

# Electroanalysis of Oenological Products for Fingerprinting: a Brief Overview

Pedro Fonseca Soares Rodrigues<sup>1</sup>, Paulo Fernando Guimaraes Morando Marzocchi Tierno<sup>2</sup>, Gustavo Augusto Couto Carvalho<sup>3</sup>

<sup>1</sup> Osasco Regional Hospital

335 Ari Barroso, Osasco, São Paulo State, 02675-031, Brazil

<sup>2</sup> Barueri Municipal Hospital

354 Rua Ângela Mirella, Vila Dom José/Boa Vista, Barueri, Brazil

<sup>3</sup> Beneficência Portuguesa São Paulo

637 R. Maestro Cardim, Bela Vista, São Paulo, 01323-001, Brazil

DOI: [10.22178/pos.102-21](https://doi.org/10.22178/pos.102-21)

LCC Subject Category: [RM1-950](#)

Received 21.02.2024

Accepted 25.03.2024

Published online 31.03.2024

Corresponding Author:

Pedro Fonseca Soares Rodrigues

[pedrodafonseca1992@gmail.com](mailto:pedrodafonseca1992@gmail.com)

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**Abstract.** The oenology industry faces challenges in maintaining wine authenticity amidst diverse environmental factors and production methods. Electroanalytical wine fingerprinting emerges as a promising solution to authenticate and validate products. Integrating electrochemical techniques with multivariate analysis enables rapid on-site testing, pattern recognition, and fraud detection. Emerging trends include miniaturisation, nanomaterial utilisation, and machine learning, driving innovation towards sustainable practices. This overview describes current trends and achievements in using electroanalysis to fingerprint oenological products.

**Keywords:** Oenological industry; Electroanalytical techniques; Wine fingerprinting; Authentication; Sustainability.

## INTRODUCTION

The oenology industry moves millions worldwide and encompasses many technologies based on traditional and contemporary production methods. From the grape harvest to commercialising finished products, wine commerce fosters jobs and revenue throughout its production chain. In this regard, the contribution of this industry to several populations around the world is remarkable, and wine has been intrinsically linked to regional tradition in numerous nations. Some noteworthy instances are the acknowledged viticulture heritage of European countries, as well as the contribution of awarded African [1], Asian [2], Oceanian [3] and American [4] wineries to the oenological scenario worldwide.

Overall, the organoleptic profile of wines is pretty variable according to edaphological and microclimate influences during grape growth. It has been reported that subtle variations in soil pH and humidity significantly affect wines' final flavour and aroma profile [5]. Several feedback

mechanisms depend on environmental conditions, as proven elsewhere [6, 7], regulating the production of secondary metabolites. Likewise, wine astringency is deeply affected by mechanic disturbances on the plant, hence the role of polyphenolic compounds such as tannins in hindering the animal foraging of plant tissues.

Although the chemical variability provided by plant secondary metabolism and its rich feedback mechanisms is noteworthy, the profound influence of fermentation and the production method must be mentioned on wine's chemical identity. Concerning the fermentation protocols usually employed by wine producers worldwide, selected strains or wild colonies are chosen according to historical factors and industrial scalability [8]. This last factor, in particular, considers various nutritional and microenvironmental requirements of the strains, which must be carefully addressed to standardise more significant production and avoid off-flavours that can tarnish wine quality. Fermentation is a critical point

in the production chain of many beverages and foods [9]. Regarding oenological products, it is usually conducted in two steps to improve the resulting aroma and taste.

The first fermentation encompasses the consumption of sugars by the microorganisms in the bioreactor and their controlled growth. Owing to the sudden spike in the amount of biomass in the must, there must be enough macro and micronutrients to sustain the balanced proliferation of selected strains and avoid those leading to foul aromas to thrive [10]. The first fermentation yields ethanol and several byproducts that contribute to wine flavour and mouthfeel, such as malic acid, whose dicarboxylic nature strongly contributes to acidity [11]. To hinder this sharp flavour, many producers follow on with a second fermentation step, wherein malic acid will undergo bioconversion to a monocarboxylic derivative, i.e., lactic acid. This process also contributes to managing the growth of microorganisms in the must and dramatically enhances the organoleptic complexity of oenological products. On the other hand, it lengthens the production time and raises the price of the final product.

