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Reviews

Dedicated to Professor Gheorghe Maria
on the occasion of his 70th anniversary

MODERN ANALYTICAL TECHNIQUES FOR VINEGAR AUTHENTICATION AND QUALITY ASSESSMENT: A COMPREHENSIVE REVIEW

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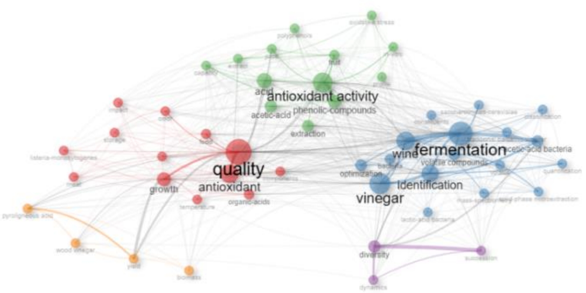

The review aims to provide a summary of the highly advanced analytical techniques used for vinegar characterization, as well as to offer a wide overview over specific solutions for picking extraction techniques that are the more effective for the advancement of vinegar technology. The benefits of contemporary analysis methods derive their effectiveness from the fact that they do not require reagents and are conducted directly on the sample. Utilizing these approaches, qualitative and quantitative information regarding chemical characteristics can be determined from spectral data (spectroscopic techniques: Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR), Ultraviolet–visible spectrophotometry (UV-Vis), Near-infrared spectroscopy (NIR); chromatographic techniques: Gas Chromatography (GC), Gas Chromatography-Mass Spectrometry (GC-MS) and High Performance Liquid Chromatography (HPLC) in less time than with traditional analytical methods. These methods, when paired with chemometric techniques (*e.g.* Principal Component Analysis (PCA), Linear Discriminant Analysis (LDA), Artificial Neural Networks (ANN), are beneficial for determining several parameters concurrently and rapidly, during vinegar production, detecting potential frauds, authenticating vinegars and characterizing vinegars originating from various source materials.

INTRODUCTION

The term vinegar is originated from the French word “vinaigre”, which means sour wine because vinegar is produced through the spontaneously aerobic oxidation of ethanol, typically present in wine, getting sour. Archaeological and historical records suggest that vinegar has been known since at least 3000 BC, since there have been exiting non-distilled alcoholic drinks.[1] Throughout history, vinegar has been employed as a beverage, condiment, preservative and medicinal treatment.[2]

Vinegar is an acetic acid solution obtained through a two-stage bioprocess involving the fermentation of

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starches and sugars with yeast converting them into ethanol. Subsequently, acetic acid bacteria oxidize ethanol into acetic acid, imparting the characteristic sensory properties of vinegar.[3,4] Parameters such as temperature, pH, yeast strain, sugar concentration, oxygen and production methods significantly influence production rate and final properties.[5] During the fermentation process, a cellulose-rich biofilm is formed by acetic acid bacteria at the liquid-air interface, indicating substrate integrity and often high quality.[6] The modern production method involves inoculating *Saccharomyces cerevisiae* yeast and lactic acid bacteria in pressurized fermentation tanks.[7]

Technological advancements have led to the replacement of traditional vinegar production methods with industrial-scale processes. Submerged culture fermentation is currently employed for the production of commercial vinegars, enabling faster processing times compared to conventional surface fermentation techniques. In this case, acetic acid bacteria are directly inoculated into the fruit juice substrate, allowing for efficient oxidation of ethanol to acetic acid under controlled conditions.[8]

The objective of this study is to evaluate the potential of advanced spectroscopic techniques (such as NMR, FTIR, UV-Vis, and NIR) and chromatographic methods (GC and HPLC) for the authentication, traceability, and quality control of vinegar. The study aims to highlight the complementary nature of these analytical tools and their integration with chemometric modeling, in order to develop robust, standardized approaches that support regulatory compliance, industrial quality assurance, and consumer protection.

