounded by a stator. It sucks air and pumps liquid, creating an air-liquid emulsion which is ejected through the stator, radially outward at a given speed, chosen so that the turbulence of the stream causes a uniform distribution of the air over the whole cross-section of the fermenter in commercial scale.[15]

The vinegar production process is generally carried out in a semi-continuous manner, and the final product reaches 12–15% acetic acid concentration at the end of this process. The process continues in cycles that start with the addition of fresh mash to the fermenter and 1/3 of this fermenter is filled with the previous fermentation product to obtain 7–10% acetic acid and ca. 5% ethanol concentration. When an alcohol concentration is in the range of 0.05–0.3% in the fermenting liquid, a quantity of vinegar is discharged from the fermenter and it is refilled with fresh mash.

In the literature, there are limited number of studies that compare the properties of traditional and commercial vinegars. In several comparison studies, physicochemical properties, phenol profiles, antioxidant and antimicrobial properties, volatile components, and sensory properties of vinegars produced with different techniques were assessed. As a result, differences in almost all tested characteristics were observed between commercial and traditional techniques.[11,16–18]

Composition

Composition of vinegar is directly related with its raw materials' composition, as a result, it depends on factors, such as variety and growing conditions of raw material and also production techniques of the product. Major raw materials used in the production of vinegar are grape, apple, and wine. Total acidity of vinegars produced from different raw materials varies between 3.9% and 12.2% (as acetic acid equivalent) and the rest of the medium is organic acids, alcohols, polyphenols, amino acids, etc.[13] Acetic acid is the most dominant component of vinegar; however, citric, formic, lactic, malic and succinic acids are also present.[19,20] Concentrations of organic acids and reducing sugars are quite high in TBV. Although tartaric acid is one of the main components of grape, it is not present in high concentrations in TBV.[20] The total amount of glucose and fructose ranges between 43 and 63 g/100 g, while the sum of organic acids and sugars is more than 50% of the composition. Acetic acid, other organic acids, esters, ketones, and aldehydes are the sources of the distinctive aroma of vinegar and these aromatic compounds form especially during acetic acid fermentation.[21] In a study conducted with different classes of Sherry vinegars, 58 aroma, and 80 odor compounds were identified using gas chromatography/mass spectrometry (GC-MS) and gas chromatography/olfactometry (GC-O), respectively.[7] While the presence of some of the aroma compounds, such as ethyl heptanoate, ethyl furoate, ethyl benzoate, and sotolon were known; ethyl 2-methylbutyrate, ethyl heptanoate, ethyl furoate, ethyl benzoate, acetophenone, and nonanoic acid were recorded in the samples for the first time. Besides, research team was able to discriminate Sherry vinegars from other types of vinegars according to their aroma compounds using multivariate statistical analysis techniques.[7]

Vinegar is a good source of various phenolic compounds, such as gallic acid, catechin, vanillic acid, syringic acid, and caffeic acid. The total phenolic contents of different vinegars were determined in several studies. According to Bakir et al.,[22] balsamic vinegar had the highest total flavonoid (960 mg catechin equivalent (CE)/L) and total phenolic contents (2550 mg gallic acid equivalent (GAE)/L).

This study was supported by another research conducted in which the amount of total phenolic contents of commercial apple, rice, balsamic, red wine, rose, white wine, grape and pomegranate vinegars were investigated, and the highest total phenolic content was measured in balsamic vinegar with 2141.64 ± 25.07 mg GAE/L while rice vinegar contained the lowest with 14.36 ± 0.16 mg GAE/L.[23] Several chemical and functional properties of BVM and TBVM were determined.[24] The mean of total phenolics, total flavonoids, and total tannins for TBVM, extra old TBVM, and BVM were determined as 7515 ± 3768, 1771 ± 963, and 1291 ± 724 mg CE/L, respectively. The results of this study also showed that extra old TBVM had the highest phenolic content. This was associated with evaporation of water and diffusion of phenolics from barrel to vinegar. Phenolic contents and antioxidant capacities of eight commercial vinegars and 10 homemade vinegars were also examined in another study[25] and it was concluded that polyphenol content of the examined vinegar samples showed significant variations due to their raw materials and the production techniques. Total phenolic and total flavonoid contents of homemade red wine and red balsamic vinegars were considerably higher than other samples. Anthocyanin content of red wine vinegar was investigated in another study[4] and 20 anthocyanin compounds such as catechyl, pyranocyanidin-3-glucoside, acetyl vitisin B, and coumaroyl vitisin B were determined in this type of vinegar. Twenty traditional home-made and five industrial vinegars, produced from grape, grape wine, apple, artichoke, pomegranate, lemon, and sour cherry, were inspected by Ozturk et al.[16] Vinegars had extremely variable total phenolic content values, ranging between 42.04 and 2228.79 mg GAE/L. The total phenolic content of traditional home-made vinegars was higher than commercial vinegars. The highest total phenolic content was obtained in grape vinegars among traditional vinegar samples and in sour cherry vinegar among industrial vinegars.