Another highly influential factor in the construction of wine aroma is ageing. The controlled ageing of oenological products has been subject to extensive investigation, as it is considered a science and art [12]. In Italy, in particular, the culture of wine ageing led to the creation of a highly lucrative industry altogether, i.e., the balsamic vinegar (Italian: "aceto balsamico"), a Modena region staple in Emilia-Romagna. The ageing process involves many microenvironmental variables: temperature and aeration. The last, in particular, needs to be maintained at deficient levels, i.e., micro aeration, so that a finely controlled oxidation of phenolic compounds may lead to their polymerisation, dramatically changing the product's organoleptic features. Overall, aged wines are darker, paler and less astringent than younger ones; hence, the tannins that would otherwise promote astringency have now undergone polymerisation and are thence no longer able to extensively form complexes with salivary proteins and change oral osmolarity [13].

Considering the chemical complexity of wines and the variety of influences on the aroma and flavour of this product, legal frameworks were developed to ensure the authenticity of wines and link them to the particular organoleptic features consistent with specific production regions

and methods. In this regard, many countries adopted the denominations of controlled origin and indication of geographical origin to standardise the classification of oenological products according to their sourcing area [14]. Nevertheless, producers from the same region may have distinct products, and even the same producer may have contrasting wines according to crop and harvest variations, climate changes, and other factors. In this regard, the legal frameworks provide a valuable attempt to establish criteria to classify the authenticity of products but need to be backed by strategies that consider the variability within producing regions [15].

To all accounts, wine is a living product, which continues to evolve from the harvest of the grape until the very moment it is consumed. These characteristics make this beverage versatile and more likely to please more significant demographics, as showcased by the widespread commercialisation of oenological products worldwide and the multimillion market in which moves [16]. On the other hand, this also evidences that the sheer chemical variety of wines leads to a somewhat subjective evaluation of their characteristics, which may lead to fraud that can incur massive financial losses [17]. Several multimillion scam accounts involved making wine look like legitimate products, and many customers were defrauded [18]. In this regard, there is an urge to develop authentication tools capable of fingerprinting wines according to their geographical origin, grape variety, vintage, and other identification parameters.

## RESULTS AND DISCUSSION

*Fingerprinting of oenological products.* Due to wine industry revenue, the investigation of methods to authenticate and validate the origin of oenological products is a highly debated topic. To all accounts, the history and cultural tradition associated with particular wines dramatically raise their equity, leading to products that can reach millions in auctions. Conversely, the lack of portable technologies to verify the authenticity of these products in a point-of-need setting makes this industry very susceptible to scams [19].

Although numerous reports in the literature detail the metabolomic and chemometric profiling of wines and their identity according to highly relevant attributes such as geographical origin and grape variety, these technologies are still re-

stricted in terms of application [20]. Owing to the high cost and infrastructural requirements of mass spectrometry and spectroscopic devices, these techniques are relegated to costly oenological products. They are unlikely to be applied for mass testing. Moreover, the very requirement of refined and large analytical instruments hinders portability.

Regardless of the limitations in cost and portability, the analysis of wines by standard techniques significantly contributed to a better understanding of their chemical profiles and ways to classify their origin and quality according to the type and proportion of chemical constituents. Overall, wine authentication can be performed by assessing mineral content, volatile metabolites, phenolic constituents, amino acid profile, isotopic ratios, and NA analysis [20]. Indeed, several outreaches employed organic and mineral profiling with refined multivariate analysis and classification tools based on machine learning to establish objective thresholds for authenticity. Furthermore, some of these technologies even led to the development of innovative ways to assess wine quality.