VINEGAR PRODUCTION FROM VARIOUS RAW MATERIALS

In recent years, the vinegar industry has experienced substantial growth, utilizing diverse raw materials such as wine, fruits, cider, alcohol, grains, malt and honey. The vinegar can be obtained from substandard fruit, seasonal agricultural surpluses, by-products from food processing and fruit waste, without adversely affecting the quality of the final product. Currently, the term "vinegar" refers to all acetic acid solutions produced from various substrates through fermentation processes.[9] The preparation of raw materials or substrates is a critical step in the vinegar production process, as it is directly influenced by the concentration of fermentable sugars. Processing methods vary depending on the type of raw material used. Fruits are highly perishable due to their elevated water content and must be processed promptly to prevent microbial contamination, which could compromise the quality of the final product or lead to the formation of harmful toxic compounds.[3] On the market there are also some expensive vinegars, such as: traditional balsamic vinegar from Modena in Italy or sherry vinegar from Spain.[10] Certain types of vinegar possess higher added value due to specific manufacturing and maturation processes, as well as the protection conferred by a Protected Geographical Indication (PGI) or a Protected Designation of Origin (PDO). Consequently, these factors contribute to distinctive and personalized product characteristics.[11]

Vinegar has a variety of functional proprieties, including antioxidant, antibacterial, anti-inflammatory, anticancer activities, antidiabetic, anti-obesity, cholesterol-lowering and also to treat wound inflammation, cough, ulceration and infectious disorders because of the phenolic compounds.[12–15]

Using the Web of Science database and RStudio software for bibliometric analysis, a total of 1,991 articles published between 2015 and 2025 were identified, focusing on vinegar research within the fields of Food Science and Technology, Chemistry, and Agriculture.

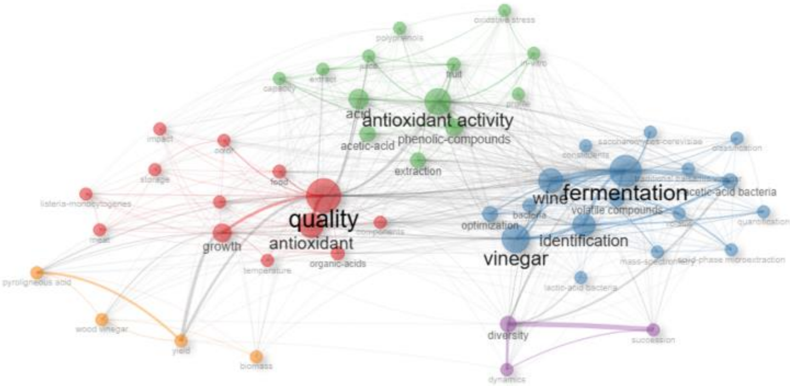

Fig. 1 – The co-occurrence network of all keywords.

Figure 1 illustrates the co-occurrence network of keywords derived from a bibliometric analysis of publications between 2015 and 2025 (Web of Science, processed using RStudio). This method highlights the main research trends in the vinegar field and the relationships among key concepts used in the scientific literature.

The network shows that the most frequent terms (nodes with larger sizes and multiple connections) are associated with:

– "acetic acid," "fermentation," and "vinegar quality," reflecting research interest in process optimization;

– "antioxidant activity" and "phenolic compounds," emphasizing the growing attention to functional and bioactive properties of vinegar;

– "authentication" and "adulteration detection," indicating an increasing focus on traceability and food fraud prevention.

The density of connections among terms demonstrates strong interdisciplinarity, with intersections between food technology, analytical chemistry, and functional nutrition. Distinct thematic clusters can also be observed: one related to technological processes and raw materials, and another focusing on functional properties and potential medical applications. This figure confirms that, in the past decade, vinegar research has expanded beyond technological aspects, increasingly incorporating metabolomic and spectroscopic approaches for authentication and bioactive compound evaluation.

VINEGAR ANALYSIS USING SPECTROSCOPIC AND SPECTROMETRIC TECHNIQUES

The combination of spectral data and chemometric techniques enables rapid and minimally invasive characterization of vinegar samples. With increasing demand for fast, accurate and cost-effective methods, these approaches support authentication, adulteration detection and quality control.[14] Due to economic motives, vinegar is often subject to counterfeiting. Multivariate statistical tools such as ANOVA, PCA, cluster analysis (CA) and (ANN) enhance both qualitative and quantitative analysis[15].

