



## Current state of electrochemical sensors in wine analysis for early diagnosis

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### ABSTRACT

The assurance of the quality of a wine, both from the point of view of tasting and food safety, and its compliance with current regulations have led to the development of electrochemical sensors for the analysis of several analytes during the last five years. On one hand, the content of glucose, alcohol, acetaldehyde, organic acids, phenolic compounds, sulphur dioxide, mercaptans, biogenic amines, food preservatives and some yeast can affect the stability and the organoleptic properties. On the other hand, some of them can cause harmful effects on the health of the consumer. So, early diagnosis is extremely important in wine samples. Enzymatic and non-enzymatic electrochemical sensors, which generally uses nanostructured materials or chemically modified electrodes to enhance both sensitivity and selectivity, have been reported with this aim. The ability of these types of sensors to be miniaturized and their ease of use make them ideal candidates for point-of-care devices.

### 1. INTRODUCTION

The wine sector is strategic for many regions, not only in economic terms but also socially due to the amount of labour it generates. The elaboration of high-quality products, which are capable of standing out in a highly competitive market, is of vital importance to consolidate its excellent international reputation and further improve its prospects. In this way, parameters related to wine composition, namely alcoholic strength, density, total acidity, volatile acidity, pH, sugars, sulphur dioxide or L-malic acid, have usually been studied in oenology laboratories. The actual wine market, increasingly understood and demanding, and the current oenological practices have led these analyses towards targets not only related to the quality of the product and its compliance with current regulations from a tasting point of view, but also from food safety, considering the hazard of many of them [1,2]. As an alternative to the official analytical methods established with these purposes, that is refractive index, enzymatic colorimetric kits, spectrophotometric methods or HPLC, electrochemical sensors provide fast, accurate and low cost analysis that would help winemakers to determine the final flavour and quality of a wine [3]. In this way, some of the problems related to these traditional analytical techniques, such as their high instrumental cost, operational capacity and long-time of analysis, can be

solved. In addition, these techniques, specially voltammetry and amperometry, enable the development of miniaturized systems, mostly using screen-printed based sensors and biosensors, without interfering in the sensitivity of the analysis [4]. In fact, hundreds of works have been devoted to the electrochemical detection of analytes of interest in wines for early diagnosis. Special attention has been paid in recent years to fine-tuning electrochemical sensors for the selective determination of glucose, ethanol, acetaldehyde, organic acids, polyphenols, sulphur compounds, biogenic amines, mycotoxins, and, to a lesser degree, allergenic proteins, food preservatives, yeast or pesticides. Thus, this work reviews the different designs of transducer systems used in these new applications during the last 5 years, including disposable devices orientated towards point-of-care analysis (Table 1). Regarding their selectivity and sensitivity, a substantial improvement has been observed by means of the incorporation of bioreceptors, including enzymes, antibodies and aptamers, and/or nanomaterials, polymers and mixtures of both. Among the possible modifications of these electrochemical sensors and biosensors, the use of nanostructured materials appears as the most interesting alternative in the analysis of different compounds in wine, due to their excellent properties related to their high surface area and conductivity (Fig. 1), regardless of their nature. In this way, a homogeneous distribution between the use of carbon and metal oxides nanomaterials, as well as metallic nanoparticles has been found (Fig. 2).

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## ABBREVIATIONS

(E <sub>ap</sub> )	Applied potential
(CNTs)	Carbon nanotubes
(CPEs)	Carbon paste electrodes
(COOH-MWCNTs)	Carboxylated multiwalled carbon nanotubes
(LOD)	Detection limit
(GCE)	Glassy carbon electrode
(ITO)	Indium tin oxide
(NPs)	Nanoparticles
(NAD <sup>+</sup> )	Nicotinamide adenine dinucleotide
(NADH)	Nicotinamide adenine dinucleotide reduced disodium salt
(MIP)	Molecularly imprinted polymer
(E <sub>pOx</sub> )	Oxidation peak potential
(PEDOT)	Poly(3,4-ethylenedioxythiophene)
(E <sub>pRed</sub> )	Reduction peak potential
(rGO)	Reduced graphene oxide
(SPCEs)	Screen-printed carbon electrodes
(SPAuEs)	Screen-printed gold electrodes

## 2. APPLICATION OF ELECTROCHEMICAL SENSORS IN WINE ANALYSIS

Enzymatic and non-enzymatic electrochemical sensors have lately been reported for the analysis of the content of glucose, alcohol, acetaldehyde, organic acids, phenolic compounds, sulphur compounds, biogenic amines, mycotoxins, allergens, food preservatives, some yeast or pesticides that can affect the stability and the organoleptic properties of a wine. These works have then been summarized in the following sections according to the target analyte.

## 2.1. GLUCOSE

The amount of sugar influences considerably the growth of yeasts responsible for the fermentation process, affecting the fermented sugar to the ethanol content and the non-fermented sugar to the sweetness of wines [5]. Therefore, the analysis of glucose in wine is extremely important, both in the final product and during the different stages of the fermentation process, in order to help producers to take corrective actions to avoid slow or stagnant fermentations, or even bottle fermentations. In this way, sensitive biosensors have been traditionally used for the accurate and sensitive analysis of glucose, based on the immobilization of glucose oxidase on gold [41] and sonogel-carbon electrodes [42] previously modified by conducting polymers. The combination of this enzyme with poly(3,4-ethylenedioxythiophene) (PEDOT) [41] or gold nanoparticles (AuNPs) modified polyaniline [42] has led to the amperometric (Applied potential (E<sub>ap</sub>) of  $-0.20$  V in phosphate buffer solution pH 7, detection limit (LOD) of  $41 \mu\text{M}$ ) and cyclic voltammetric (Reduction peak potential (E<sub>pRed</sub>) at  $-0.45$  V in phosphate buffer solution pH 6.8, LOD of  $56 \mu\text{M}$ ) analysis of glucose in wine, respectively. Selectivity and electrical properties have been merged to achieve a considerable improvement of the LOD of the biosensors in comparison with the previously described ones based on more complex architectures.

Enzyme degradation limits the enzyme-based biosensors lifetime. Thus, long-term stability non-enzymatic amperometric sensors have also been developed for analysis of sugar content. A graphene-like material (MoS<sub>2</sub>) was used as support for the synthesis of NiCo<sub>2</sub>O<sub>4</sub> nanorods by an easy ionothermal method using deep eutectic solvents for the modification of a glassy carbon electrode (GCE). The constructed sensor was satisfactory applied in the analysis of glucose in red wines (E<sub>ap</sub> of  $+0.57$  V in a  $0.1$  M NaOH solution, LOD of  $0.23 \mu\text{M}$ ). The modification by metal oxides nanomaterials considerably improves the electronic properties of

the sensor [43]. Very sensitive and stable glucose sensors based on the deposition of Cu<sub>x</sub>Co<sub>y</sub>O with variable Co/Cu atomic ratio on commercial carbon fibre paper substrate have been reported as well (E<sub>ap</sub> of  $+0.5$  V in a  $0.1$  M NaOH solution, LOD of  $0.1 \mu\text{M}$ ) [7]. Moreover, screen-printed carbon electrodes (SPCEs) modified with cobalt phthalocyanine, graphene and ionic liquid composite have also allowed the analysis of glucose with high sensitivity and selectivity (E<sub>ap</sub> of  $+0.7$  V in a  $0.1$  mg mL<sup>-1</sup> NaOH solution, LOD of  $0.64 \mu\text{M}$ ) [6].

SPCEs have also been selected for the joint determination of glucose and fructose in wine. The modification of the working electrode was carried out in this case with nitrogen-doped graphitic carbon-coated Cu/Co/CoO NPs, showing even a better LOD using a lower working potential (E<sub>ap</sub> of  $+0.4$  V in a  $0.2$  M NaOH solution, LOD of  $0.2 \mu\text{M}$ ). This ultrasensitivity was related to the catalytic effect and the synergy between the different modification materials [5].

The high sensitivity and selectivity, but also the low price and disposability of the non-enzymatic devices [5–7], make them candidates for on-site monitoring analysis during fermentation processes, that is, suitable point-of-care systems.

## 2.2. ALCOHOL CONTENT

Although many alcohols appear during the production process of a wine, only a few of them have an appropriate concentration to affect its characteristics. Among them, ethanol, which is the main compound generated during the wine fermentation process, can negatively affect yeast growth when found in high concentrations [44,45]. The analysis of this compound in wine has been carried out using both enzymatic and non-enzymatic systems. In this way, a photoelectrochemical miniaturized biosensor based on the immobilization of the enzyme alcohol dehydrogenase on a SPCE, previously modified with a mixture of carbon black, TiO<sub>2</sub> and KuQuinone, has been used for the successful analysis of ethanol in white wine samples. The registered analytical response was the amperometric signal obtained after the irradiation of the working electrode with LED laser light (530 nm). The presence of carbon black substantially improved the photoelectrochemical response of the sensor due to its high conductivity (E<sub>ap</sub> of  $+0.4$  V in Tris buffer solution pH 8.8, LOD of  $62 \mu\text{M}$ ) [8]. Recently, a non-enzymatic sensor using screen-printed gold electrodes (SPAuEs) has been developed for the flow injection amperometric analysis of ethanol vapours in wine. A room temperature ionic liquid embedded in a paper crown was placed over the electrodic system. This disposable system allowed the direct amperometric analysis of ethanol in a home-made closed gas cell using nitrogen as the carrier gas and a gas-tight microsyringe for the injection of the gas sample (E<sub>ap</sub> of  $+0.8$  V, LOD of  $0.55\%$  v/v) [9].

Glycerol is another of the alcohols whose concentration influences the characteristics of a wine, contributing considerably to both flavour and viscosity. The presence of high amounts of this alcohol in wine is usually assigned to deterioration processes of raw materials and alterations in the production process, that even include the adulteration of the sample [44,46]. The rapid and sensitive determination of this compound has been performed using gold modified electrodes with three-dimensional nanoporous gold using glycerol kinase and glycerol-3-phosphate oxidase as biorecognition elements, following the oxidation peak obtained by cyclic voltammetry (Oxidation peak potential (E<sub>pOx</sub>) at  $+0.2$  V in phosphate buffer solution pH 7, containing  $20$  mM Adenosine triphosphate,  $8$  mM ferrocene methanol, and  $8$  mM MgCl<sub>2</sub>, LOD of  $77.08 \mu\text{M}$ ), according to the mechanism shown in Fig. 3. The use of nanoporous gold avoids successfully inactivation and denaturation of the enzymes, so this biosensor enables to perform diagnostic tests by frequent and consistent measurements that can provide immediate information, being considered as well as a potential point-of-care alternative in food analysis [46].

The simultaneous analysis of both alcoholic species has been carried out even in the presence of glucose using non-enzymatic systems based on the modification of a GCE with nickel NPs on nitrogen-doped

graphene. The modified sensor showed higher electrocatalytic activity compared with the bare GCE in the amperometric detection of both ethanol ( $E_{ap}$  of +0.55 V in 0.5 M NaOH solution, LOD of 30  $\mu\text{M}$ ) and glycerol ( $E_{ap}$  of +0.95 V in 0.5 M NaOH solution, LOD of 100  $\mu\text{M}$ ) [45].

### 2.3. ALDEHYDES

The presence in wine of reactive carbonyl compounds such as aldehydes is frequent due to different enzymatic processes occurring during fermentation and storage steps. Acetaldehyde, which constitutes more than 90% of a wine's aldehyde content [47], has been identified as an indicator of wine quality since it has a negative impact on colour, stability and aroma of wines when it is present in high concentrations. Moreover, it presents genotoxic and neurotoxic effects, having been classified as a carcinogenic compound whose determination in wine is really important [10,11,48]. Thus, different amperometric aldehyde dehydrogenase modified SPEs have then been developed for the early detection of this compound [10,11]. This enzyme was immobilized together with diaphorase for the development of a two-enzyme sensor

system which used the combination of electrochemistry and UV-vis spectroscopy in a sole experiment. Aldehyde dehydrogenase catalyses the oxidation of the aldehyde to carboxylic acid using nicotinamide adenine dinucleotide hydrate ( $\text{NAD}^+$ ) as a cofactor and, subsequently, diaphorase reoxidises the cofactor to nicotinamide adenine dinucleotide reduced disodium salt ( $\text{NADH}$ ) and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  to  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , which is finally reoxidised on the electrode surface at +0.4 V in 0.1 M phosphate and 0.1 M KCl buffer solution (pH 8), according to the scheme shown in Fig. 4.