*Electroanalysis for Wine Fingerprinting.* In recent years, electroanalytical techniques have emerged as promising tools for the authentication and characterising oenology products [21]. These techniques, which encompass a variety of methods, including voltammetry and electrochemical impedance spectroscopy through electrochemical sensors, offer several advantages over traditional analytical methods.

One of the critical advantages of electroanalysis is its simplicity and portability, making it suitable for on-site testing and rapid analysis [21]. Unlike mass spectrometry and spectroscopic techniques, which often require expensive instrumentation and trained personnel, electroanalytical methods can be implemented using compact and relatively inexpensive devices. Some of these platforms were reported to reach values lower than \$30 [22], highlighting their affordability in contrast with chromatographic devices. Another noteworthy point of electroanalysis is portability. This attribute is particularly advantageous for the wine industry, where performing real-time analysis directly in the vineyard or winery can facilitate quality control and, when performed at point-of-sale or auctions, could assist in fraud detection.

Voltammetry, in particular, has shown great promise for wine fingerprinting due to its ability to provide detailed information about the electrochemical behaviour of wine components [23]. By measuring the current response as a function of applied potential, voltammetry can identify and quantify specific electroactive species present in the sample [24]. This includes redox-active compounds such as polyphenols, which are crucial in determining wine quality and authenticity [25]. Polyphenols, abundant in various natural sources like fruits [26], vegetables [27], and beverages, have drawn considerable attention for their health benefits [28–30]. The structure of polyphenols has also been extensively used in the pharmaceutical industry as a building block for many medicines [31–33]. Voltammetry offers a promising method for their detection. In voltammetric analysis, polyphenols undergo oxidation or reduction at specific potentials [34], producing characteristic electrochemical signals. By monitoring changes in current or potential during these reactions, voltammetry enables precise and selective detection of polyphenols, even in complex matrices [35]. Its high sensitivity, rapidity, and relatively low cost make voltammetry a valuable tool for assessing polyphenol & antioxidant content in food, beverages, and biological samples, contributing to research in nutrition and medicine.

Moreover, voltammetric techniques can be easily adapted to target specific analytes of interest, allowing for selective detection of essential compounds associated with geographical origin, grape variety, and production methods [23]. For example, cyclic voltammetry can characterise phenolic compounds' redox behaviour ], while differential pulse voltammetry can enhance sensitivity and selectivity for trace analysis [37]. Furthermore, voltammetry has been proven to allow susceptible and selective compound detection and is increasingly used in chemical and pharmaceutical industries for quality control [31, 38–40] and environmental monitoring [41–43].

In addition to voltammetry, electrochemical sensors offer a promising approach to fingerprinting [33, 44]. These sensors, which typically consist of an electrode modified with a selective recognition element, can provide rapid and sensitive detection of target analytes. By leveraging the unique electrochemical properties of wine components, such as their redox activity and charge transfer kinetics, electrochemical sensors can

achieve high specificity and accuracy in wine analysis.

Electroanalytical techniques offer a powerful approach to wine fingerprinting, providing rapid, sensitive, and selective analysis of oenological products [45]. By leveraging the electrochemical properties of wine components, these methods can facilitate quality control, fraud detection, and traceability throughout the production chain. As such, electroanalysis holds great promise for ensuring the authenticity and integrity of wines in a global market characterised by increasing demand and diverse consumer preferences.

*Integration of Electroanalytical Techniques with Multivariate Analysis.* Integration with multivariate analysis methods is highly beneficial to fully exploit the potential of electroanalytical techniques for wine fingerprinting [46]. Multivariate analysis allows for the simultaneous interpretation of complex datasets containing information from multiple electrochemical measurements and complementary analytical techniques such as chromatography and spectroscopy.