According to the International Organization of Vine and Wine (OIV), a *Compendium of International Methods of Analysis for Vinegar* has been established, comprising a wide range of standardized methodologies for the analysis of wine vinegars. These include procedures for the determination of total polyphenols content, alcohols and organic acids.[16]

SPECTRAL TECHNIQUES FOR VINEGAR EXAMINATION

The combined application of UV-Vis, FT-IR and FT-NIR spectroscopic (Fourier Transform Near-Infrared) techniques with linear discriminant analysis enables the efficient authentication of white wine vinegar and the detection of adulteration with spirit vinegar.[17]

Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy, combined with chemometric methods, is a powerful technique that can be successfully applied to vinegar analysis, providing quantitative information with high reproducibility on a wide range of compounds present in vinegar. NMR analysis is widely applied in food quality control due to its minimal sample, non-destructive nature, rapid data acquisition and high selectivity and accuracy, enabling molecular identification and precise quantification with excellent reproducibility.[18,19]

The following section presents a series of vinegar analyses performed using NMR spectroscopy. The aim of these investigations is to achieve a comprehensive molecular characterization of vinegar samples, to identify specific metabolic profiles and to discriminate between different types, origins or processing methods of vinegar.

Low-Field Nuclear Magnetic Resonance (LF-NMR), combined with chemometric analysis, has demonstrated high accuracy in discriminating authentic white wine vinegars from those adulterated with alcohol vinegar, offering a rapid and non-destructive approach for food authenticity assessment.[20]

Caligani *et al.*[21] used the ^{1}H-NMR method with water suppression to enable the rapid and sequential quantification of carbohydrates (glucose and fructose), organic acids (acetic, formic, lactic, malic, citric, succinic and tartaric acids), alcohols and polyols (ethanol, acetoin, 2,3-butanediol, hydroxymethylfurfural) and volatile compounds (ethyl acetate) in several balsamic vinegar samples.[21] The existence of organic acids and carbohydrates has been validated by FT-IR. Also, the phenolic compounds such as gallic acid, catechin, epicatechin, chlorogenic acid, caffeic acid and p-coumaric acid were determinate using ^{1}H-NMR, being confirmed by GC-MS.[22]

The Nuclear Magnetic Resonance Partial Least Squares Discriminant Analysis (NMR-PLS-DA) approach achieved the highest predictive accuracy among the tested methods, with accuracy values ranging from 92.3% to 100% while FT-IR and UV-Vis methods yielded values between 80.8% and 96.0% and NIR provided accuracy ranging from 69.2% to 84.0%. Nevertheless, all of the aforementioned spectral fingerprinting techniques have been shown to be effective for vinegar classification.[11]

Wang *et al.*[23] developed a non-destructive and comprehensive method for ^{13}C isotope assessment based on ^{1}H -NMR spectroscopy, applied to nine commercial vinegar and three lab-fermented samples. The results show that the carbon isotope distribution (CID) is in natural abundance. Spectra were recorded at room temperature (298 K) on a Bruker AVANCE 600 MHz spectrometer, processed with TopSpin 3.0 and aligned to the glucose signal at 5.24 ppm using Amix 3.9.14. The peak area ratio (PAR) between ^{1}H-NMR spectra with and without ^{13}C decoupling was used to calculate CID. Fermented vinegars showed PAR values between 0.97 and 1.04, while mixed vinegars and broths ranged from 0.94 to 1.09. Results were validated by Isotope Ratio Mass Spectrometry (GC-IRMS), confirming the method's potential for discrimination and authentication of fermented food matrices.[23]

Thomas and Jamin[24] investigated the ^{2}H/^{1}H ratio at the methyl site of acetic acid using Site-Specific Natural Isotope Fractionation studied by Nuclear Magnetic Resonance (SNIF-NMR) and the ^{13}C/^{12}C ratio using Isotope ratio mass spectrometry (IRMS) to determine the botanical origin of vinegar and detect adulteration with synthetic acetic acid. In wine vinegar, the ^{18}O/^{16}O ratio of water measured by IRMS enables distinction from vinegar made from dried grapes. SNIF-NMR has also proven effective in identifying counterfeit rice vinegars. Using a Bruker DMX 600 ^{2}H-NMR spectrometer with tetramethylurea (TMU) as internal standard, Hsieh *et al*.[25] detected adulteration with synthetic acetic acid in three rice vinegar samples.[27,28]