Several studies monitored the changes in compositional parameters, particularly bioactive compounds, during vinegar production. Effect of acetification process on phenolic profile and total phenolic content of cider, red and white vinegar production was studied and up to 50% decrease in phenolic content was observed.[26] The effects of production techniques on the composition of the vinegar were also investigated. It was shown that vinegars produced from the same raw material (Ulugbey Karasi grapes) using different techniques (traditional surface and industrial submerge methods) had different phenolic contents.[17] Vinegar, produced by the traditional surface method, contained 2690 mg GAE/L, while industrial vinegar had 2461 mg GAE/L total phenolic content. Two vinegars also differed by the amounts of catechin and chlorogenic acid.

Aging is a part of vinegar production and this section of production also has an effect on the chemical composition of vinegar. Through NMR spectroscopic investigation, it was found out that vinegars, aged in acacia (*Robinia pseudoacacia*) wood barrels, contained (+)-dihydrorobinetin.[8] Amount of (+)-dihydrorobinetin in vinegar was proportionally increased with aging duration; however, limited migration was observed in toasted barrels.[8]

Functional properties

Vinegar has not only antioxidant and antibacterial properties but also has a role in the acceleration of glycogen repletion and calcium absorption in the human body. Studies have shown that vinegar consumption provides protection from hypertension and decreases the serum cholesterol levels. A brief summary of these functional properties of vinegars is provided in this section.

It was shown that chronically alcoholic rats having vinegar supplemented diet had reduced serum triglycerides, total cholesterol, and liver total cholesterol concentration.[27] In another study, the effect of dietary vinegar consumption on calcium absorption was investigated.[28] Experimental results of the study on ovariectomized rats fed on a low-calcium diet suggested that dietary vinegar improved intestinal calcium absorption by increasing calcium solubility and by the trophic effect of the acetic acid. The effect of the vinegar uptake on aiding the recovery from fatigue in rats was also investigated.[29] Studies showed that rats with a diet containing acetic acid had enhanced glycogen repletion in muscles and liver. Tests done on spontaneously hypertensive rats indicated that acetic acid lowered blood pressure and renin activity; however, any change in concentration of angiotensin I-converting enzyme activity was not observed. Kondo et al.[30] concluded that anti-hypertensive benefits of vinegar are due to acetic acid content and its mechanism caused lowering of renin activity in blood plasma.

Antioxidant properties of vinegar are shown in several studies. One of the famous traditional Chinese vinegar, Shanxi vinegar, was investigated for its antioxidant effect on hydrogen peroxide-induced oxidative stress, superoxide dismutase, catalase and glutathione levels. Vinegar treatment in cells treated with H_2O_2 reduced reactive oxygen species significantly.[31] Similarly, antioxidant effects of soy vinegar on Swiss albino male mice was also studied.[32] These mice were treated with allopurinol (10 mg/kg) and soy vinegar (100, 200, and 400 mg/kg) once a day for seven days. The control group and experimental group which were fed with 400 mg/kg vinegar daily had the same xanthine oxidase activity. Moreover, this study showed that vinegar might be an alternative treatment to allopurinol for potassium oxonate-induced hyperuricemic mice.

The effect of apple vinegar uptake in 70 patients with type 2 diabetes and dyslipidemia was observed by Gheflati et al.[33] Any significant differences in the blood pressure and homocysteine concentration were not noted. However, daily consumption of apple vinegar showed a reducing effect on glycemic indices and an increasing effect in the total antioxidant capacity. Clinical nutrition studies conducted on three men and seven women, aged between 22 and 51, with normal body mass showed that vinegar supplemented diet significantly lowered the postprandial glucose and insulin levels.[34] In another study, Ostman et al.[35] inspected the effect of vinegar supplementation to lower the glycemic index of a starchy meal, and the dose-response relationship of postprandial glucose and insulin levels on 12 healthy participants. As a result, vinegar containing diet reduced postprandial responses of blood glucose and insulin.

Additionally, 24 obese mice were monitored during 10 weeks to observe the effect of vinegar consumption on body weight.[36] In this period, mice were divided into three groups. The control group was fed with a high-fat diet while two other experimental groups' diets were supplemented with 0.08 mL and 2 mL coconut vinegar per kg body weight. At the end of 10 weeks, approximately 8.7–17.9% reductions in body weights were detected.

There are also studies that indicate the immune system support of vinegar. Active group, control group, and placebo group, consisting of people aged between 30 and 60 years, were observed during 8 weeks and change in the rate of release of secretory immunoglobulin A was recorded in the study.[37] Uptake of active food (vinegar with mashed garlic) was closely correlated with an increase in the release of secretory immunoglobulin A in saliva. Responses of the immune system to persimmon vinegar uptake were investigated in the intestinal system of mice at different doses for 20 days.[38] Concentration of Immunoglobulin A in intestinal fluids and feces was recorded four times higher than in the control group. In both studies, consumption of vinegar did not show any adverse or cytotoxic effect.