A spectroscopic detection was simultaneously carried out based on the UV-vis signals obtained at 310 and 420 nm for  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . The combination of both analytical techniques allowed the autovalidation of the analysis in a single experiment [10]. The  $\text{NADH}$  formed during the catalysed enzymatic reaction described above can be also followed by amperometric measurements using SPCEs modified with carbon nanotubes (CNTs) and a new recombinant aldehyde dehydrogenase enzyme ( $E_{ap}$  of +0.5 V in phosphate 0.1 M solution, LOD of 10  $\mu\text{M}$ ). This new cold-active bacterial aldehyde dehydrogenase showed a higher specificity towards acetaldehyde than the ones obtained from other sources

**Table 1**  
Disposable electrochemical devices used in wine analysis.

Analyte	Working electrode	Modification material	LOD	Ref.
Glucose	SPCE	Nitrogen-doped graphitic carbon-coated Cu/Co/CoO NPs	0.20 $\mu\text{M}$	[5]
		Cobalt phthalocyanine, graphene and ionic liquid composite	0.64 $\mu\text{M}$	[6]
Ethanol	Carbon fiber electrode	$\text{Cu}_x\text{Co}_y\text{O}$ with variable Co/Cu atomic ratio	0.10 $\mu\text{M}$	[7]
	SPCE	A mixture of carbon black, $\text{TiO}_2$ and KuQuinone and alcohol dehydrogenase enzyme	62 $\mu\text{M}$	[8]
Acetaldehyde	SPAuE	RTIL:1-butyl-3-methylimidazolium hydrogen sulfate	0.55% v/v	[9]
	SPCE and SPAuE	Aldehyde dehydrogenase and diaphorase enzymes	–	[10]
Lactate	SPCE	CNTs and Aldehyde dehydrogenase enzyme	10 $\mu\text{M}$	[11]
	SPCE	PtNPs and Lactate oxidase enzyme	0.75 $\mu\text{M}$	[12]
		A mixture of PtNPs and PdNPs and Lactate oxidase enzyme	0.1 $\mu\text{M}$	[13]
		Reduced graphene oxide and $\text{N}_3\text{N}'$ -Bis(3,4-dihydroxybenzylidene)-1,2-diaminobenzene hybrid nanomaterials and Lactate oxidase enzyme	2.9 $\mu\text{M}$	[14]
Gallic acid	SPCE	–	32 $\mu\text{M}$	[16]
		$\text{Co}_3\text{O}_4$	4.8 nM	[17]
Gentisic acid	inkjet-printed graphene electrode	Amino-montmorillonite	330 nM	[18]
Caffeic acid	SPCE	NiWO <sub>4</sub> NPs and PEDOT–polystyrenesulfonate nanocomposites	74 nM	[19]
		Nafion/Lacasse/graphene nanoplatelets and MnO <sub>2</sub> NPs	1.9 $\mu\text{M}$	[20]
Phenolic compounds	SPCE	A 3D-printed structure combined with a microfluidic system	0.8 $\mu\text{M}$	[4]
		CNTs	–	[21]
<i>Trans</i> -resveratrol	SPCE	Polypyrrole	–	[22]
Quercetin	SPCE	Mesoporous carbon	473 nM	[23]
4-ethylphenol	SPCE	–	51.6 nM	[2]
4-ethylguaiacol	SPCE	$\text{C}_{60}$	400 $\mu\text{gL}^{-1}$	[24]
$\text{SO}_2$	SPCE	$\text{C}_{60}$	200 $\mu\text{gL}^{-1}$	[25]
	SPCE coupled with a porous oxygen filter	–	–	[26]
Planar gold sensor chip	Screen-printed graphene electrode	Polyaniline	6 $\mu\text{gL}^{-1}$	[27]
		Teflon gas diffusion membrane.	1.5 $\text{mgL}^{-1}$	[28]
$\text{SO}_3^{2-}$ ions	Nanoporous gold microelectrode	–	0.34 $\mu\text{M}$	[29]
Mercaptans	SPCE	AuNPs	1.6 $\mu\text{gL}^{-1}$	[30]
Ethanedithiol	SPCE	Phthalocyanine	12.5 $\mu\text{gL}^{-1}$	[31]
Ovalbumin	SPCE	MIP based on the electropolymerization of polydopamine	0.46 $\text{mgL}^{-1}$	[32]
			$\text{mgL}^{-1}$	
Lysozyme	SPAuE	AuNPs	0.32 $\text{mgL}^{-1}$	[33]
	SPCE	Poly-L-lysine	2 pM	[34]
<i>Saccharomyces cerevisiae</i>	SPCE	Protofibril and graphene oxide	1 nM	[35]
		Graphene oxide functionalized with propionic acid and polyclonal antibody	4 CFU $\text{mL}^{-1}$	[36]
<i>Brettanomyces bruxellensis</i>	SPCE	Core-shell $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ superparamagnetic NPs modified with anti- <i>Brettanomyces bruxellensis</i>	8 CFU $\text{mL}^{-1}$	[37]
<i>Botrytis cinerea</i>	SPAuE	–	0.5 U $\text{mL}^{-1}$	[38]
2,4,6-Trichlorophenol	SPCE	Double perovskite oxide $\text{Gd}_2\text{NiMnO}_6$ nanostructures	23 nM	[39]
Iron	SPCE	Deferoxamine	0.87 $\text{mgL}^{-1}$	[40]

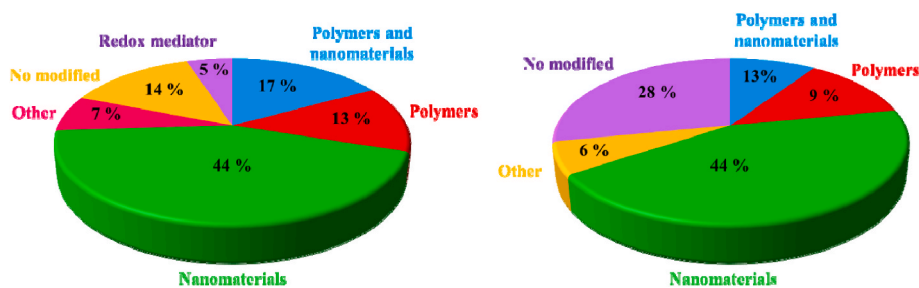


Fig. 1. Percentage distribution diagram of materials used in the development of electrochemical sensors (left) and biosensors (right) in wine analysis.

[11]. Non-enzymatic devices have also been employed in this kind of analysis, following the decrease in the differential pulse voltammetric signal recorded by copper nitroprusside modified GCEs in presence of acetaldehyde. The developed sensor showed good selectivity towards acetaldehyde in both synthetic and red wine samples and even a higher sensitivity than the enzymatic sensors described above ( $E_{pOx}$  at  $-0.03$  V in phosphate buffer solution pH 7.4, LOD of  $0.41$   $\mu$ M) [48].

#### 2.4. ORGANIC ACIDS

The analysis and control of the amount of organic acids in wine samples is relevant in each of the stages involved in a winemaking process, since, for example, acidity is one of the main factors that affects the flavour and aroma of a wine. Among them, lactic acid is of analytical interest since also plays an important role in wine stabilization during storage, preventing the growth of [13,49]. Thus, several lactic electrochemical biosensors have recently been described based on the immobilization of lactate oxidase [12–14,49] or lactate dehydrogenase [15] on different electrode surfaces.

Lactate oxidase biosensors are usually based on the direct electrochemical detection of the  $H_2O_2$  enzymatically produced (Fig. 5). This analytical response is often improved by means of the modification of the electrode surface with materials that exert a catalytic effect on the redox reaction, including metallic ones [12,13]. The amperometric analysis of lactate has been performed at lower potential with higher selectivity when lactate oxidase was immobilized onto PtNPs modified SPCEs ( $E_{ap}$  of  $+0.15$  V in phosphate buffer solution pH 7.0, LOD of  $0.75$   $\mu$ M) instead of onto SPCEs ( $E_{ap}$  of  $+0.6$  V in phosphate buffer solution pH 7.0, LOD not shown) [12] or onto a mixture of PtNPs and PdNPs modified SPCEs ( $E_{ap}$  of  $+0.6$  V in phosphate buffer solution pH 7.2, LOD of  $0.1$   $\mu$ M) [13]. Hybrid nanomaterials consisted of reduced graphene oxide and  $N,N'$ -Bis(3,4-dihydroxybenzylidene)-1,2-diaminobenzene have also been used in the modification of SPCEs for the development of amperometric transducers ( $E_{ap}$  of  $+0.1$  V in phosphate buffer solution pH 7.0, LOD of  $2.9$   $\mu$ M) for the analysis of lactate in white wine samples. In this case, the selective analysis was achieved due to the electron acceptor function of the quinone/hydroquinone moiety in the modified SPCEs, although the sensitivity was lower than that obtained using the metallic NPs modified electrodes described above [14]. The addition of a second enzyme, such as horseradish peroxidase, can also significantly improve the selectivity of the biosensor, although complicates the process for preparing working electrodes and, moreover, decreases their stability. To avoid these drawbacks, synthesized peroxidase-mimetic nanoenzymes, lower in cost and less affected by the nature of the surrounding environment, have been developed. Carbon microfibers modified with hemin and AuNPs or PtNPs, generated as synthetic enzymes, have been deposited on a graphite-rod working electrode to which the lactate oxidase enzyme was finally incorporated. PtNPs modified transducers resulted preferable for the amperometric analysis of lactate ( $E_{ap}$  of  $-0.1$  V in  $50$  mM phosphate buffer with  $100$  mM  $Na_2SO_4$  pH 6.8 solution, LOD of  $2.0$   $\mu$ M), being selected for the real samples testing [49].

Lactate dehydrogenase-based biosensors, which are usually based on

the electrochemical detection of NADH as co-product of the enzymatic reaction (Fig. 6), present important advantages related to a lower cost, higher stability and better substrate recycling than lactate oxidase-based biosensors [15].

The advantages of dehydrogenase-based electrochemical systems can be increased through the use of nanomaterials for the modification of the surface of the working electrode. Thus, the analysis of lactic acid has been carried out successfully by using modified SPCEs with a ternary composite based on a poly(allylamine) hydrochloride, reduced graphene oxide and AuNPs where lactate dehydrogenase was crosslinked. The developed amperometric biosensor ( $E_{ap}$  of  $+0.5$  V in  $0.1$  M phosphate buffer pH 7.5 solution containing  $8$  mM  $NAD^+$ , LOD of  $1$   $\mu$ M) was extremely robust being stable for seven weeks [15].

Nonenzymatic sensors, with higher stability and repeatability than enzymatic biosensors, have recently been described for the determination of lactic acid content in different wine samples by cyclic voltammetry based on the modification of GCEs with different nanomaterials. Thus, the use of cobalt polyphthalocyanine/carboxylated multiwalled carbon nanotubes (COOH-MWCNTs) [50,51] has improved the sensitivity of these sensors ( $E_{pRed}$  at  $-0.1$  V in phosphate buffer solution pH 4.0, LOD of  $2.0$   $\mu$ M) in relation to the ones modified only by NiO NPs ( $E_{pOx}$  at  $+0.47$  V in  $0.1$  M NaOH solution, LOD of  $5.7$  mM) [52].