Papotti *et al.*[19] analyzed using a Bruker FT-NMR Avance 400 spectrometer at 400.13 MHz 23 samples of Traditional Balsamic Vinegar of Modena (TBVM) aged >25 years, 17 aged between 12–25 years and 36 samples of Balsamic Vinegar of Modena (BVM) aged <3 years. Spectral data obtained from ^{1}H-NMR analysis were processed using principal component analysis (PCA), general discriminant analysis (GDA), and classification tree analysis (CTA). The most discriminative variables were identified as 5-hydroxymethylfurfural (5-HMF), fructose, glucose, 6-acetyl glucose, and 2,3-butanediol. Among the tested models, GDA demonstrated the best performance, accounting for 98.6% of the total variance and achieving a predictive accuracy of 98.4%, with clear separation between clusters.[19]

Fourier Transform Infrared spectroscopy (FTIR)

Fourier Transform Infrared with Attenuated Total Reflectance (ATR-FTIR) spectroscopy is among the most widely employed screening techniques for the detection of food fraud.[26] FTIR spectroscopy as a quantitative analytical method and stastical analysis has significantly expanded, being widely recognized for its efficacy in vinergar authentication and classification purposes.[27]

In a recent study,[27] the FTIR spectra of 67 vinegars registered under the Protected Designation of Origin (PDO) were analyzed using a Bruker Vertex 70 spectrometer equipped with a DGTS detector. The Principal Component Analysis (PCA) was performed on the spectral region 1500–900 cm^{-1}, using triplicate measurements, and explained 93.98% of the total spectral variance. The results demonstrated a clear separation among PDO vinegar samples, indicating that vinegars produced in accordance with PDO regulations possess enhanced quality and distinct compositional profiles.[27]

Natera *et al.*[28] analyzed 83 vinegar samples to evaluate their phenolic composition, aromatic profile and organic acid content. The samples were classified using multivariate analytical methods according to raw material origin (white wine, red wine, apple, honey, alcohol, balsamic, malt) and production method (with or without wood aging). Linear Discriminant Analysis (LDA) achieved an 88% discrimination rate based on wood aging.[28]

Öztürk conducted a study using FTIR on household vinegars produced from organically grown fruits and vegetables (pumpkin, wild plum, pear and cabbage), cultivated without pesticides and harvested at full maturity. The absorption spectra exhibited highly consistent patterns among the traditional vinegar samples, with minor variations attributed to differences in phenolic content. Characteristic peaks corresponding primarily to acetic acid and water confirmed the expected chemical composition. Additionally, weaker signals associated with ethyl alcohol, hydroxyl groups, C–C, C–O and C–H bonds further supported the structural integrity of the samples. These findings indicate that traditionally produced vinegars are safe for consumption and comparable in quality to their industrially manufactured counterparts.[8]

FTIR spectroscopy has also shown potential in the rapid determination of antibacterial activity of vinegar. Measurements were performed using a FTIR spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector and ATR single-reflection diamond crystal. Results indicated that grape vinegar has the greatest antibacterial effects against *S. aureus*, *E. coli* and *P. aeruginosa*, with no statistically significant differences observed among the other samples.[13]

Near Infrared (NIR) spectroscopy

Near-infrared (NIR) spectroscopy is an emerging analytical technique distinguished by its low operating costs, non-destructive and rapid analysis, as well as high precision, accuracy, repeatability, and reproducibility. The method is based on the absorption of electromagnetic radiation within the 780–2500 nm wavelength range [36–38]. NIR spectroscopy has been widely applied to monitor fermentation processes, including the characterization of vinegar during storage and the quantification of key chemical constituents, such as organic acids, reducing sugars, total procyanidins, ethanol, acetic acid, soluble solids, and pH.[39,40]

Liu *et al.*[41] investigated the potential of near-infrared (NIR) spectroscopy for the simultaneous determination of organic acids and pH in fruit vinegars. Given that both the composition and concentration of organic acids are key indicators of vinegar quality and authenticity, the study analyzed three types of fruit vinegar (apple, lemon, and peach) using an FT-IR-4100 spectrometer.