Principal component analysis (PCA) is one of the most commonly used multivariate analysis techniques for wine authentication. PCA enables the visualisation of high-dimensional data by identifying patterns and correlations among variables, thereby reducing the dimensionality of the dataset while preserving the most relevant information [47]. By plotting samples in a lower-dimensional space defined by principal components (PCs), PCA can reveal similarities and differences between wine samples based on their electrochemical profiles. Several works have detailed the use of this technique to gather more insights into product development in several industries, such as unfermented consumer goods and pharmaceuticals [36, 48]. Furthermore, PCA can be combined with hierarchical clustering analysis (HCA) to classify wine samples into distinct groups or clusters based on their electrochemical characteristics. HCA utilises similarity measures to group samples with similar profiles together, providing insight into the underlying structure of the dataset. This approach can facilitate the identification of outliers and the detection of fraudulent or adulterated wines [49].

In addition to unsupervised methods like PCA and HCA, supervised classification techniques such as linear discriminant analysis and support vector machines can be employed to build predictive models for wine authentication. These

techniques leverage labelled training data to learn discriminative features that distinguish between authentic and counterfeit wines, allowing for highly accurate classification of unknown samples [50]. These artificial intelligence strategies have already established themselves in the medical and pharmaceutical industries, hence the possibility of thoroughly analysing complex datasets and extracting classification parameters that allow disease diagnosis [51, 52]. Moreover, feature selection algorithms can be used to identify the most informative electrochemical variables for wine fingerprinting. By prioritising variables that contribute the most to the discrimination between wine samples, feature selection can enhance the efficiency and interpretability of the analysis. This can lead to more robust and reliable authentication models capable of handling complex and heterogeneous datasets.

Integrating electroanalytical techniques with multivariate analysis methods represents a powerful approach to wine fingerprinting and authentication [23]. By combining electrochemistry's analytical capabilities with multivariate analysis's data processing capabilities, this integrated approach enables a comprehensive and objective assessment of wine authenticity, helping to ensure consumer confidence and preserve the reputation of the oenological industry.

*Emerging Trends in Electroanalytical Wine Fingerprinting.* As the field of electroanalytical wine fingerprinting continues to evolve, several emerging trends are shaping this research area's future. These trends encompass technological advancements, methodological innovations, and interdisciplinary collaborations aimed at addressing key challenges and expanding the capabilities of wine authentication and quality control.

a) Miniaturisation and Portable Devices. One prominent trend is the miniaturisation of electroanalytical devices and the development of portable instrumentation for on-site wine analysis. Miniaturisation enables the integration of multiple sensing elements into compact and user-friendly platforms, allowing for rapid and convenient testing in diverse settings such as vineyards, wineries, and distribution centres. Portable devices equipped with electrochemical sensors and microfluidic systems offer real-time monitoring capabilities, empowering stakeholders across the wine supply chain to make in-

formed decisions about product quality and authenticity [53].

b) Nanomaterials and Sensing Enhancements. Another trend involves the utilisation of nanomaterials and nanotechnology-based approaches to enhance the sensitivity, selectivity, and stability of electrochemical sensors for wine fingerprinting [54, 55]. Nanomaterials such as carbon nanotubes, graphene, metal nanoparticles, and molecularly imprinted polymers exhibit unique electrochemical properties that can be leveraged to improve the performance of sensors for detecting specific wine components. Nonetheless, all these techniques have been extensively subjected to proof-of-concept through applications in fermented and unfermented consumer goods [45], pharmaceutical [35, 56–58], medical [59] and chemical industries, which highlights the benefits of designing recognition surfaces to enhance analytical response.