Antimicrobial effect of vinegar was also demonstrated and it was shown that 18 vinegar types (apple, grape, pomegranate, balsamic, blueberry, rosehip, gilaburu, lemon, blackberry, artichoke, mulberry, rice, apricot, date, and hawthorn vinegars) were effective on the inhibition of *Salmonella typhimurium, Staphylococcus aureus*, and *Escherichia coli*.[16] In another study, inhibitory effects of acetic and lactic acids on of *Salmonella enteritidis* and *E. coli* were examined and the results showed that the undissociated organic acids have antimicrobial activity.[39] Besides, synergism was observed between acetic and lactic acids. Food poisoning is one of the main reasons for outbreaks; therefore, bacteriostatic and bactericidal effects of vinegar on 17 strains of food-borne pathogenic bacteria including *E. coli* (EHEC, EPEC), *S. enteritidis, Vibrio parahamolyticus, Aeromonas hydrophila, S. aureus, Bacillus cereus* were studied.[40] The growth inhibition of all strains was observed at 0.1% (w/w) acetic acid concentration. Moreover, sodium chloride and treatment temperature had synergistic effect with acetic acid concentration on bacterial growth. Besides to its un-dissolved organic acid content, phenolic and volatile compounds of vinegars also provide antimicrobial activity. A study in the literature indicated that grape vinegar samples had higher antimicrobial activity against *S. aureus,* *E. coli*, and *Pseudomonas aeruginosa* than apple vinegar samples and this was associated with the higher antioxidant capacity of grape vinegar compared with apple vinegar.[41] Due to its antimicrobial effect, vinegar can be used as a cleaning and disinfection agent in home environmental surfaces. Cleaning and disinfection effects of various agents including vinegar, bleach, club soda, and tea tree oil on common home surfaces, and against two common bacteria, *S. aureus* and *E. coli*, were compared in an investigation.[42] The mixture of vinegar, club soda, and tea tree oil was found to be an adequate alternative to bleach for cleaning, in the cases of which complete elimination of microorganisms was not required. Vinegars produced from physalis (*Physalis Pubescens L.*) and red pitahaya (*Hylocereus Monacanthus*) were also reported to have antimicrobial effects due to both acetic acid and phenolic contents. *E. coli, Listeria monocytogenes, S. aureus*, and *S. enteritidis* were subjected to vinegar produced from these raw materials. The minimum inhibitory concentrations and minimal bactericidal concentration of vinegars were determined as 0.5% and 1%, respectively.[43]

Authentication

Different types of adulteration practices exist for vinegar, and the main type of economic adulteration is the use of an ingredient of lower value or cost than the authentic product. Adding edible alcohol made from molasses or glacial acetic acid to vinegar and declaring the product as traditional vinegar is a common practice.[44] Although grape must caramel (E-150d) is legal to add even into more expensive special type of vinegars it could be also used in vinegars with the purpose of imitating a longer storage time or covering undesirable attributes.[45]

Differences in the production processes between and within Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI) categories are reflected in their commercial price.[46] The products such as foodstuffs, agricultural products, and wines registered as PDO are produced, processed and prepared in a specific region. PGI label shows, on the other hand, at least one of the stages of production, processing or preparation takes place in a specific geographic region where quality, reputation or characteristic is linked to.[47] Labeling non-PDO or non-PGI products as PDO or PGI is a type of fraud. In addition, false labeling of the age of vinegar, in which the quality is associated with, is another problem. Labeling vinegar obtained from dried grapes with the addition of water as wine vinegar is reported as another type of authentication case.[48]

Vinegar with many different varieties is a complex liquid; therefore, detection of adulteration has become even more of a daunting task with the increasing number of adulterants that are mixed with the pure product. Adulteration detection methods can be grouped as targeted and non-targeted techniques. Targeted adulteration testing is based on the detection of specific compounds that can be used to trace abnormality. As an example, the presence or absence of certain pigment or phenolic compounds could be an indication of adulteration. However, most of the targeted compounds have low concentrations in food products and this could be regarded as a weakness for targeted analysis because adulteration techniques are becoming more sophisticated and can be undetectable by small changes. Amounts of targeted compounds in food products could be directly measured with any suitable analytical method such as chromatographic techniques.

Non-targeted analysis, on the other hand, has a holistic approach and aims to obtain an overall measurement of the analyzed food product. There is a variety of non-targeted techniques currently available: especially spectroscopic methods, such as Fourier transform infrared (FTIR), near-infrared (NIR), hyperspectral imaging, Raman and nuclear magnetic resonance (NMR), are the important non-targeted analysis tools, although some of these techniques could also be used in targeted measurements. In spectroscopic measurements, differences between spectra could be too complicated to detect visually. Chemometrics is a useful multivariate statistical analysis tool to extract the information from the data to differentiate classes and to eliminate unnecessary elements of the data. Chemometrics can be used to identify food samples based on geographical origin, species variety as well as highlighting the contamination and adulteration of a sample and it is very commonly used in combination with spectroscopic techniques to evaluate the data.

Table 1. Studies performed with various non-targeted approaches for authentication of vinegars.