The analysis of tartaric acid in wine is also interesting considering its important applications in wine industry as acidification and antioxidant agent, and even due to its influence in the stability and the organoleptic features of a wine. Its detection in red wines samples has been achieved by cyclic voltammetry using modified GCEs with copper, polytryptophan and Nafion ( $E_{pOx}$  at  $0$  V approx. in phosphate buffer solution pH 3, LOD of  $0.5$  mM) [53]. Besides, this carboxylic acid has also been analysed considering the electrocatalytic activity of a cobalt phthalocyanine modified carbon paste electrode (CPE) by square wave voltammetry, detecting lower concentrations and avoiding interferences from other organic acids in wines samples from different origins and types of grapes, thanks to the use of multiway calibrations ( $E_{pOx}$  at  $+1.15$  V in acetic acid/sodium acetate buffer solution pH 4.5, LOD of  $7.29$   $\mu$ M) [54].

Malic acid is consumed by lactic bacteria during the malolactic fermentation process carried out mainly by red wines to soften and stabilize them microbiologically. So, this acid is considered as a wine component of analytical interest due to its contribution to the taste,

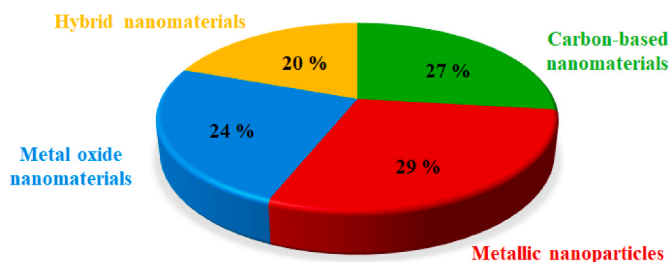


Fig. 2. Percentage distribution diagram of nanomaterials used in the development of electrochemical sensors and biosensors in wine analysis.



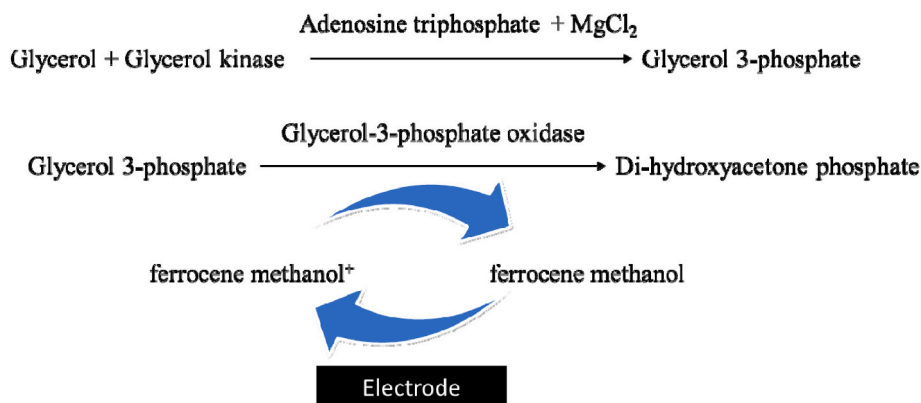


Fig. 3. Schematic diagram of the electrochemical signal obtained for glycerol detection using glycerol kinase/glycerol-3-phosphate oxidase-based biosensors [46].

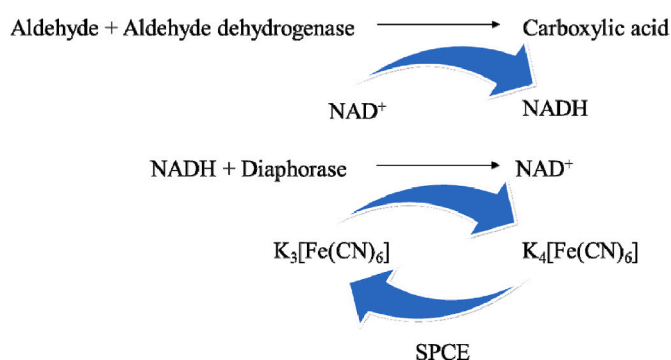


Fig. 4. Schematic diagram of the electrochemical signal obtained for aldehyde detection using aldehyde dehydrogenase/diaphorase-based biosensors [10].

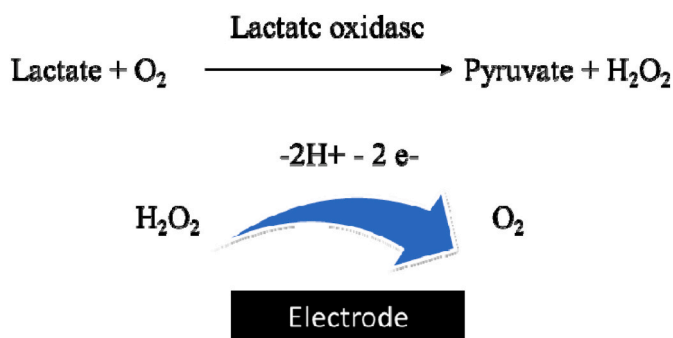


Fig. 5. Schematic diagram of the electrochemical signal obtained for lactic acid detection using lactate oxidase-based biosensors [12].

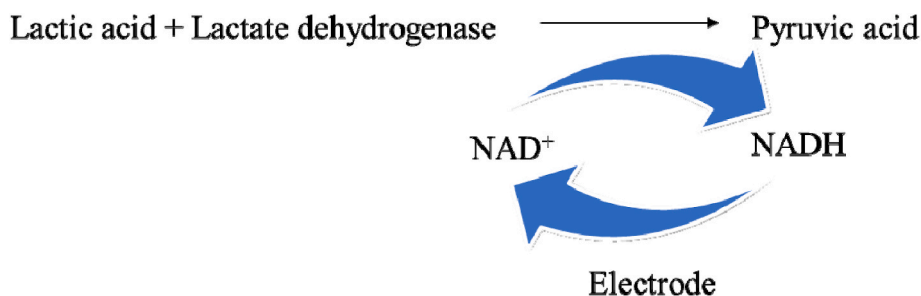


Fig. 6. Schematic diagram of the electrochemical signal obtained for lactic acid detection using lactate dehydrogenase-based biosensors [15].

ageing and stability of the finished wine [55]. A chiral selector sensor that is able to distinguish between malic acid enantiomers by differential pulse voltammetry has recently been described, using a CPE modified with CNTs and different carbon matrices. Accordingly, the sensor resulted selective toward D-malic acid when carbon nanopowder or graphene were used, while the use of graphite gave rise to a L-malic selective sensor [56].

Ascorbic [57] and glutamic acids [51], both compounds related with the aging process of wine rice samples, are often analysed in wine as well. Ascorbic acid is also added as food preservative and is regulated as oenology practice. Thus, GCEs modified with conducting polymer nanocomposites based on poly neutral red and copper have been used for the development of glutamic acid sensors. The analysis was performed by cyclic voltammetry in a phosphate buffer solution pH 4.0 (LOD of 3.0  $\mu\text{M}$ ) [51]. A higher sensitivity was achieved using a combination of the conducting polymer acid chrome blue K and AuNPs using GCEs as well. This great sensitivity for the determination of ascorbic acid was due to the high electrocatalytic effect and electrical conduction that produces the combination of both modifier materials using differential pulse voltammetry as the analytical technique ( $E_{\text{pRed}}$  at approx + 0.3 V in phosphate buffer solution pH 4.0, LOD of 2.0  $\mu\text{M}$ ) [57].

The total acid content in wine has also deserved attention. A portable voltammetric device, based on a 3-electrode configuration together with a potentiostat, an electrochemical cell and a monitor, has been developed for this aim. The reduction peak of 3,5-di-*t*-butyl-1,2-benzoquinone (Fig. 7), observed at  $-0.1$  V using a plastic formed carbon working electrode by linear sweep voltammetry in ethanol containing 0.1 M  $\text{LiClO}_4$  solution, shifts to more positive values in the presence of both organic and inorganic acids, giving a prepeak suitable for the analysis of the total acid content. Low sample volumes and short analysis times are required. These properties together with their ease handling have made them suitable for point-of-care applications in food analysis [58].

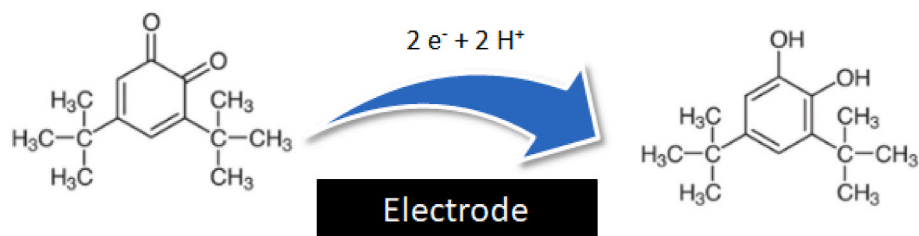


Fig. 7. Scheme of the electrochemical reduction of 3,5-di-t-butyl-1,2-benzoquinone [58].

The analysis of organic acids, such as tartaric [53], ascorbic [57,59], lactic [51], glutamic [51] and gallic [59] acids in wines, together with other species such as glucose [51,53], or tyrosine [57,59], has also been used in the development of voltammetric electronic tongues based on multivariate analysis methods to realize wine classifications based on their origin or aging. Thus, highly-selective sensors based on Nafion/poly-tryptophan/Cu/GCE and polyaspartic acid/NiO/GCE for tartaric acid and glucose detection, respectively, combined with a propagation neural network procedure have been used for the discrimination of different wines according to their origin [53]. In the same way, both ascorbic and glucose contents have been analysed together with tyrosine, using a polymer acid chrome blue K/AuNPs/GCE, polymer aspartic acid/PtNPs/GCE and polymer sulfanilic acid/AuNPs/GCE [58]. The control of the three analytes content allowed to carry out a wine age classification with multi-frequency rectangle pulse voltammetry and multi-frequency staircase pulse voltammetry, selected as the analytical techniques, and principal components, locality preserving projections and differential financial analysis for data analysis, being the later the most adequate for wine classification. The presence of lactic acid, glutamic acid and glucose can also be related with the aging process rice wines. Thus, three different sensors have been constructed based on the modification of a GCE with cobalt polyphthalocyanine/COOH-MWCNTs, poly neutral red/Cu/and poly aspartic acid/NiO nanocomposites for the selective determination of lactic acid, glutamic acid and glucose, respectively. The aging information obtained by these systems by means of cyclic voltammetry was analysed by multivariate techniques, namely principal components, locally linear embedding, and locality preserving projection, which offered the best results to classify the wine samples [51].

## 2.5. PHENOLIC COMPOUNDS

The presence of phenolic compounds affects colour, astringency, bitterness, and antimicrobial properties of wines, playing then an important role in their organoleptic properties and, therefore, in their quality and stability [1,3,21,60,61]. Much of the oxygen absorbed by must or wine is consumed in oxidative reactions with phenols [21,47], whose content is considered to be a good indicator of the antioxidant capacity [3,61,62]. These antioxidants, capable of reducing lipid oxidation, could be responsible for protective effects against cardiovascular diseases and cancer in wine consumers [1]. Accordingly, the physiological effects of a wine have been demonstrated above all through the content of phenolic compounds, usually reported for a reference polyphenol [61]. Thus, the electrochemical determination of non-flavonoids (gallic acid, vanillic acid, sinapic acid, syringic acid, caffeic acid, 4-ethylphenol, 4-ethylguaicol, *trans*-resveratrol), anthocyanins (e.g., malvidin-3-glucoside), flavonols (quercetin, rutin), flavanols (catechol derivatives), and many others polyphenols has continued to be extremely active in recent years to assess routinely their presence in wine for characterization and classification purposes.