c) Multimodal Sensing and Data Fusion. Multimodal sensing approaches, which combine multiple sensing modalities within a single analytical platform, are gaining traction for comprehensive wine analysis. By integrating electrochemical sensors with complementary techniques such as spectroscopy, chromatography, and mass spectrometry, multimodal sensing systems offer a holistic view of wine composition and quality [54]. Data fusion techniques enable the integration of information from different sensors and analytical methods, enhancing the robustness and accuracy of wine fingerprinting models. Multimodal sensing and data fusion facilitate synergistic analysis of wine samples, enabling comprehensive characterisation of complex matrices and identifying subtle variations associated with geographical origin, grape variety, and production methods.

d) Machine Learning and Artificial Intelligence. Advancements in machine learning and artificial intelligence are revolutionising the field of wine fingerprinting by enabling automated data analysis, pattern recognition, and predictive modelling. Machine learning algorithms such as deep learning, random forests, and support vector machines can extract meaningful insights from large datasets, identify relevant features, and classify wine samples based on their electrochemical profiles. These algorithms learn from historical data to develop robust authentication models capable of detecting anomalies, predicting wine quality, and identifying counterfeit products with high accuracy and efficiency [47, 60].

e) Interdisciplinary Collaborations and Knowledge Integration. Interdisciplinary collaborations between researchers in chemistry, material science, engineering, viticulture, and data science drive innovation in electroanalytical wine fingerprinting. By combining expertise from diverse disciplines, interdisciplinary teams can tackle complex challenges, develop novel sensing technologies, and elucidate fundamental relationships between wine composition, sensory properties, and production parameters. Knowledge integration across disciplines fosters a holistic understanding of wine authenticity and quality, paving the way for holistic solutions that address the multifaceted nature of wine analysis and authentication. In conclusion, the future of electroanalytical wine fingerprinting is characterised by ongoing advancements in miniaturisation, nanotechnology, multimodal sensing, machine learning, and interdisciplinary collaboration [17, 49, 54]. These trends promise to enhance the efficiency, accuracy, and accessibility of wine authentication and quality control, ultimately ensuring consumer confidence, safeguarding industry integrity, and promoting sustainability in the global wine market.

## CONCLUSIONS

The oenological industry stands at the intersection of tradition and innovation, where centuries-old winemaking practices merge with cutting-edge technologies to produce exceptional quality and character wines. Throughout this review, we have explored the intricate nuances of wine production on a high level, from the influence of terroir on grape composition to the role of fermentation and ageing in shaping wine aroma and flavour profiles. The organoleptic complexity of wines arises from many factors, including environmental influences, fermentation protocols, and ageing processes. As such, ensuring the authenticity and quality of wines presents a multifaceted challenge that requires a comprehensive understanding of their chemical composition and sensory attributes. In response to these challenges, electroanalytical wine fingerprinting has emerged as a powerful tool for authentication, quality control, and traceability in the wine industry. By leveraging electrochemical techniques such as voltammetry and impedance spectroscopy in customised electrochemical sensors, researchers and producers can obtain detailed insights into the composition and characteristics of

wines, enabling them to differentiate between authentic products and counterfeit imitations, as well as potentially harmful contaminants or adulteration. Moreover, integrating electroanalytical methods with advanced data analysis techniques such as multivariate analysis, machine learning, and blockchain technology has further enhanced the capabilities of wine fingerprinting, enabling real-time monitoring, predictive quality control, and transparent supply chain management.

Looking ahead, the future of electroanalytical wine fingerprinting holds immense promise, driven by ongoing advancements in sensor technology, data analytics, and interdisciplinary collaboration. By harnessing the power of electro-

chemistry and embracing innovative approaches to wine analysis and quality assurance, the industry can continue to uphold its reputation for excellence while meeting the evolving demands of consumers and regulatory authorities alike. In conclusion, electroanalytical wine fingerprinting represents a valuable tool for preserving the integrity and authenticity of wines, safeguarding the heritage of the oenological tradition, and ensuring a sustainable future for the global wine industry. Through continued research, innovation, and collaboration, we can unlock new possibilities in wine analysis and quality control, enriching the appreciation and enjoyment of this timeless beverage for generations to come.

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