Aim	Type of Vinegar	Method	Result	Reference
Classification of products according to aging process	Traditional balsamic vinegar of Modena	Head-space mass spectrometry (HS-MS)	Reasonable classification with respect to ageing was accomplished	[49]
Prediction of the ageing	Balsamic and traditional balsamic vinegar of Modena	1H Nuclear magnetic resonance spectroscopy (1H NMR)	1H NMR spectra combined with PLS-DA and Naive Bayes approaches showed their strong classification and prediction capability	[50]
Classification of production methods and prediction of vinegar properties such as total acidity	Vinagres de Montilla-Moriles; produced by submerged culture and Orleans methods	Near infrared reflectance spectroscopy	Submerged culture and Orleans methods were differentiated and vinegar properties were predicted with high accuracy	[51]
Developing and comparing robust classification models for the identification of adulterated aged vinegars	Authentic Shanxi aged vinegars and synthetic vinegars samples adulterated with glacial acetic ranging from 10 to 100%	Excitation-emission matrix (EEM) fluorescence spectroscopy	Adulterated samples were recognized with a rate of 100% in both training and prediction sets	[52]
Classification of vinegars with respect to their types	White and red, balsamic, sherry and cider vinegars	Headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography (GC)	Use of HS-SPME/GC in combination with chemometrics provided a simple, fast and reliable discrimination between different vinegar types on the basis of their total volatile profiles	[53]
Discrimination of origins of vinegars	Vinagre de Jerez, Vinagre de Montilla-Moriles, and Vinagre de Condado de Huelva, Industrial Balsamic Vinegar	UV–visible and fluorescence spectroscopy	Well discrimination of vinegar origins was obtained	[54]
Characterization and classification of PDO wine vinegars	Vinagre de Jerez and Vinagre Condado de Huelva	Fourier transform mid infrared spectroscopy (FTIR) with attenuated total reflectance	FTIR analysis was useful for a simple characterization of the established aging categories of high quality wine vinegars protected under PDO	[55]
Characterization and classification of PDO wine vinegars	Vinagre de Jerez, Vinagre de Condado de Huelva and Vinagre de Montilla-Moriles	Mid-infrared spectroscopy (MIR), near infrared spectroscopy (NIR), excitation-emission multidimensional fluorescence (EFM), 1H-Nuclear Magnetic Resonance (1H-NMR) spectroscopy	Application of data fusion methods improved the characterization and authentication of PDO wine vinegars	[56]
Characterization and authentication of Spanish PDO wine vinegars	Vinagre de Jerez, Vinagre de Montilla-Moriles and Vinagre de Condado de Huelva	Fluorescence analysis	Fluorescence spectroscopy and chemometrics combination was proposed as a potential routine analysis for PDO regulatory councils	[57]
Classification of PDO wine vinegars and their discrimination from commercial wine vinegars	Vinagre de Jerez, Vinagre de Condado de Huelva and Vinagre de Montilla-Moriles of different categories, and wine vinegars without PDO	Near infrared spectroscopy (NIR)	Combination of NIR with chemometrics was useful for a rapid characterization and classification of the Spanish PDO wine vinegars with >90% correct classification	[58]

(*Continued*)

Table 1. (Continued).

Aim	Type of Vinegar	Method	Result	Reference
Differentiation of aged and PDO wine vinegars from commercial (rapid) vinegars	Vinagre de Condado de Huelva, Vinagre de Jerez, Vinagre de Montilla-Moriles and 20 wine vinegars without PDO	UV–visible spectroscopy	Hierarchical classification model developed using UV–visible spectra showed promising classification of aged and PDO vinegars	[59]
Determination and quantification of adulterants in Sherry vinegar	Sherry vinegar adulterated with molasses, rice, cider and wine vinegars	Laser diode fluorescence spectroscopy	Adulteration ratios of Sherry vinegar were determined with small mean absolute percentage errors	[60]

Non-targeted analyses

Non-targeted analyses are attracting attention due to their rapid, low cost and small amounts of sample and minimum amounts of chemicals requiring nature.Especially in the past 15 years, various scientific studies aiming to detect the origin of the vinegar, to classify according to raw material, to characterize, and to authenticate the quality of vinegar have been published. In this part of the review, researches that were performed using non-targeted techniques will be discussed first. These techniques have been mostly used in detection of mixtures and identifying false labeling frauds (Table 1).