Gallic acid exhibits strong antioxidant properties, as well as anti-cancer, anti-aging and bacteriostatic effects. The determination of this benzoic acid in wine has been considered essential and, thus, different electrochemical strategies have been attempted, using mainly

voltammetric techniques. This acid shows a first oxidation peak attributed to the oxidation of the *ortho*-diphenol group by a two steps procedure to quinone, and a second one corresponding to the third phenol group [21]. Badea et al. [16] describe electroanalytic devices based on screen-printed carbon sensors coupled with a mobile PalmSens device using differential pulse voltammetry for gallic acid determination ( $E_{pOx}$  at +0.17 V in phosphate buffer pH 7, LOD of 32  $\mu$ M), highlighting their potential use in point-of-care applications or in rapid food analysis control, without pre-treatment of surface electrodes. Gallic acid can also be oxidized using different nanostructured modified transducers with improved sensitivity and selectivity compared to that of bare electrodes: CPEs modified by trihydrate alumina ( $E_{pOx}$  at +0.7 V in 0.1 M HCl, LOD of 0.8  $\mu$ M) [62], nanographene oxide-SiO<sub>2</sub> NPs ( $E_{pOx}$  at +0.45 V in phosphate buffer pH 2, LOD of 2.1  $\mu$ M) [63], ZrO<sub>2</sub>NPs ( $E_{pOx}$  at +0.5 V in phosphate buffer pH 2, LOD of 0.1  $\mu$ M) [64] or Co<sub>3</sub>O<sub>4</sub>NPs ( $E_{pOx}$  at +0.55 V in phosphate buffer pH 2, LOD of 0.1  $\mu$ M) [65]; GCEs coated by ZnO ( $E_{ap}$  of +0.48 V in phosphate buffer pH 3, LOD of 20 nM) [66] or by Au nanospheres/Mo<sub>3</sub>Se<sub>4</sub>/β-Ni(OH)<sub>2</sub> ( $E_{pOx}$  at +0.47 V in phosphate buffered saline pH 2, LOD of 5 nM) [67] and carbon ceramic electrodes modified with reduced graphene oxide (rGO) by a via sol-gel method ( $E_{pOx}$  at +0.57 V in Britton Robinson buffer pH 2, LOD of 86.7 nM) [68]. Poly L-methionine electropolymerized onto CNTs modified GCEs have also been reported for gallic acid oxidation ( $E_{pOx}$  at +0.5 V in Britton Robinson buffer pH 2.2, LOD of 3.1 nM). The combination of polymers and nanomaterials as modifiers has showed to have a synergistic effect that has led to an increase in the catalytic activity of the surface, achieving a better LOD for gallic acid [69].

Genticic acid is also a hydroxybenzoic acid spread out in red and white wines. Dongmo et al. [18] developed a sensor based on an amino-montmorillonite-modified inkjet-printed graphene electrode for the voltammetric determination of this acid ( $E_{pOx}$  at +0.23 V in Britton Robinson buffer pH 2, LOD of 330 nM). This technique can allow the preparation of miniaturized and mass-produced organoclays sensors, with enhanced properties as mechanical stability, large surface area, microporosity and chelating ability for various analytical applications.

Hydroxycinnamic acid derivatives are also an important class of polyphenolic compounds that receives a significant importance in quality control analysis of wines. Thus, the antioxidant capacity of different wines has also been quantified using caffeic acid as standard. This compound is accountable for maintaining colour and protecting this beverage from oxidative deterioration [70]. Several electrochemical sensors with high electrocatalytic activity have been reported to record anodic voltammetric currents related to the two-electron transfer oxidation of caffeic acid to *o*-quinone (Fig. 8), reaching even better LODs than those obtained for gallic acid: from simple and low-cost biochar based CPE ( $E_{pOx}$  at +0.4

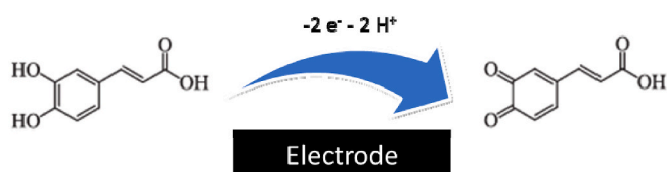


Fig. 8. Scheme of the electrochemical oxidation of caffeic acid [71].

V in phosphate buffer pH 5, LOD of 31 nM [71] or porous carbon material from *Tetrapanax papyriferus* modified GCE ( $E_{pOx}$  at +0.2 V in phosphate buffer pH 6.6, LOD of 5.3 nM [72] to  $Co_3O_4$  modified SPCEs ( $E_{pOx}$  at +0.2 V in phosphate buffer pH 7, LOD of 4.8 nM [17] and modified GCEs by CuONPs ( $E_{ap}$  of +0.32 V in phosphate buffer pH 7, LOD of 40 nM [73], hierarchical mesoporous graphite oxide film ( $E_{ap}$  of +0.3 V in phosphate buffer pH 7, LOD of 4 nM [74] or fluorine-doped graphene oxide ( $E_{pOx}$  at +0.45 V in phosphate buffer pH 2.65, LOD of 1.8 nM [70]. Antioxidant estimation based on caffeic acid oxidation has also been achieved using an arrangement of six carbon fibre ultramicroelectrodes assembled in a glass capillary as working electrode and Ag/AgCl as reference/auxiliary electrode, in absence of supporting electrolyte ( $E_{pOx}$  at +0.5 V, LOD of 410 nM [75]. Higher caffeic acid oxidation peak currents have been reported combining hybrid nanostructures. In this way, GCEs have been modified by  $SnO_2$  decorated graphene ( $E_{pOx}$  at +0.15 V in phosphate buffer pH 7, LOD of 80 nM [76],  $MoS_2$  decorated graphene aerogel ( $E_{pOx}$  at +0.25 V in phosphate buffer pH 6, LOD of 0.3 nM [77], CuO and ZnO/CNTs ( $E_{ap}$  of -0.2 V in phosphate buffer pH 7, LOD of 155 nM [78], CoFeSe<sub>2</sub>/carbon nanofibers ( $E_{pOx}$  at +0.2 V in phosphate buffer pH 7, LOD of 2 nM [79],  $Cu_2O$  supported PdNPs/COOH-MWCNTs ( $E_{pOx}$  at +0.2 V in phosphate buffer pH 2, LOD of 2 nM [80], Ce doped  $TiO_2$ /CNTs ( $E_{pOx}$  at +0.25 V in phosphate buffer pH 6, LOD of 0.3 nM [81], N-doped carbon quantum dots@hexagonal porous  $CuO_2$  decorated CNTs ( $E_{pOx}$  at +0.2 V in phosphate buffer pH 7, LOD of 4 nM [82] flower-like hierarchical graphene/CuO@Cu-1,3,5-Benzene-tricarboxylate ( $E_{pOx}$  at +0.45 V in phosphate buffer pH 4, LOD of 7 nM [83] composites modified GCEs. Polymers have been used as well as surface modifiers to improve the stability of both nanomaterial and electrode. Like this, Chitosan protected carbon black and rGO hybrid layer dropped cast onto GCEs provides currents due to the caffeic acid oxidation at +0.3 V in phosphate buffer pH 3, with a LOD of 0.03 nM [84]. Moreover, the hybridisation of metal oxides with conducting polymers has also been stated to provide mechanical flexibility, thermal stability and enhancement in conductivity. In the case of  $NiWO_4$ NPs on PEDOT-polystyrenesulfonate nanocomposites on SPCEs, a  $E_{pOx}$  at +0.3 V in phosphate buffer pH 7.2 was observed, with a LOD of 74 nM [19]. Enzymatic biosensors, which have been widely studied to determine polyphenols in beverages, have also been used for the assessment of wine polyphenol index and antioxidant capacity, using caffeic acid as reference polyphenol, at PEDOT-Tyrosinase/sonogel-carbon electrodes ( $E_{ap}$  of +0.2 V in phosphate buffer pH 7, LOD of 4.3  $\mu$ M [85] and at Nafion/Lacasse/graphene nanoplatelets and  $MnO_2$ NPs/SPCEs ( $E_{ap}$  of +0.4 V in acetate buffer pH 4.6, LOD of 1.9  $\mu$ M [20].

Nowadays, battery waste is being generated in large quantities due to the high demand for this type of product. The effective reduction of battery waste is therefore desirable worldwide. Zinc-carbon batteries are 100% recyclable, including their graphite rods that possess good electrical conductivity to be used as electrode in cost-effective and environment-friendly electrochemical experiments. In fact, electrochemical sensors based on waste-battery graphite electrodes have already been reported for the analysis of tannic acid in wines ( $E_{ap}$  of +0.38 V, LOD of 3.13 ppb) [86].

*Trans*-resveratrol is a natural polyphenolic compound, whose presence in wines is especially valuable in order to bolster their potential health [23,87,88] electrochemical behaviour in Britton–Robinson buffer solution pH 2.0 on poly(L-lysine) modified GCEs has been investigated. The anodic peak recorded at +0.6 V with this sensing platform led to the effective detection of *trans*-resveratrol in red wines (LOD, 60 nM [90]. Flexible laser-induced porous graphene electrodes ( $E_{pOx}$  at +0.45 V in Britton Robinson buffer pH 5, LOD of 160 nM [89], graphene- $MoS_2$ /SPCEs ( $E_{pOx}$  at +0.15 V in Britton Robinson buffer pH 5, LOD of 450 nM [88] and ordered mesoporous carbon/SPCEs ( $E_{ap}$  of +0.21 V in Britton Robinson buffer pH 5, LOD of 473 nM [23] have been used with this aim as well. In order to improve measuring sensibility, sensors have also been built using molecularly imprinted polymers (MIPs) as

artificial recognition elements, characterized by their simplicity and reusability compare with natural biological receptors [90,91] Polyacrylamide based MIPs have been assembled onto graphene-AuNPs/GCEs, measuring the signals change recorded with potassium hexacyanoferrate (III) as redox probe in absence and presence of resveratrol (LOD, 4.4 nM [90], and onto polyaniline/AuNPs/GCEs ( $E_{pOx}$  at +0.3 V in phosphate buffer pH 4, LOD of 87 nM [91]. Polyaniline films coupled to AuNPs produce sensing interfaces with enhanced electrochemical performance, allowing direct resveratrol assays in wine.

The flavonol quercetin has the already mentioned advantages for human health, but also side effects. In high dose it leads to headaches, kidney cancer, inflammation and DNA structure damage. Therefore, it is important to monitor its concentration in wine. Quercetin shows a weak oxidation peak at +0.3 V (Citrate buffer solution pH 5.6, LOD of 5 nM) and a reduction peak at +0.2 V at both GCE and polysaccharine O/GCE, being the peak intensities remarkably enhanced at the modified electrode [92]. Analogously, electrochemically pretreated SPCEs at +1.2 V for 5 min in a saturated sodium bicarbonate solution have shown a great performance towards the joint detection of quercetin ( $E_{pOx}$  at +0.2 V in phosphate buffer solution pH 7, LOD of 51.6 nM) and the pesticide carbendazim [2]. Rutin and morin have also been analysed in red wines by using PdNP-decorated triazine-urea-based porous organic polymer modified GCEs ( $E_{pOx}$  at +0.4 V in phosphate-buffered saline solution pH 5, LOD of 0.006 nM [93] and Ni(II) phthalocyanine modified CPES ( $E_{pOx}$  at +0.1 V in phosphate-buffer pH 7, LOD of 2 nM [94], respectively.

Enzymatic and non-enzymatic electrochemical sensors (Fig. 9) have correspondingly been described for the quantification of catechol and catechol derivatives in wine. Ag nanowires, acting as electron mediators, incorporated at indium tin oxide (ITO) substrates have been used as platform for the immobilization of tyrosinase ( $E_{pOx}$  at -0.2 V in phosphate buffer pH 7, LOD of 2.7  $\mu$ M [95]. Similar LOD was reached when using non-enzymatic flow injection devices coupled with amperometric detection based on PdNPs-Chitosan ITO modified electrodes ( $E_{ap}$  of +0.4 V in phosphate buffer pH 7, LOD of 8.25  $\mu$ M [96]. MIPs have also been used with this aim by electropolymerization of chitosan onto boron doped diamond electrodes (LOD of 0.7  $\mu$ M [97] and onto AuNPs decorated CNTs cross-linked to boron doped diamond electrodes (LOD of 37  $\mu$ M [98]. Cyclic voltammetric responses of these sensors reveal anodic and cathodic signals corresponding to the oxidation of catechol and reduction of quinone. The LOD in the oxidation range of both MIPs highlights that not always the most complex transducer modification leads to the best results.