Optimal partial least squares (PLS) models were established using different spectral preprocessing techniques. In parallel, least squares-support vector machine (LS-SVM) models were constructed by incorporating wavelet transform (WT), latent variables, and effective wavelengths (EWs) as input parameters. Comparative analysis revealed that LS-SVM models exhibited superior predictive performance over PLS models for acetic, tartaric, and formic acid contents, as well as for pH determination. These findings highlight the potential of LS-SVM as a reliable approach for process control and real-time monitoring in fruit vinegar production.[41]

Several studies have explored the use of near-infrared (NIR) spectroscopy for quantifying key constituents in different vinegar types, including ethanol and acetic acid in rice vinegar, as well as organic acids and other quality-related parameters in wine vinegar. Guan *et al.*[42] integrated NIR spectroscopy with high-performance liquid chromatography (HPLC) to determine the production season of aromatic vinegar and to quantify lactic acid, malic acid, and L-pyroglutamic acid. Additionally, a partial least squares (PLS) regression model, developed based on NIR spectral data, accurately predicted 14 quality parameters of wine vinegar, including total acidity, volatile and non-volatile acids, individual organic acids, L-proline, dry matter, ash content, and chloride concentration.[30]

Fan *et al.*[43] evaluated the potential of NIR spectroscopy for distinguishing between fermented and blended vinegars. A total of 100 commercial samples (50 fermented and 50 blended vinegars) were analyzed. For classification purposes, 11 relevant wavelengths were selected. A partial least squares discriminant analysis (PLS-DA) model was developed based on the selected variables, yielding an average error rate of 6.95% as determined by repeated pairwise cross-validation. These results demonstrate that near-infrared (NIR) spectroscopy, when coupled with optimized wavelength selection, represents a rapid and reliable approach for vinegar authentication.[43]

Ji-Yong *et al.*[44] evaluated the applicability of NIR spectroscopy for non-destructive analysis of Chinese vinegars using 95 samples of various origins. While fruit and white vinegars were distinctly separated, LS-SVM was required to classify overlapping categories such as mature, aromatic and rice vinegars. Total acidity, used as a quality descriptor, was predicted with good accuracy using LS-SVM regression models, outperforming PLS methods. The results confirm the potential of FT-NIR spectroscopy combined with LS-SVM for vinegar quality assessment.[44]

Casale *et al.*[45] analyzed 95 vinegar samples of various origins collected from the industry and supermarkets in northern Spain. Spectral data were acquired both immediately after opening the bottles and after a storage period. Using LDA for classification, the study demonstrated that NIR spectroscopy can differentiate vinegars based on compounds developed during aging, with satisfactory classification and prediction rates.[45]

In conclusion, the application of near infrared (NIR) spectroscopy has been successfully applied for monitoring fermentation processes, identifying key chemical constituents such as organic acids and ethanol, and distinguishing between different types and qualities of vinegar. When coupled with multivariate calibration and classification techniques, NIR spectroscopy proves to be a reliable and efficient tool for vinegar analysis.

Ultraviolet and Visible spectroscopy (UV-Vis)

UV-Vis spectroscopy is used for the determination of various characteristics of vinegars. Owing to its simplicity, reproducibility and cost-effectiveness, UV-Vis spectroscopy has found extensive applications in food science and food processing research.[29] When coupled with advanced chemometric methods, this technique allows for the simultaneous determination of multiple physicochemical parameters directly from spectral data, which is particularly valuable in real-time monitoring of vinegar production processes.[30]

H. Xie *et al.*[15] investigated the applicability of UV-Vis spectroscopy for discriminating against vinegar samples produced from different raw materials and via distinct fermentation methods (liquid and solid-state fermentation). Data interpretation was performed using principal component analysis (PCA) and artificial neural networks (ANN), applied as multivariate pattern recognition techniques.