Cocchi et al.[49] aimed to discriminate TBVM "affinato", aged at least 12 years, and "extravecchio", aged at least 25 years, using whole volatile profiles obtained by head-space mass spectrometry and evaluating the data with multivariate analysis techniques. Score plots showed that reasonable classification with respect to aging was obtained. The potential of non-targeted methods combined with multivariate statistical techniques was also shown in another study.[53] Wine vinegar, balsamic, sherry and cider vinegar samples were analyzed with headspace solid-phase microextraction/gas chromatography to classify four types of vinegars. Again based on their distinctive overall volatile profiles, samples were differentiated successfully. Nuclear magnetic resonance (NMR) spectroscopy combined with chemometrics is one of the other spectroscopic methods used to classify vinegars and predict their properties. Seventy-two balsamic vinegar samples having different ages were successfully classified and predicted with high precision with this technique.[50] Hierarchical projection to latent structure discriminant analysis of NMR data provided differentiation of samples as young (<12 years), old (between 12 and 25 years) and extra old (>25 years). Fluorescence spectroscopy is the other technique to produce data used in the classification of vinegars. Determination of synthetic vinegars in Shanxi aged vinegars, a traditional Chinese vinegar type, was performed with excitation-emission matrix fluorescence spectroscopy and evaluation of the data with parallel factor analysis (PARAFAC) and multi-way partial least square discriminant analysis resulted in 100% correct classification of adulterated vinegars.[52] Rios-Reina et al.[57] used multidimensional fluorescence spectroscopy with parallel factor analysis and partial least squares-discriminant analysis to characterize and authenticate Spanish PDO wine vinegars. Results showed that the combination of these techniques can be the standard for PDO investigations. Following this study, same group completed other classification and authentication studies using Fourier transform mid-infrared, NIR, UV–visible, excitation-emission multidimensional fluorescence, and ^{1}H-NMR spectroscopy as analytical tools combined with various chemometric methods and obtained successful results for the characterization and authentication of PDO wine vinegars.[55,56,58,59] In one of these studies, data from various spectroscopic techniques including NIR, Mid-IR, ^{1}H-NMR, and multidimensional fluorescence spectroscopy were fused to improve the classification performance of these techniques for Spanish PDO wines.[56] Mid-level data fusion and common component and specific weights analysis multi-block method were the two data fusion approaches used in this study.

In addition to the identification of raw material or detection of aging duration, non-targeted methods can be used to determine high-quality products. la Haba et al.[51] aimed to characterize Vinagres de Montilla-Moriles wine vinegars, which were protected with PDO certification, using NIR reflectance spectroscopy. Submerged culture and Orleans methods were differentiated and also prediction of vinegar properties was performed with high accuracy in the same study. In a study that aimed to detect and quantify cheaper and low-quality vinegars from molasses, rice, cider and white wine in high-quality sherry vinegars, laser diode fluorescence spectroscopy was used and the