New technologies have also been developed to detect simultaneously different phenolic compounds. The antioxidant capacity of wines, with

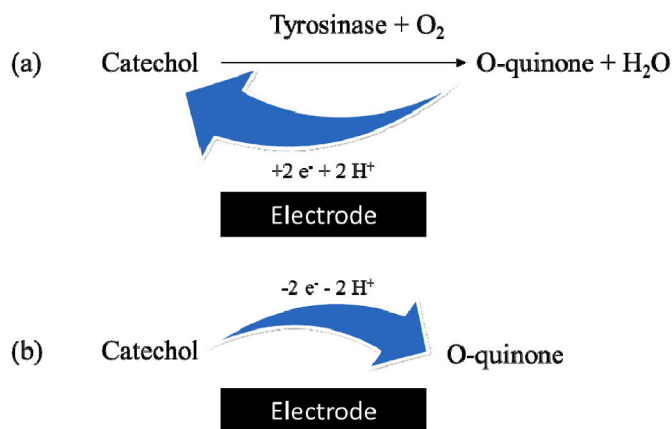


Fig. 9. Scheme of the electrochemical reaction of catechol using (a) enzymatic biosensors [99] and (b) non-enzymatic sensors [96].

caffeic and gallic acid as standards, has been studied using a portable analytical system based on the combination of SPCEs and a 3D-printed structure of microfluidic system ( $E_{ap}$  of +0.3 V in phosphate buffer pH 2, LOD of 0.8 and 1.5  $\mu\text{M}$  for caffeic and gallic acid, respectively) [4]. Standard polyphenols (gallic acid, caffeic acid, catechin and malvidin-3-glucoside) have also been characterized in red wines through the three anodic peaks recorded at CNTs/SPCEs, ascribed to the oxidation of catechol and galloyl groups of polyphenols ( $E_{pOx}$  at +0.13–0.15 V in model wine solution pH 3.6, LOD not shown), malvidin anthocyanins ( $E_{pOx}$  at +0.33–0.37 V in model wine solution pH 3.6, LOD not shown) and flavonoid phenolic groups ( $E_{pOx}$  at +0.58 V in model wine solution pH 3.6, LOD not shown). The total peaks area obtained with this procedure has been used to successfully evaluate the total antioxidant capacity of different wine samples [21]. In the same way, the electro-sensitive determination of rutin ( $E_{pOx}$  at +0.38 V in acetate buffer solution pH 4.8, LOD of 80 nM), sinapic acid ( $E_{pOx}$  at +0.42 V in acetate buffer solution pH 4.8, LOD of 220 nM) and syringic acid ( $E_{pOx}$  at +0.58 V in acetate buffer solution pH 4.8, LOD of 260 nM) in red and white wines has been attempted at CPEs modified with  $\text{Fe}_3\text{O}_4$  NPs [99]. Multisensors systems, based on the combination of an array of four CPEs, three of them modified by metal oxide NPs ( $\text{CeO}_2$ , NiO, and  $\text{TiO}_2$ ), with a multivariate data software, have also been described to monitor phenolic ripening, providing responses toward caffeic acid, vanillic acid, catechol and pyrogallol present in wines ( $E_{pOx}$  between +0.6 and +0.8 V, LOD of 80 nM) [100].

The oxidation of different phenolic compounds, together with chemometric analysis, has also been used to classify wine samples according to their grape variety and maturation process. The voltammetric signals were recorded using a hydrodynamic voltammetric technique with CNTs/polyvinylpyrrolidone-modified GCEs [61], a cyclic voltammetric technique with polypyrrole/SPCEs [22] and a differential pulse technique with iridium electrodes [101].

An array of CPEs made of different forms of carbon (graphite, CNTs and activated biochar) has also been developed as an electronic tongue by using chemometric processing, not only for discrimination, but also for stripping voltammetric determination of catechol, 4-ethylcatechol and 4-ethylguaiacol phenolic compounds in wine samples. The detection of ethylphenols in foods and drinks is extremely important since they can be related with undesired aromas and flavours, becoming a problem when the content exceeds the value of 0.50  $\text{mgL}^{-1}$ , the lower limit detected by the human gustatory system [102]. Sensors modified with MIPs tailor-made for 4-ethylphenol and 4-ethylguaiacol, as specific bio-recognition elements, have also been incorporated into voltammetric arrays. The specific polymers were synthesized using co-polymerization standard protocols and immobilized onto the surface of a graphite epoxy composite electrode via a sol-gel membrane. Their combination with Artificial Neural Networks able to quantify these

4-ethylphenols even in presence of different polyphenolic compounds present in wine, such as gallic acid or quercetin, even though their analogue chemical structure [103]. Different methodologies have been reported for the preparation of MIPs, being electropolymerization highly advantageous considering its easy preparation and control of film thickness and morphology. Polypyrrole tailor-made for 4-ethylphenol have been built onto GCEs (Fig. 10) for the differential pulse voltammetric determination of this compound in wines ( $E_{pOx}$  at +0.6 V in Britton Robinson buffer pH 6, LOD of 24  $\mu\text{gL}^{-1}$ ) [104].

4-ethylphenol and 4-ethylguaiacol are characterized by their volatility, which facilitates their determination in gas phase improving the sensitivity of the sensors, since the number of interfering species in this phase is reduced. Both 4-ethylcompounds have been determined using activated fullerene  $\text{C}_{60}$  modified SPCEs, which has shown to be a high electroactive material with good conductivity, by a two-step procedure: the sensors were first placed at the headspace of a sealed cell to let the analyte be accumulated at the working electrode and next, the supporting electrolyte solution was dropped onto the incubated sensors to carry out the corresponding differential pulse voltammograms. The direct contact between the electrochemical device and the wine sample is thus avoided, which is very advantageous in order not to alter the product [24,25]. In this way, 4-ethylphenol ( $E_{pOx}$  at +0.15 V in Britton Robinson buffer pH 5.8, incubation time of 360 s at 54 °C, LOD of 400  $\mu\text{gL}^{-1}$ ) [24] and 4-ethylguaiacol ( $E_{pOx}$  at +0.45 V in Britton Robinson buffer pH 2.3, incubation time of 360 s at 70 °C, LOD of 200  $\mu\text{gL}^{-1}$ ) [25] have successfully been quantified in wine samples.

## 2.6. SULPHUR COMPOUNDS

Winemaking is a very complex process that requires the addition of several substances to achieve high quality products and to prevent undesirable effects, such as oxidation or browning. Among them, sulphur dioxide ( $\text{SO}_2$ ) is generally used due to its important antioxidant, anti-septic and preservative characteristics that prevent microbial reactions. However, the presence of high concentrations of  $\text{SO}_2$  have been related to the appearance of allergic effects with asthmatic and anaphylactic episodes in some individuals, so the content of this compound in wine is limited by law and, therefore, its analysis is mandatory. In wine,  $\text{SO}_2$  is present in three forms including molecular ( $\text{SO}_2$ ) and its ionized forms, hydrogen sulphite ( $\text{HSO}_3^-$ ) and sulphite ( $\text{SO}_3^{2-}$ ) ions, being the ionization process affected by temperature, pH and alcohol concentration of the wine sample [26,27,105]. Different accurate and sensitive electrochemical sensors have lately been developed for the determination of the molecular and the sulphite forms.

$\text{SO}_2$  can be extracted from wine samples using core/shell CdS/ $\text{SiO}_2$  NPs absorbents. The decrease of the intensity of the peak potential obtained at -0.775 V, in a 1 M KCl solution using a platinum rod electrode

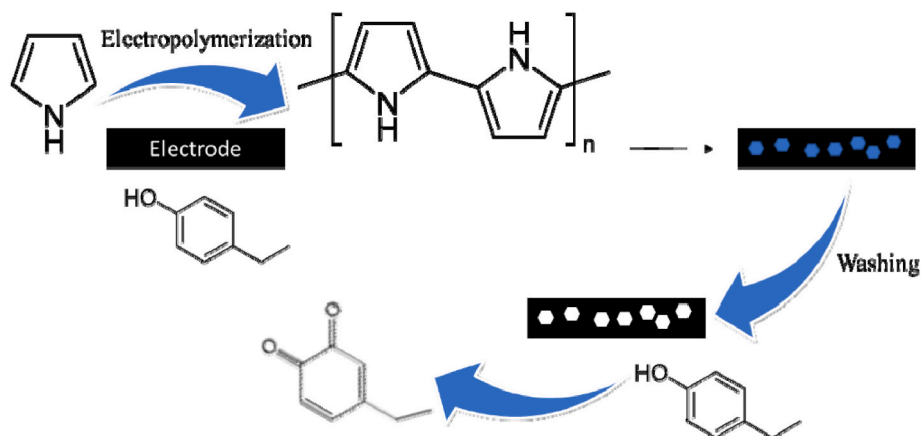


Fig. 10. Scheme of the electrochemical detection of 4-ethylphenol using MIP-based sensors [104].



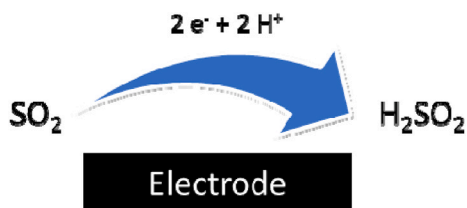


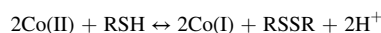
Fig. 11. Scheme of the electrochemical reduction of  $\text{SO}_2$  [26].

by means of cyclic voltammetry, has been used for the study of the efficiency of the elimination of  $\text{SO}_2$  from wine samples [105]. Moreover, free  $\text{SO}_2$  content in wine has also been detected following the reduction of this compound under acidic conditions using different electrodes (Fig. 11) [26,28]. In this way, a novel 3D electrochemical cell has specifically been designed for the amperometric determination of free  $\text{SO}_2$  in complex wine samples, based on the integration of a SPCE electrochemical system coupled with a porous oxygen filter, constructed with several layers of platinum mesh. The use of this oxygen filter allowed to separate the amperometric signals of oxygen and  $\text{SO}_2$  obtained in up to 27 different acidized wine samples ( $E_{\text{ap}}$  of  $-0.65$  V in HCl pH 1.6, Limit of quantification of  $7.5 \text{ mg L}^{-1}$ ) [26]. A higher sensitivity was obtained when using a planar gold sensor chip modified with polyaniline for the analysis of  $\text{SO}_2$  [27]. The developed sensor was based on the interaction between PANI and  $\text{SO}_2$ , which results in the reduction of PANI. The successive oxidation of this molecule at the electrode generates a response associated with the analyte concentration. The polyaniline coating has proven to be an excellent electrocatalytic membrane to the direct analysis of  $\text{SO}_2$  in small volumes of wine samples by cyclic voltammetry ( $E_{\text{pOx}}$  at  $+0.4$  V, LOD of  $6 \mu\text{g L}^{-1}$ ), obtaining fast, simple, precise and inexpensive results [27]. The reduction of  $\text{SO}_2$  can also be followed using a gas sensor based on the construction of a gas chamber, containing a screen-printed graphene electrode covered with a Teflon gas diffusion membrane. After filling the chamber with the wine sample, the system is completely covered with a paper-based microfluidic cap. Then an acid reagent is deposited on top of the microfluidic system, which drops it in a reproducibly way into the chamber with the wine sample. The generated  $\text{SO}_2$  gas diffuses then through the Teflon membrane and is detected by giving a selective cathodic signal by square wave voltammetry ( $E_{\text{pRed}}$  at  $-0.78$  V, LOD of  $1.5 \text{ mg L}^{-1}$ ). The sensor resulted poorly sensitive but, highly selective as it has been above-mentioned, since gas sensors reduce the risk of interference [28].