PC1 and PC2 accounted for 90% and 100% of the variance, respectively, while ANN achieved a classification accuracy of 85.71%. The UV-Vis approach successfully grouped the samples within 30 minutes, highlighting its efficiency and potential for rapid analysis.[15]

In another study, González-Domínguez *et al.*[31] used UV-Vis spectroscopy combined with chemometric techniques to discriminate wine vinegar samples according to their geographical origin. The spectral profiles obtained from 71 vinegar samples were analyzed using linear discriminant analysis (LDA), which revealed a distinct clustering of samples according to their protected designation of origin (PDO). The model achieved a high classification accuracy of 98.6%.[31]

Also, Ríos-Reina *et al.*[32] successfully developed a hierarchical classification model with the primary objective of distinguishing between "aged" and "non-aged" wine vinegars, as well as between PDO and non-PDO samples and even among different maturation categories within the same PDO. Notably, this study represents the first attempt in which all vinegar types were concurrently classified using a unified analytical procedure combined with a chemometric modelling strategy.[32]

The method proposed by Ríos-Reina *et al.*[33] offers a valuable tool for the assessment of balsamic vinegars, particularly for monitoring the addition of caramel (E150d). The study demonstrated that UV-Vis spectroscopy, combined with multivariate calibration, is effective for detecting caramel concentrations below 2% v/v in both balsamic and PDO wine vinegars, in accordance with legal requirements. Due to its rapid, non-destructive, and robust nature, this method is well-suited for large-scale quality control applications.

In a related study, Yalçın *et al.*[34] employed UV-Vis spectroscopy to perform qualitative and quantitative analyses on six types of organic vinegars (apple, hawthorn, artichoke, grape, rosehip and blackberry) produced using deep culture fermentation. Rosehip vinegar exhibited the highest absorbance at 215 and 285 nm, attributed to its elevated content of amino and organic acids, while grape vinegar showed the lowest values. However, due to the applied method, the ethyl alcohol content was found to be significantly higher, up to 30 times, compared to vinegars obtained through traditional methods. Despite this, UV spectral data confirmed the high quality and suitability of these vinegars for human consumption.[34]

In relation to the health-promoting effects of grape vinegar components, another study focused on the immunomodulatory potential of a nano-polysaccharide (VBCP2.5) extracted from vinegar-baked *Radix Bupleuri*. Using a U-2910 UV spectrophotometer (200–400 nm range), the study demonstrated that VBCP2.5 significantly enhanced immune responses by promoting NO release, phagocytosis and the production of TNF-α and IL-6 in RAW264.7 cells.[35]

CHROMATOGRAPHIC METHODS OF VINEGAR ANALYSIS

The quality of the vinegars was also using chromatographic techniques, but these procedures may have certain drawbacks: time-consuming and expensive.[13]

Gas chromatography (GC)

Gas chromatography (GC) is widely employed for the qualitative and quantitative analysis of food composition, natural products, food additives, aroma compounds, transformation products and contaminants.[46,47] Xie and Chai[48] developed a rapid and straightforward method using head-space gas chromatography (HS-GC) to determine the total acid content in vinegar. The method demonstrated high precision and accuracy, with a relative standard deviation of 1.73% in repeatability tests and a relative difference of 4.81% compared to the reference titration method. This approach proves suitable not only for process monitoring but also for quality control of commercial vinegar samples.

Vinegar contains 2,3,5,6-tetramethylpyrazine (TMP), a compound with health benefits, yet its formation in vinegar is not well understood. A comprehensive study on 137 global vinegar samples employed gas chromatography coupled with flame ionization detection (GC-FID) showed that acetoin and ammonium are TMP precursors.[49] Additionally, GC-FID combined with GC-olfactometry and SAFE-GC-MS was used to compare Sichuan modern (SMV) and traditional (STV) vinegars. The SAFE-GC-MS analysis showed that STV aroma is dominated by high levels of alcohols, ketones and pyrazines, whereas SMV aroma is characterized by elevated concentrations of acids, esters, aldehydes, lactones, acetals, sulphides and phenols.[50]