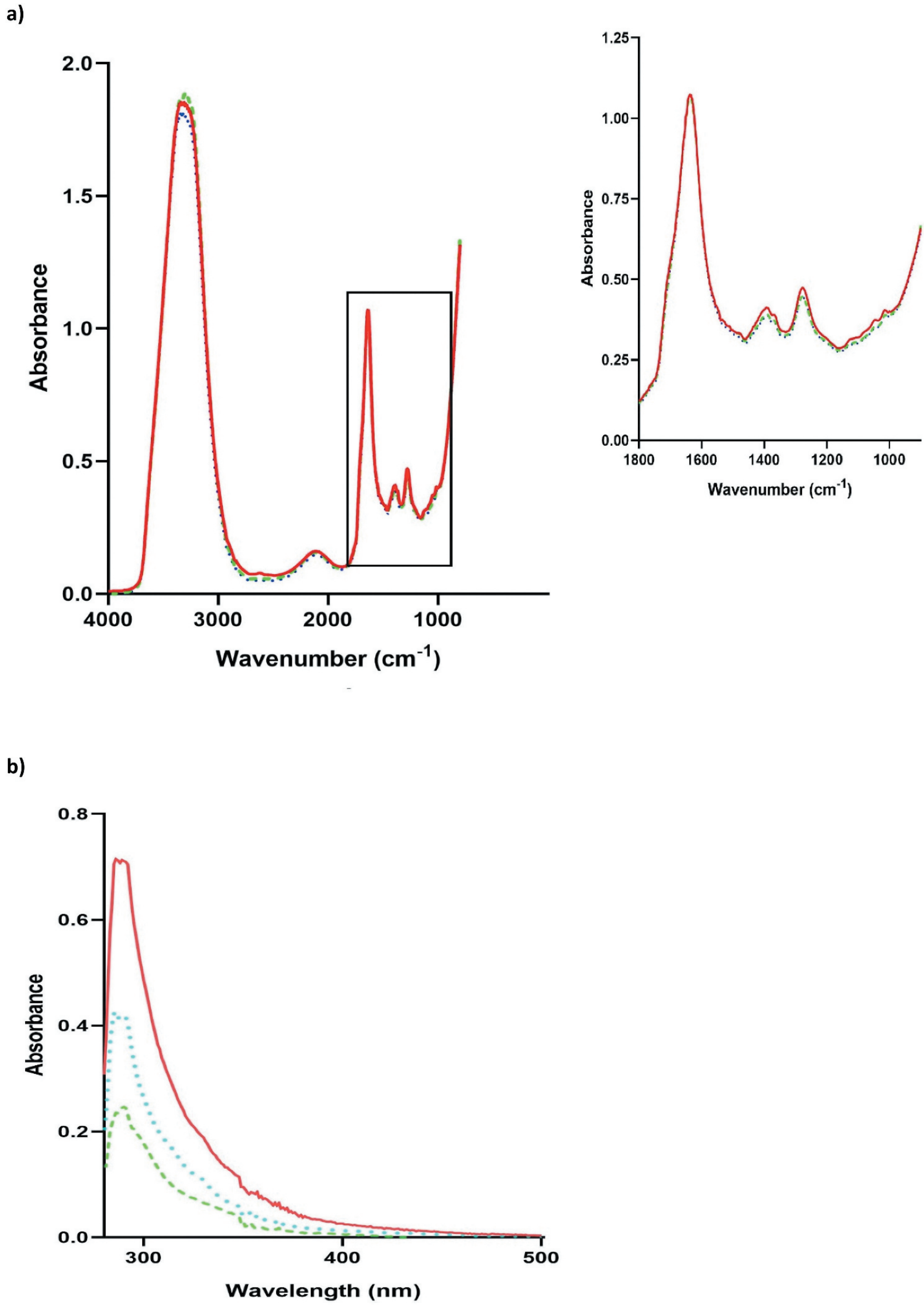

Figure 1. (a) Mid-infrared spectra of pure apple vinegar (–), apple vinegar adulterated with spirit vinegar (––) and apple vinegar adulterated with synthetic vinegar (......); (b) UV–visible spectra of pure apple vinegar (–), apple vinegar adulterated with spirit vinegar (––) and apple vinegar adulterated with synthetic vinegar (......).

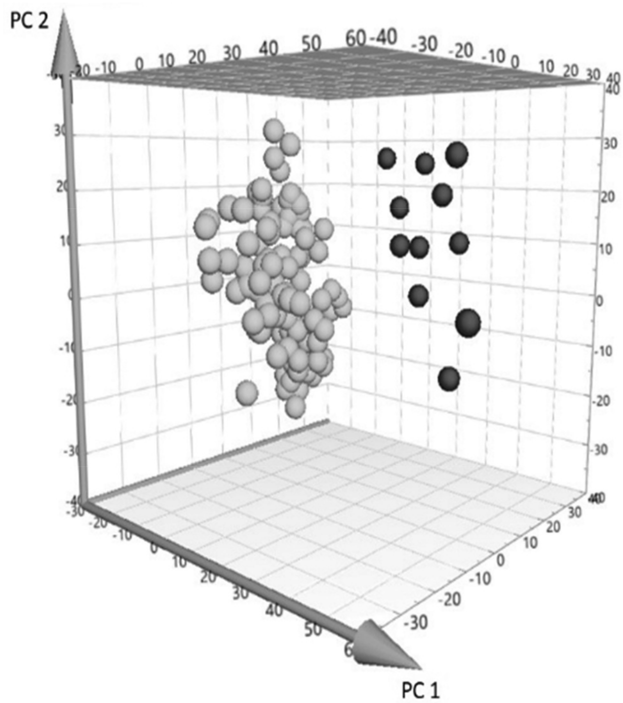

Figure 2. Orthogonal partial least square discriminant analysis model built with using combined mid-infrared and UV–visible spectral data and showing discrimination between pure apple vinegars (dark color) and apple vinegar adulterated with spirit vinegar and synthetic vinegars (light color).

data were evaluated with varying success using several intelligent chaotic algorithms.[60] Argentinean, Italian and Spanish vinegars were examined using a combination of UV–visible and fluorescence spectroscopies, aiming discrimination of their origins. Data were analyzed using principal component analysis and parallel factor analysis. Well discrimination of vinegar origins was reported.[54] As part of our still ongoing study, evaluation of the second derivative of combined FTIR and UV–visible spectral data with orthogonal partial least square discriminant analysis provided a good separation between pure apple vinegars and apple vinegars adulterated with spirit vinegar and synthetic vinegar (diluted acetic acid) separately. Figures 1 and Figures 2 show mid-IR and UV–visible spectral differences between vinegar and adulterated vinegars and differentiation of apple vinegar and adulterated samples regardless of adulterant, respectively.

Targeted analyses

Targeted testing, on the other hand, aims to differentiate products with respect to their specific properties and constituents and has been used in various authentication studies of vinegar (Table 2). Since molecular isotope ratios provide information regarding the precursor molecules, measurement of stable isotope ratio was introduced as a useful tool to differentiate the botanical and geographical origin of food products. Therefore, it could be possible to classify the fermentation of raw materials with respect to their sources in the case of vinegar production with this technique. For this purpose, 14 vinegars, fermented from 7 different raw materials, were examined using headspace solid-phase microextraction combined with gas chromatography-high temperature conversion or combustion–isotope ratio mass spectrometry to provide differentiation according to raw materials.[64] Hydrogen and carbon isotope ratios were determined as effective parameters to discriminate the botanical origins of the acetic acid. The difference between C3 and C4 plants was

Table 2. Studies performed with various targeted and combination of targeted and non-targeted approaches for authentication of vinegars.