The electrochemical oxidation of the  $\text{SO}_3^{2-}$  ions present in wine to  $\text{SO}_4^{2-}$  can be followed using different electrochemical systems. Among then, GCEs have been recently used as the electrochemical platform for the deposition of different nanomaterials with high electrocatalytic properties [106–108] this way, Cu-based metal oxide NPs ( $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  and  $\text{CuNa}_2(\text{OH})_4$ ) have been synthesized by a simple one-step chemical method and deposited on the working electrode surface, being CuO/GCEs those that generated a greater oxidation current in the determination of  $\text{SO}_3^{2-}$  by means of differential pulse voltammetry ( $E_{\text{pOx}}$  at  $+0.47$  V in phosphate buffer solution pH 7.0, LOD of  $1.42 \mu\text{M}$ ) [106]. Higher sensitivity was obtained by modifying the working electrode with a hybrid nanomaterial consisted of  $\text{LaFeO}_3$  and graphene. The incorporation of  $\text{LaFeO}_3$  resulted in a substantial increase in the conductivity and stability of the sensor since it avoided the graphene aggregation, giving a sensor with a better performance ( $E_{\text{pOx}}$  at  $+0.6$  V in phosphate buffer solution pH 7.0, LOD of  $0.21 \mu\text{M}$ ) [107]. Better LOD has even been achieved with a sensor based on a GCE modified with carbon coated- $\text{NiCo}_2\text{O}_4$  ( $\text{C@NiCo}_2\text{O}_4$ ) nanoflowers. The  $\text{C@NiCo}_2\text{O}_4/\text{GCEs}$  showed higher electrocatalytic activity than the  $\text{NiCo}_2\text{O}_4/\text{GCEs}$  due to the supplementary electrical conductivity given by the carbon coating, which also resulted in an increase of the accessible surface area for the sensitive oxidation of the analyte by amperometry ( $E_{\text{ap}}$  of  $+0.42$  V in  $0.1$  M KCl solution, LOD  $0.05 \mu\text{M}$ ) [108].

Among the sensors developed for the analysis of sulphite, it is worth mentioning those that have been used in the determination of this compound in the presence of other species such as ferulic acid, ascorbic acid, hydrazine and  $\text{NO}_2^-$  ions. These sensors, based on a CPE, took advantage of the benefits of using nanomaterials to obtain well-defined and separated oxidation peaks for each compound. The incorporation of a  $\text{MgO}/\text{CNTs}$  nanocomposite together with 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide into the carbon paste matrix allows the simultaneous sensitive determination of  $\text{SO}_3^{2-}$  and ferulic acid, antioxidant added to wine samples, by differential pulse voltammetry ( $E_{\text{pOx}}$  between  $0$  V and  $+1.5$  V in phosphate buffer solution pH 4.5, LOD (ferulic acid) of  $3 \text{ nM}$  and LOD ( $\text{SO}_3^{2-}$ ) of  $50 \text{ nM}$ ) [109]. The joint determination of  $\text{SO}_3^{2-}$  ions ( $E_{\text{pOx}}$  at  $+0.35$  V in acetate buffer solution pH 5.0, LOD of  $0.58 \mu\text{M}$ ) and the common interferent ascorbic acid ( $E_{\text{pOx}}$  at  $+0.9$  V in acetate buffer solution pH 5.0, LOD not shown) has been described as well using a CPE modified by a metal-organic framework based on chromium-terephthalate. Due to the increase in porosity and surface area that this excellent mediator confers to the sensor, an enhanced analytical oxidation response of  $\text{SO}_3^{2-}$  ions has been obtained by square wave voltammetry [110]. Moreover, a nanoporous gold microelectrode that does not require the use of any type of mediator or added modification, has achieved enough sensitivity and selectivity for the analysis of  $\text{SO}_3^{2-}$  ions in the presence of the pesticide hydrazine and  $\text{NO}_2^-$  ions, often used as antimicrobial agent, by differential pulse voltammetry in commercial beverages, including wine samples. Three well-defined oxidation peaks at  $+0.03$  V (LOD of  $0.91 \mu\text{M}$ ),  $+0.3$  V (LOD of  $0.34 \mu\text{M}$ ) and  $+0.72$  V (LOD of  $1.44 \mu\text{M}$ ) for hydrazine,  $\text{SO}_3^{2-}$ , and  $\text{NO}_2^-$ , have been found in phosphate buffer solution pH 6.5, respectively [29].

Electrochemical sensors have also been reported to point out the presence of traces amounts of mercaptans in wines. Although this fact is only due to a small anomaly in the biochemistry of fermentation, the sensory impact of mercaptans is notable and detrimental, since it can alter the aroma of bottled wines. Taking into account the strong covalent bond that is easily formed between the sulphur and gold atoms, the analysis of ethanethiol, representing volatile mercaptans, has been approached using AuNPs modified GCEs ( $E_{\text{pRed}}$  at  $+0.1$  V in Britton Robinson buffer pH 4.2, LOD of  $3.3 \mu\text{g L}^{-1}$ ) and AuNPs modified SPCEs ( $E_{\text{pRed}}$  at  $+0.3$  V in Britton Robinson buffer pH 3, LOD of  $1.6 \mu\text{g L}^{-1}$ ) in different white and red wines by differential pulse voltammetry [30]. In order to improve even more the selectivity of this type of sensors, GCEs have been modified not only with AuNPs but also with electro-synthesized molecularly imprinted polypyrrole for the quantification of ethanethiol in wines ( $E_{\text{pOx}}$  at  $+0.6$  V in Britton Robinson buffer pH 2, LOD of  $7.2 \text{ mg L}^{-1}$ ) [111]. Undoubtedly, headspace measurements of ethanethiol would contribute to the reduction of interferences in wine matrices, since only volatile analytes reach the working electrode, and the wine sample is not altered as it has previously been mentioned. A procedure based on the reaction of thiols and Co(II) has been developed for the quantification of these compounds, being an oxidation current registered at the working electrode,



In this case, the whole measurement procedure has been carried out in gas phase: the supporting electrolyte pH 2.6 was pre-loaded onto a cobalt phthalocyanine modified SPCE by a procedure as simple as adsorption. Then, amperometric measurements were recorded at the headspace of sealed cell applying a constant potential of  $+0.8$  V, under stirring conditions (LOD of  $12.5 \mu\text{g L}^{-1}$ ) [31].

## 2.7. BIOGENIC AMINES

Biogenic amines appear in wine as a result of the decarboxylation of amino acids or by the amination of aldehydes and ketones during the

fermentation and aging stages. A high concentration of these compounds in wine not only produces a decrease in the quality of the product, but can also have harmful effects on the health of the consumer due to its toxicological potential [112]. Therefore, knowledge of the content of biogenic amines in wine is of the utmost importance.

Histamine, which is the most common biogenic amine present in wine, has been related to pathological processes that include headache or hypotension. The analysis of this compound has been performed using highly sensitive sensors based on the combination of the analytical properties of graphene nanoribbons and AuNPs deposited on an edge plane of pyrolytic graphite electrode. The analysis in wine was carried out following the oxidation signal obtained by means of square wave voltammetry ( $E_{pOx}$  at +0.94 V in phosphate buffer solution pH 7.2, LOD of 49 nM) [113]. In the same way, less sensitive, but highly selective electrodes towards histamine, have been developed based on the modification of different working electrodes with MIPs. Thus, differential pulse voltammetric measurements of histamine were performed using graphite epoxy composite electrodes modified with MIP bead particles, generated by combining methacrylic acid, ethylene dimethacrylate and 2,2'-azobis(2,4-dimethylvaleronitrile) ( $E_{pOx}$  at +1.1 V in phosphate buffer solution pH 7.0, LOD of 1.7  $\mu$ M) [114]. A simpler and more sensitive MIP based sensor has also been developed for an outstanding analysis of histamine even in the presence of other structural analogues. In this case, a GCE was previously modified with AuNPs on which the MIP was electrochemically generated using *p*-amino-benzene sulfonic acid as the functional monomer. The developed sensor resulted also highly stable in comparison with biological receptors-based sensors, giving an oxidation signal by differential pulse voltammetry ( $E_{pOx}$  at +1.3 V in phosphate buffer solution pH 5.5, LOD of 0.6  $\mu$ M) [115].

An increase in the toxicity of histamine due to the presence of tryptamine by inhibiting histamine-detoxifying enzymes has been described. Thus, the simultaneous determination of both biogenic amines is mandatory to evaluate the quality of a wine sample and avoid intoxication problems. This analysis has been recently performed using a CPE modified with nickel phthalocyanine, which may be considered as an excellent electrocatalyst material producing a significantly increase in the oxidant peak current obtained by square wave voltammetry for both amines (Histamine- $E_{pOx}$  at +1.0 and Tryptamine- $E_{pOx}$  at + 0.75 V in phosphate buffer solution pH 8.5, Histamine-LOD of 0.168 ng mL<sup>-1</sup>, Tryptamine-LOD of 0.038  $\mu$ g mL<sup>-1</sup>) [112].

Tyramine, which comes up from the decarboxylation of tyrosine, is another electroactive biogenic amine frequently found in wine associated with diverse health problems, including severe migraines. An enzymatic sensor has recently been described for the analysis of this compound by differential pulse voltammetry in wine based on the immobilization of the enzyme tyrosinase on a carbon graphite lead previously modified with electropolymerized 4-mercaptophenylacetic acid ( $E_{pOx}$  at +0.15 V in phosphate buffer solution pH 7.2, LOD of 3.16  $\mu$ M) [116]. A much simpler and even more sensitive method has been developed for the fast analysis of tyramine in wine, which implies the use of non-modified pencil carbon graphite electrodes. Two different electrochemical techniques, differential pulse and square wave voltammetry, were applied for the measurement of tyramine oxidation at +0.64 V in phosphate buffer solution pH 7.4, obtaining a similar good LOD value for both techniques: 0.5  $\mu$ M for DPV and, 0.6  $\mu$ M for SWV [117].

## 2.8. MYCOTOXINS

Aflatoxins, produced by some moulds, are mycotoxins often present in wine due to grape contamination. These compounds are considered highly harmful, being aflatoxin B1 type the most toxic and carcinogenic species [118]. An important number of electrochemical sensors have been developed for its determination, being immunosensors often selected mainly owing to their specificity, but also to their good efficacy

and sensitivity. Thus, a carbon felt electrode coated with a PdNPs-boron nitride film has been developed for the incorporation of an anti-aflatoxin B1 antibody, giving rise to a very sensitive immunosensor (LOD of 2.7 nM). The analytical signal used was the electrochemical response obtained by cyclic voltammetry for ferricyanide, which intensity decreases in the presence of the target analyte due to the formation of the antibody-aflatoxin B1 complex and, the high sensitivity was explained by the improvement of the specific surface area of the sensor by PdNPs [118].

Despite the great sensitivity and selectivity obtained with immunosensors, they have some drawbacks related to the tedious production, cost, and stability of antibodies. Thus, the use of aptamers (synthetic oligonucleotides), which can overcome these limitations, has attracted growing [119–122]. In this way, competitive analytical sensors, based on the hybridization process between aptamers and complementary DNA strands, have been developed for the analysis of aflatoxin B1. Most of these sensors are based on the use of gold electrodes, where thiolated aptamers or DNA strands are immobilized through the well-known gold-sulphur chemistry. The analytical signal is achieved by means of a redox tag attached to one end of the aptamer, being methylene blue often selected as redox label in the determination of aflatoxin B1 in wine samples (Fig. 12). The presence of the target analyte prevents the binding of the methylene blue labelled-aptamer with the DNA strand, producing a change in the square wave voltammetric electrochemical response of redox probe [119,120]. The modification process selected in the generation of this type of competitive sensors does not affect the sensitivity of the analytical method, since similar results have been obtained for sensors in which the aptamer was immobilized on the electrode surface [119], as for sensors in which the immobilized species was the DNA strand [120] ( $E_{pRed}$  at -0.25 V in phosphate buffer solution pH 7.5 containing 20 mM MgCl<sub>2</sub>, LOD of 2.0 nM).