To better understand the compounds responsible for vinegar's distinctive aroma, GC-O with modified frequency (MF, %) analysis was applied to traditional Modena balsamic vinegars (TB) and Modena PGI vinegars. Thirty-four key aroma compounds were identified. Statistical analysis using (ANalysis Of VAriance) ANOVA ($p < 0.05$) and PCA (PC1 = 55.45%) showed that TB aroma is mainly influenced by high levels of 2-methyloxolan-3-one and vanillin (4-hydroxy-3-methoxybenzaldehyde), while PGI aroma is characterized by higher concentrations of propanoic acid, octanoic acid and vanillin. The analyses were performed using an Agilent 7890B GC coupled with a 5977A MS and an ODP3 olfactory detection port, equipped with a DB-Wax capillary column (60 m × 0.25 mm, 0.25 μm).[51]

The analysis of aldehydes and acids (the most abundant compunds) in traditional Chinese rose vinegar was conducted using Gas chromatography-olfactometry (GC-O) combined with Headspace Solid-Phase Microextraction Gas Chromatography Mass Spectrometry (HS-SPME-GC-MS) and Silylation-GC-MS to investigate their contribution to the vinegar's aroma. The analysis employed an Agilent 7890B GC coupled with a Triple Quad 7000C MS, a Sniffer 9000 olfactometer, a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm) and a 75 μm CAR/PDMS SPME fiber. The study identified 48 aroma compounds and 78 metabolites, but the aldehydes were linked to floral and fruity notes, while hydroxides enhanced aroma and mitigated acetic acid's acidity.[52] In conclusion, based on the examples provided, gas chromatography is suitable for determining the aromatic profile of vinegars.

Gas cromatography – mass spectroscopy (GC-MS)

In volatile compound analysis, gas chromatography coupled with mass spectrometry (GC-MS) is widely employed. Ubeda *et al.*[53] developed a GC-MS method to monitor key volatile compounds during fruit vinegar production, using samples from raw materials, fruit wine, and fruit vinegar. Nine main volatiles were identified, including acetaldehyde, propanol, 2-methyl-1-butanol, ethyl acetate, methanol, isobutanol, 3-methyl-1-butanol, and isoamyl acetate. These compounds contribute directly to the aroma profile, either through specific notes or as precursors, such as acetaldehyde, which forms acetoin. Additionally, vinegars obtained from acetification in wooden barrels showed improved volatile profiles, with higher levels of most compounds except acetaldehyde.[53]

Kim *et al.*[54] applied a GC-MS-based metabolomic approach to monitor metabolic variations during alcoholic (FA) and acetic acid fermentation (FAA) phases. Principal component analysis (PCA), performed using SPSS Statistics 23.0, was applied to evaluate the variations in metabolite composition. The analysis revealed that fermentation-associated aroma (FAA) exerted a stronger influence on the levels of ethylene glycol, malonic acid, glutamic acid, glutaric acid, linoleic acid, butyric acid, and glycerol monostearate, whereas fermentation aroma (FA) predominantly affected **lactic acid** content (93.8% contribution compared to 6.2% from FAA). Conversely, FAA accounted for 97.0% of the variation in glutamic acid levels.

Furthermore, both strain type and fermentation temperature significantly modulated metabolite concentrations. These findings highlight the potential of this analytical approach for monitoring and controlling the formation of nutritional and bioactive compounds in vinegar.

Pinu *et al.*[55] demonstrated the effectiveness of a metabolomic approach in identifying a wide range of metabolites, some of which can be used to differentiate balsamic vinegar samples by origin and potential quality. Three GC-MS methods (methyl chloroformate (MCF), trimethylsilyl derivatization (TMS) and residual standard deviation (RSD) values were optimized for the analysis of commercial balsamic vinegar, demonstrating excellent reproducibility and linearity across all evaluated parameters. TMS was used to analyze sugars, alcohols, and amino sugar derivatives, while MCF targeted amino and non-amino organic acids, primary amines, and alcohols. Overall, over 1500 features were detected, with 123 metabolites precisely identified, including amino acids, carboxylic acids, sugars, fatty acids, vitamin, tripeptide and numerous aromatic compounds.[55]