Aim	Type of Vinegar	Targeted/ Both	Method	Result	Reference
Authentication of high quality Spanish wine vinegars	Wine vinegars from Vinagre de Jerez, Vinagre de Condado de Huelva, and Vinagre de Montilla-Moriles	Targeted	Headspace sorptive extraction gas chromatography-mass spectrometry analysis (HSSE-GC–MS)	Successful classification was obtained using individual volatile compounds	[61]
Authentication of high quality Italian and Spanish wine vinegars	Vinagre de Jerez, balsamic vinegars of Modena and traditional balsamic vinegars of Modena	Targeted	High-performance liquid chromatography (HPLC) analysis	The amino acid and biogenic amine composition can be used to authenticate high quality Italian and Spanish vinegars	[62]
Determination of carbon isotope distribution in vinegar acetic acid	Commercial Japanese vinegars	Targeted	Improved gas chromatography-pyrolysis-gas chromatography-combustion-isotope ratio mass spectrometry (GC-Py-GC-C-IRMS) combined with headspace solid-phase microextraction (HS-SPME)	Low concentrations of acetic acid in complex media such as food products were measurable by the SPME technique	[63]
Discrimination of raw materials used in fermentation	Rice vinegar, tomato vinegar, apple vinegar, pineapple vinegar, lychee vinegar, grain vinegar, wheat vinegar	Targeted	Head space solid-phase microextraction (HS-SPME) combined with gas chromatography-high temperature conversion or combustion-isotope ratio mass spectrometry (GC-TC /C-IRMS)	Hydrogen and carbon isotope ratios were good parameters to discriminate the botanical origins of the acetic acid. The difference between C3 and C4 plants was clearly shown.	[64]
Identification of the adulteration by addition of molasses spirit vinegar and synthetic acetic acid into rice vinegar	Rice vinegar	Targeted	Site-specific natural isotopic fractionation by nuclear magnetic resonance (SNIF-NMR)	Deuterium to hydrogen ratio of acetic acid varies with the source of vinegar	[65]
Classification of balsamic vinegars	Balsamic vinegar of Modena (BVM) and traditional balsamic vinegar of Modena (TBVM)	Targeted	1H Nuclear magnetic resonance (1H NMR) spectroscopy	Constituents such as acetic acid, ethanol, formic acid, 5-hydroxylmethylfurfural, lactic a., malic a., succinic a. and tartaric a. were effective in BVM and TBVM characterization and quality control	[66]
Characterization and classification of PDO wine vinegars	Traditional balsamic vinegar of Modena and the industrial balsamic vinegar of Modena products	Targeted	High-performance liquid chromatography (HPLC) analysis, gas chromatographic-combustion-Isotopic ratio mass spectrometry (GC-C-IRMS)	Carbon isotopic ratio of glycerol polyalcohol varied with origin, varietal or provenance; therefore, the discriminating potential of these species could be useful to elucidate balsamic vinegar production process	[67]
Detection of adulterations of balsamic vinegars through addition of water, acetic acid not only from wine, and/or other sugars to grape must	Balsamic vinegar	Targeted	Gas chromatography isotope ratio mass spectrometry (GC-IRMS) validated by 1H NMR	A stepwise procedure based on different isotopes was validated	[68]
Detection of addition of rehydrated grapes to fermentation medium	14 groups of authentic samples including wine vinegars, raw vinegars, diluted vinegars	Targeted	$^{18}O/^{16}O$ ratio analyses by isotope ratio mass spectrometers	$^{18}O/^{16}O$ ratio values were determined for authenticated vinegars and vinegars produced from rehydrated grapes	[69]

(*Continued*)

Table 2. (Continued).

Aim	Type of Vinegar	Targeted/ Both	Method	Result	Reference
Determination of origin of vinegars from different parts of Spain	Vinagre de Condado de Huelva, Vinagre de Jerez, Vinagre de Montilla-Moriles and commercial vinegars from Northern Spain	Targeted	Stable isotope analysis ($\delta^{13}C$ and $\delta^{18}O$)	$\delta^{18}O$ ratio analysis provided better results than the $\delta^{13}C$ for determination of origin of vinegar	[70]
Authentication of high quality Spanish wine vinegars	Wine vinegars from Vinagre de Jerez, Vinagre de Condado de Huelva and Vinagre de Montilla-Moriles	Targeted	Headspace sorptive extraction gas chromatography-mass spectrometry analysis (HSSE-GC–MS)	Classification using individual volatile compounds have high success for authentication of Spanish wine vinegars	[61]
Determination of types and aging times of Chinese vinegars	Chinese traditional cereal vinegars	Targeted	CdTe-TGA sensor array and fluorescence spectroscopy	Types and aging time of Chinese vinegars were successfully predicted using organic acids and melanoidins	[71]
Authentication of Italian PDO vinegars	Traditional balsamic vinegar of Modena (TBVM), balsamic vinegar of Modena (BVM)	Targeted	^{13}C NMR spectroscopy	Glucose and fructose isoforms were measured and fructose isoforms were found effective in determination of fraud	[72]
Detection of addition of synthetic acetic acid into spirit vinegar	Spirit vinegar	Targeted	Isotopic ratios, $^{2}H/^{1}H$ and $^{13}C/^{12}C$, individual volatile compounds, sensory analysis	Isotopic ratios provided the most successful identification of the presence of acetic acid in spirit vinegar	[73]
Detection and quantification of grape-must caramel in vinegars	Vinagre de Jerez PDO and Vinagre de Montilla-Moriles	Both	Fluorescence spectroscopy, high-performance liquid chromatography (HPLC) analysis, sensory analysis	Multidimensional fluorescence coupled with a suitable chemometric method identified as a valuable tool for detecting and quantifying the addition of grape-must caramel to wine vinegars without sample treatment	[45]
Classification of vinegars	Wine vinegars and alcohol vinegars	Both	Near-infrared (NIR) spectroscopy, high-performance liquid chromatography	Vinegar NIR spectra is closely related to sample origin	[44]