Better sensitivity values have been obtained when using a reagent-less aptamer-based sensor that does not require the addition of DNA strands and, therefore, neither competition binding steps. Methylene blue was also used as the redox tag, which in the absence of aflatoxin B1 displays a slow electron transfer efficacy related to its position away from the electrode surface. However, the presence of the analyte produces a change in the conformation of the aptamer, bringing methylene blue closer to the electrode and increasing the electron transfer rate, thus generating the analytical response by means of square wave voltammetry ( $E_{pRed}$  of -0.25 V in 10 mM Tris-HCl buffer solution pH 7.5 containing 20 mM MgCl<sub>2</sub>, LOD of 6.0 pM). The non-competitive sensor not only showed higher sensitivity but also presented important advantages related to the easy fabrication procedure and fast response, as well as a high regeneration efficiency [121]. This high sensitivity has even been increased by means of more complex aptasensors based on the immobilization of carboxylated polystyrene nanospheres together with an aptamer and the enzyme horseradish peroxidase on a carbon nanofiber/carbon felt electrode. The obtained electrochemical biosensor had an excellent performance by means of differential pulse voltammetry, due to the exceptional structures as well as their synergistic effects, giving an enhanced electrochemical response based on the previous oxidation of hydrogen peroxide catalysed by the enzyme ( $E_{pRed}$  at -0.35 V in phosphate buffer solution pH 7.4, LOD of 0.05 pM) [122].

Ochratoxin A has also been classified as a possible human carcinogen, having severe toxic effects, including hepatotoxicity, carcinogenicity and nephrotoxicity. This compound is widely found in cereals as well as in drinks, including wine, and being, subsequently, its rapid detection at trace levels of high importance for human health [123,124]. Numerous electrochemical sensors, mostly based on the use of selective aptamers, have been then described with this aim. Thus, a very sensitive sensor has been constructed based on the co-immobilization of a DNA strand and an ochratoxin-aptamer on a gold electrode surface. The presence of ochratoxin A releases the DNA strand, which reacts with the graphite-like carbon nitride nanosheets incorporated to the electrochemical cell giving rise to a mimetic enzyme complex that catalyses

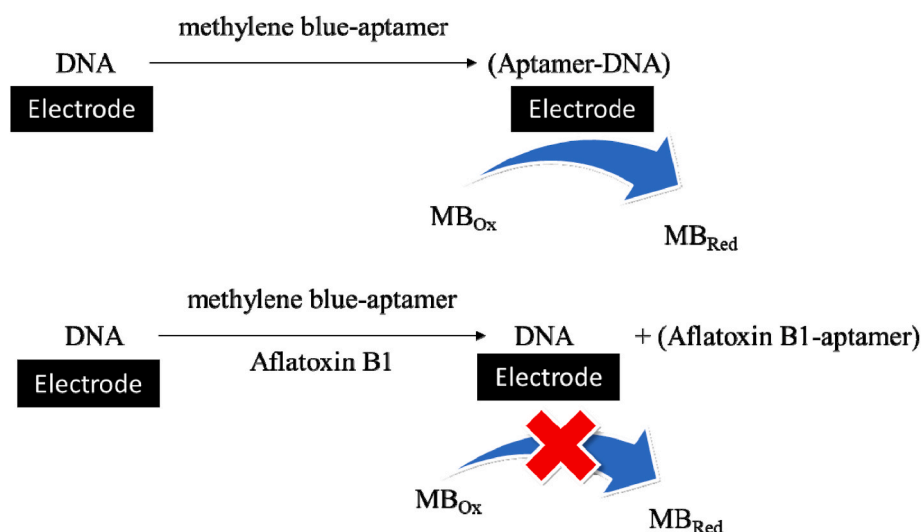


Fig. 12. Schematic diagram of the electrochemical signal obtained for aflatoxin B1 detection using an aptamer-based sensor and methylene blue as the redox probe [119,120]. [119,120]. (For interpretation of the references to colour/colour in this figure legend, the reader is referred to the Web version of this article.)

the oxidation of  $\text{H}_2\text{O}_2$  also present in the cell solution (Fig. 13). The generated current is finally followed by means of cyclic voltammetry ( $E_{\text{pOx}}$  at  $-0.8$  V in phosphate buffer solution pH 7.4 containing 10 mM  $\text{H}_2\text{O}_2$ , LOD of 0.073 nM) [123]. Similar, but more sensitive sensors, based on gold working electrodes have been developed, using ferricyanide [124] or AgPt bimetallic NPs decorated iron-porphyrinic metal-organic framework complexing systems as redox probes [125]. In the first case, in the presence of the analyte, the ochratoxin-aptamer interacts forming a complex that separates from the electrode surface, leaving free space for ferricyanide to approach the electrode and generate the sensitive analytical response by differential pulse voltammetry ( $E_{\text{pOx}}$  at  $+0.18$  V in a 4 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and 0.1 M KCl solution, LOD of 5 pM) [124]. The same mechanism is used by the sensor based on bimetallic systems, following by differential pulse voltammetry the decrease of the oxygen electrochemical reduction due to the presence of the analyte ( $E_{\text{pRed}}$  at  $-0.22$  V in phosphate buffer solution pH 6.0, LOD of 0.03 pM) [125]. Several other approaches have been developed to increase sensitivity of different aptasensors by means of the modification of the electrode with nanomaterials. The presence of the nanomaterial enhances, on one hand, the surface area of the electrode for loading more aptamer molecules so as to reinforce its binding to the target analyte, and on the other hand, elevates the conductivity, increasing the electrical signal induced by the aptamer-ochratoxin interaction. Thus,

graphene has been selected as an interesting nanomaterial for the generation of sensitive aptasensors based on different modified electrodes, including GCEs [126] and ITO electrodes [127]. In this sense, a very sensitive sensor has been obtained by means of the modification of a GCE with carboxylate graphene to anchor aptamer/ $\text{NH}_2$  Janus particles, generated by the incorporation of thiolated-ochratoxin aptamer on a gold layer deposited on aminopolystyrene microspheres. In this case, the interaction aptamer-analyte was analysed by differential pulse voltammetry, also following the decrease of the peak current value of the redox probe ferricyanide ( $E_{\text{pRed}}$  at  $+0.24$  V in phosphate buffer solution pH 7 containing 10 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , LOD of 3.3 fM) [126]. Graphene has also been used to increase the surface area of ITO electrodes using ferricyanide as the redox probe as well and, being the sensitivity of the sensor enhanced by the incorporation of chitosan. The presence of chitosan effectively increases the number of active sites for immobilization of aptamer molecules explained by the high sensitivity obtained by differential pulse voltammetry ( $E_{\text{pOx}}$  at  $+0.3$  V in phosphate buffer solution pH 7.5 containing a 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , LOD of 2.5 fM) [127]. The high sensitivity achieved by the above-described aptasensors can even be increased by using AuNPs-based nanomaterials for the modification of GCEs. Thus, an ultrasensitive aptasensor has been described based on the incorporation of AuNPs@metal carbides and nitrides together with thiol-labelled tetrahedral DNA nanostructures on a GCE

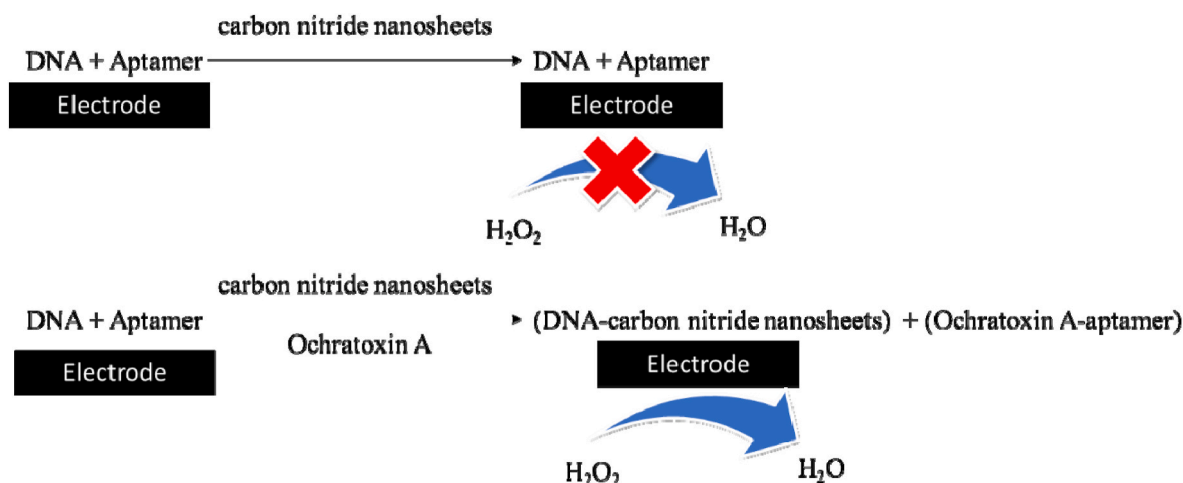


Fig. 13. Schematic diagram of the electrochemical signal obtained for ochratoxin A detection using an aptamer-based sensor [123].

surface. The analytical response of the sensor was obtained by adding DNA strands labelled with AuNPs modified cobalt metal-organic frameworks, used as the electrochemical signal probe. Moreover, toluidine blue was also added to the electrochemical cell and used as an internal reference tag. Thus, in the presence of ochratoxin A, the cobalt metal-organic frameworks signal decreased, while toluidine blue response increased, using the current ratio value between both signals for ochratoxin A detection in Tris-HCl solution pH 7 containing 50 mM MgCl<sub>2</sub> (LOD of 0.8 fM) [128]. A simpler but less sensitive aptasensor based on AuNPs nanomaterials has been developed by means of the modification of GCEs with poly 3,4-ethoxyethylene dioxy thiophene-AuNPs nanocomposites. The modified electrode was then covered with an ochratoxin-aptamer, using a DNA strand jointly decorated with PtPd nanoalloys and toluidine as the signal probe. The presence of ochratoxin A changes the aptamer configuration allowing the approach of the modified DNA strand to the electrode surface, leading to a high oxidation current obtained by the reaction of toluidine and H<sub>2</sub>O<sub>2</sub> in a Tris-HCl solution pH 7 containing 3 mM H<sub>2</sub>O<sub>2</sub> (LOD of 0.12 pM) [129]. A similar aptasensor has been described based on the incorporation of the above described AuNPs nanocomposites but using this time a GCE modified with graphene oxide and ferricyanide as the redox probe. The sensitivity obtained by this sensor, although very high ( $E_{pOx}$  at +0.3 V in phosphate buffer solution pH 6.8 containing a 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.2 M KCl, LOD of 12.1 pM), failed to exceed that of other aptamers described above [130].

Finally, the simultaneous determination of aflatoxin B1 and ochratoxin A has been performed using a paper-based dual working electrode system fabricated by screen-printing. Both carbon working electrodes were first modified with black phosphorus-gold nanocomposites, being each mycotoxin-specific aptamer subsequently immobilized on one of the working electrodes. In the presence of the target mycotoxins, the aptamers could bind with their specific mycotoxin, resulting in a decrease in the peak current, associated to the redox probe ferricyanide, obtained by differential pulse voltammetry ( $E_{pRed}$  at +0.15 V in 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 M KCl, LOD of 96.6 pM (ochratoxin A) and 73.7 pM (aflatoxin B1) [131].

## 2.9. ALLERGENS

Fining agents composed of milk or egg proteins are often used in wine production, so the determination of any residue of these compounds is extremely important in order to avoid allergic effects, considering the large number of people affected by food allergies caused mainly by these proteins [132]. Ovalbumin is a typical glycoprotein related to allergic reactions in hypersensitive individuals, which has been recently analysed using electrochemical sensors based on MIPs to obtain not only high sensitivity, but also high selectivity [32,133]. A MIP, based on the electropolymerization of polydopamine using ovalbumin as the template molecule, was synthesized on a SPCE, previously modified with AuNPs that enhanced the electrical conductivity of the polydopamine/SPCE. The analysis of ovalbumin was finally performed by differential pulse voltammetry, after template removal, using a 5 mM K<sub>3</sub>Fe(CN)<sub>6</sub> solution as the analytical probe, obtaining high sensitivity (LOD of 0.46 mg L<sup>-1</sup>) and good selectivity considering other proteins [32]. A more complex but much higher sensitive MIP structure has been developed for the analysis of ovalbumin using GCEs modified with polydopamine as well, but this time the polymer was generated on boronic acid-functionalized magnetic NPs for the final immobilization on the electrode surface. The incorporation of nanomaterials to the MIP generation clearly produces an ultrasensitive sensor for the differential pulse voltammetric analysis of ovalbumin (LOD of 3.0 fg L<sup>-1</sup>) [133].