Aromatic profile represents a fundamental sensory attribute of vinegars, alongside taste. Using a solid phase micro extraction before the GC-MS analysis Pizarro *et al.*[56] classified 43 commercial vinegar samples (white, red, balsamic, sherry, and cider) based on volatile profiles using HS-SPME-GC-MS coupled with stepwise linear discriminant analysis (SLDA). Only 14 characteristic peaks were sufficient to discriminate among cider, balsamic, sherry, and wine vinegars, whereas only three variables enabled differentiation between red and white wine vinegars. Cirlini *et al.*[57] employed HS-SPME/GC-MS to investigate the volatile profiles of Balsamic Vinegar of Modena (BVM**)** at different aging stages, achieving a minimum quality match of 98%. The volatile profile of younger BVM samples was dominated by higher levels of 3-methyl-1-butanol, 4-ethyl-phenol, and 3-methyl-1-butanol acetate, while aged BVM was characterized by increased concentrations of ethyl acetate, ethyl acetoacetate, furans, 2,3-butanediol, and 2,3-butanediol acetate.

One-way ANOVA, performed using SPSS Statistics 16.0, confirmed significant differences between the two groups. Given the legal restriction against the use of added natural or synthetic flavours in BVM, such analyses may serve as effective tools in detecting adulteration.[57]

High performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC) is a versatile separation technique suitable for compounds ranging from low to high molecular mass. Coupled with various detectors (UV-Vis, MS, NMR, Raman-FT), HPLC enables the separation, identification, and quantification of complex mixtures. Accurate identification of such constituents underpins the detection of adulteration and fraud, ensuring compliance with food authenticity regulations.[58]

Bakir *et al.*[12] employed HPLC with photodiode array detection (HPLC-PDA) to evaluate phenolic profiles in apple and grape vinegars. Results indicated high gallic acid content in grape vinegar, while p-hydroxybenzoic acid was absent in raw samples but appeared after decantation and filtering. In apple vinegar, a broader range of phenolics (catechin, syringic, caffeic, and p-coumaric acids) was detected, though their concentrations decreased after processing, unlike gallic and p-hydroxybenzoic acids. Spectrophotometric methods revealed significant phenolic changes during vinegar production. Data were statistically analyzed using SPSS and Tukey's test ($p < 0.05$).[12]

Similarly, Zong *et al.*[59] applied HPLC-PDA to determine organic acids in seven vinegars (white and black). Sample preparation involved dilution and filtration. Oxalic, lactic, succinic and D-pyroglutamic acids were present in black vinegars, while citric and propanoic acids were undetected. White vinegar contained only acetic acid. Lactic acid concentration correlated with vinegar quality, supporting HPLC-PDA as a reliable tool for authenticity assessment.[59]

Lin *et al.*[60] applied ion-exclusion HPLC to determine organic acids in various fruit vinegars (apple, sparkling apple, plum, condensed cranberry and grape). Major organic acids identified were acetic, ascorbic, citric, malic, and malonic acids, with acetic acid present at the highest concentration. Additionally, minor acids such as glutaric, oxalic, α-ketoglutaric, tartaric, lactic, pyruvic, succinic and gluconic were detected. These compounds originate either from raw materials or are formed during fermentation.[60]

CONCLUSION

This review proves that modern spectroscopic and chromatographic techniques provide powerful, complementary tools for the authentication and quality control of vinegar. NMR offers unmatched reproducibility and structural insight, while FTIR, UV-Vis, and NIR spectroscopy enable rapid screening. Chromatographic methods such as GC and HPLC remain essential for the detailed profiling of volatile and phenolic compounds, contributing to sensory characterization and traceability. When combined with chemometric modeling, these approaches enhance classification accuracy and detection of adulteration. The integration of these methods can support regulatory frameworks and industrial quality assurance protocols, ensuring consumer protection and product integrity. Future research should focus on standardizing multivariate models and exploring portable, real-time analytical platforms for in-line vinegar assessment.

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