clearly observed. Following this study, same sample composition was also used to determine $\delta^{13}C$ values of methyl and carboxyl carbons of acetic acid with gas chromatography–pyrolysis–gas chromatography–combustion–isotope ratio mass spectrometry (GC-Py-GC-C-IRMS) combined with headspace solid-phase microextraction (HS-SPME) since each carbon isotope ratios of methyl and carboxyl groups in acetic molecules could be indicators of the origin.[63] Therefore, findings of this study were expected to assist in the determination of indigenously and exogenously produced sources of acetic acid. Stable isotope methods using hydrogen, carbon and oxygen isotope analyses by isotope ratio mass and H-2-NMR spectrometry were also proposed to check the authenticity of balsamic vinegar.[63,68] Scatter plot of $\delta^{13}C$ versus $\delta^{2}H$ values of acetic acid (calcium acetate) from balsamic vinegar demonstrated successful visual discrimination of pure wine acetic acid, C4 plant acetic acid added samples, and C3 plant acetic acid added samples. $\delta^{18}O$ analysis of water with isotope ratio mass spectrometer was used to determine the production of wine vinegar through fermentation of dried gapes and dilution with tap water which is against the EU regulation (EU Regulation 555/2008).[69] Limit values for $\delta^{18}O$ which are the indications of this type of fraud were established for this purpose. Another study assessed $\delta^{18}O$ and $\delta^{13}C$ as the fingerprints for the discrimination of Spanish wine vinegars according to their origin and $\delta^{18}O$ was found useful for this purpose.[70] Site-specific natural isotopic fractionation by NMR spectroscopy was another technique used to determine the deuterium to hydrogen ratio at the methyl group of acetic acid. Hsieh et al.[65] showed that the deuterium to hydrogen ratio at the methyl group is different for rice, molasses spirit, and synthetic vinegars. Moreover, as rice vinegar was adulterated with synthetic vinegar or molasses spirit vinegar, the ratio increased proportionally and the ratio versus adulteration level had a high correlation ($R^2 > 0.97$). Another property to classify vinegars is isotropic $^{13}C/^{12}C$ ratio of glycerol in balsamic vinegar. Sighinolfi et al.[67] studied 112 TBVM and BVM using this technique and it was concluded that this approach could be used as an additional tool for balsamic vinegar authentication. Glucose and fructose isoforms in TBVM were measured through ^{13}C NMR spectroscopy and especially fructose isoforms were found useful in authentication of this type of vinegar.[72]

PDO vinegars of Spain were differentiated with respect to their individual volatile components determined with head space stir bar sorptive extraction GC-MS and it was shown that certain volatile components were inherent to each of three different vinegar types.[61] As a result, 100% correct classification for these vinegars was obtained with the evaluation of the data with a chemometric technique. Aroma profiles of Spanish PDO vinegars were also shown to have a discriminatory power.[74]

In a recent study, an acid-sensitive sensor array was used in identification of the types and ages of 32 traditional Chinese cereal vinegars and discrimination was based on organic acids and melanoidins present in vinegars.[71] Analysis of vinegar components with multivariate statistical techniques can also be used to authenticate high-quality vinegars. A total of 76 samples containing TBV and BVM samples aged for different durations were determined. Compositional properties such as brix value, concentration of acetic acid, ethanol, formic acid, 5-hydroxymethylfurfural, lactic acid, malic acid, succinic acid, and tartaric acid were analyzed using principal component analysis, factor analysis, and general discriminant analysis. Scatter plot of the first two discriminant functions of the general discriminant analysis showed very distinct groups visually.[66]

In some studies, both targeted and non-targeted methods were used together to validate each other and/or provide comparison between methods. The study performed by Rios-Reina et al.[45] is a good example for the use of targeted and non-targeted methods together. Although vinegar adulteration with grape-must caramel can be detected using multidimensional fluorescence, validation of this technique with the conventional chromatographic (HPLC) method was required.

Conclusion

Vinegar has nutritive, functional, and taste and flavor enhancing roles in the human diet. The use of vinegar provides protection of foods against microorganisms while addition to sauces enhances aroma and taste. Moreover, positive effects of vinegar consumption on human health are proven with in vivo, in vitro and clinical experiments. Raw material diversity and the presence of different production methods define classes of vinegars by their quality. With increasing demand to high-quality vinegars, adulteration practices are also in rise and fast and low-cost authentication methods are in high demand for detection of low-quality ingredients, estimation of the age of the product and identification of false labeling. Both targeted and non-targeted methods have been used for determination of different types of adulteration in vinegar. However, more studies especially using combination of different techniques and various data analysis methods particularly data fusion approaches are needed to improve the detection of adulteration of this product.

Disclosure statement

Authors declare no competing interest

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