Lysozyme has been classified as another allergic molecule that can cause even serious kidney problems and, whose presence in wine is due to its use as antiseptic, replacing [33,134] Different sensors have been

then used for the analysis of this compound in wine based on cyclic voltammetric [33], differential pulse voltammetric [34] and electrochemical impedance spectroscopic measurements [35,134] Cyclic voltammetric measurements were performed with an aptasensor consisted of an aptamer immobilized on AuNPs/SPAuEs transducers for the analysis of the decrease in the signal obtained for ferricyanide in phosphate buffer solution pH 7.4, after an incubation period with the analyte. The surface modification with AuNPs resulted highly important to achieve a considerably enhance in sensitivity due to the increase produced in the electroactive area and in the amount of immobilized aptamer (LOD of 0.32 mg L<sup>-1</sup>) [33]. Gold nanostructures have also been used in the development of an aptasensor based on a SPCE modified by means of the electropolymerization of poly-L-lysine. A lysozyme aptamer was, in this case, immobilized on the electrode surface and a sandwich-structured based on a biotin modified aptamer and streptavidin alkaline phosphatase was used for the analytical detection of lysozyme following the oxidation of naphthol by differential pulse voltammetry (Fig. 14) [34]. The combination of the polymer film and gold nanostructures demonstrated a higher catalytic effect generating a very sensitive sensor for the also selective analysis of lysozyme in wine samples (LOD of 2 pM).

Electrochemical impedance spectroscopy has demonstrated a high sensitivity recording small changes occurring in near proximity of the electrode surface through interaction between biomolecules [35]. In this way, an aptasensor has also been developed for the determination of lysozyme based on the immobilization of an aptamer on a graphite-epoxy composite electrode using again the couple [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> as redox probe (LOD of 1.67 μM) [134]. Although aptamers are often used as recognition elements, they are extremely vulnerable to external environments, including changes in pH and temperature conditions. Thus, the use of protofibril as an active material emerges as an interesting alternative in the development of electrochemical impedance spectroscopy-based sensors, since they are highly stable even in a huge range of pH and temperature conditions. Hence, high sensitivity was obtained in the analysis of lysozyme when using a protofibril and graphene oxide modified SPCE (LOD of 1 nM) [35].

## 2.10. FOOD PRESERVATIVES

In addition to the preservatives already described, such as sulphur compounds, other compounds with antifungal [135] and antioxidant [136] activities are often used in winemaking that help to preserve the final product. Among them, natamycin, a natural antifungal, is used as a food preservative in wine. However, if it is consumed in excess, it can be detrimental to health by neutralizing the action of certain antibodies, being its rapid and sensitive determination necessary [135]. The electrochemical determination of this compound presents a low sensitivity when using conventional unmodified electrodes due to its slow direct electron transfer. Therefore, different nanomaterials have been used for lowering the LOD. Among them, three-dimensional graphene oxide-CNTs have been employed for the modification of a GCE ( $E_{pRed}$  at +0.95 V in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, LOD of 0.1 nM), giving rise to a very sensitive sensor for the analysis of natamycin by linear sweep adsorptive stripping voltammetry, achieving a wider linear concentration range and a lower LOD than in previous described works. A nanomaterial based GCE has also been used in the analysis of the additive *tert*-butylhydroquinone, which presents antioxidant properties preventing wine from spoiling. Thus, a composite consisting of AuNPs decorated on tungsten carbide was deposited on a GCE for the development of an electrochemical sensor. The method resulted very simple, due to the easy ultrasonicated generation of the nanocomposite, and sensitive due to the low LOD obtained by square wave voltammetric measurements ( $E_{pRed}$  at 0 V in phosphate buffer solution pH 7.0, LOD of 0.2 nM) [136].



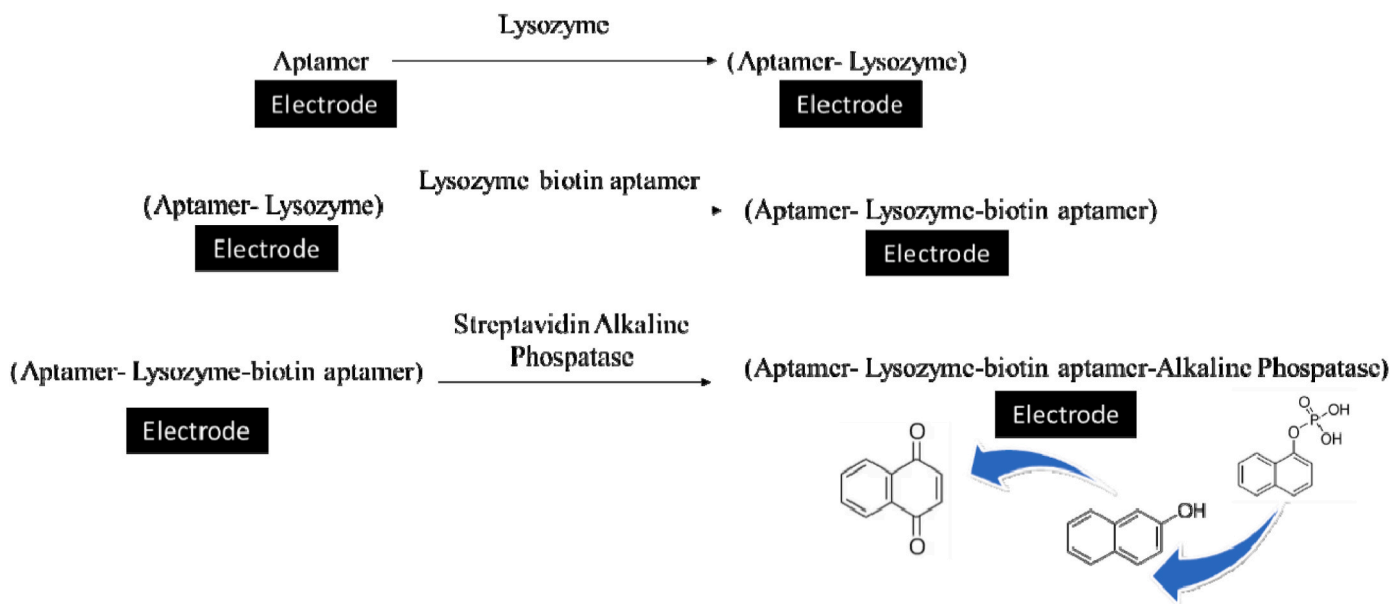


Fig. 14. Schematic diagram of the electrochemical signal obtained for lysozyme detection using an aptamer-based sensor [34].

### 2.11. YEAST

Several microorganisms, such as yeasts, are involved in wine production process, which achieve the transformation of must through complex fermentation stages. In addition, certain microorganisms are also involved in wine spoilage, which generate significant economic losses for wineries due, generally, to the modification of wine organoleptic properties. The analysis of these microbial species is therefore important to ensure not only an effective production process, but also the good quality of the final product [36–38]. *Saccharomyces cerevisiae* is the main species involved in wine production due to its capability to reach a complete fermentation of different sugars. Yet, this microorganism should be accurately removed after fermentation process to avoid uncontrolled re-fermentation stages, producing modification of the chemical composition of wine. Recently, an amperometric immunosensor has been developed for this yeast analysis based on the modification of SPCEs with graphene oxide functionalized with propionic acid [36]. These modified electrodes were finally covered with a polyclonal antibody, generating the specific analytical platform using a concanavalin A-peroxidase conjugate as the recognizing element ( $E_{ap}$  of  $-0.2$  V in phosphate buffer solution pH 7.2, containing 0.9 mM hydroquinone and 0.5 mM  $H_2O_2$ , LOD of 4 CFU  $mL^{-1}$ ). A similar procedure has been described for the analysis of *Brettanomyces bruxellensis*, another yeast often involved in wine spoilage due to its negative impact on wine aroma related to generation of phenolic compounds [37]. The analysis of this yeast was based on a capture process performed by core-shell  $Fe_3O_4@SiO_2$  superparamagnetic NPs modified with anti-*Brettanomyces bruxellensis* specific antibodies and also functionalized with a concanavalin A-peroxidase conjugate. The described captors were finally magnetically immobilized on a SPCE and the analysis of the yeast was performed by amperometry ( $E_{ap}$  of  $-0.2$  V in phosphate buffer solution pH 6.0, containing 1 mM hydroquinone and 0.5 mM  $H_2O_2$ , LOD of 8 CFU  $mL^{-1}$ ). Electrochemical sensors have also been developed for the analysis of the necrotrophic fungus *Botrytis cinerea*, which has been described as an undesirable bacterium responsible of significant economic losses in vineyards. The detection of this microorganism has been performed through the determination of one of its metabolites, laccase enzyme, using carbon fibres microelectrodes. The presence of this enzyme was detected following the evolution of the oxidation and reduction peaks of 2,20-azino-bis(3-ethylbenzothiazoline-6-sulfonic) acid, used as the enzyme substrate, by means of cyclic voltammetry.

Although the method was sensitive enough to detect laccase, it was difficult to apply it for measurements in reduced volumes. Thus, carbon fibres microelectrodes were replaced by SPAuEs using amperometry as the analytical tool ( $E_{ap}$  of  $+0$  V in acetate buffer solution pH 4.5 containing 0.4 mM 2,20-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid), LOD of 0.5 U  $mL^{-1}$ ) [38].

### 2.12. PESTICIDES

Pesticides are widely used to control pests in wine agriculture, usually with the aim of achieving increased productivity. A high number of compounds have been used in the vineyard to treat crops or even during different steps of the winemaking process. Most of these compounds are harmful to the environment and, in addition, are classified as toxic agents due to their carcinogenic properties. Besides, they are highly chemically stable, which makes their degradation and elimination from the environment considerably difficult [39,137,138]. Therefore, its control is necessary to guarantee the good quality of the product obtained in wine industry. Among the pesticides recently analysed in wine is carbendazim. The electrochemical analysis of this compound has been performed by adsorptive differential pulse stripping voltammetry using a CPE containing the protic ionic liquid 2-hydroxyethylammonium acetate. The presence of this ionic liquid facilitated the oxidation of the pesticide giving rise to a sensor with good analytical performance ( $E_{pOx}$  at  $+0.8$  V in Britton Robinson buffer pH 6.0, LOD of 1.69 nM) [137]. 2,4,6-Trichlorophenol has also been used in wineries for wood and cork conservation and even in barrels disinfection. Being a very toxic compound related to lung lesions and carcinogenic effects, its determination is of special analytical interest. Thus, different electrochemical sensors have been developed based on the modification of different electrodes with nanomaterials, including a GCE modified with a vanadium selenide/rGO nanocomposite [138] and a SPCE modified with double perovskite oxide  $Gd_2NiMnO_6$  nanostructures [39]. Vanadium selenide/rGO/GCE sensors presented exceptional electroanalytical characteristics and a high feasibility and commercial applicability for the analysis of 2,4,6-trichlorophenol in wine by means of differential pulse voltammetry. An increase of the electrocatalytic performance of the sensor was observed due to the synergistic effect achieved with the combination of vanadium selenide and rGO ( $E_{pOx}$  at  $+0.6$  V in 0.1 M phosphate buffer pH 7.0, LOD of 35.7 nM) [138]. A better sensitivity was obtained for the  $Gd_2NiMnO_6$ /SPCEs, which also showed a better

analytical performance when compared with bare SPCE being able to analyse red wine samples by means of differential pulse measurements ( $E_{pOx}$  at +0.83 V in 50 mM phosphate buffer solution pH 3.0, LOD of 23 nM) [39].

### 2.13. OTHERS

Alcoholic beverages, including wine, have also been considered as important sources of toxic and polluting substances generated as by-products during the fermentation process. Thus, carcinogenic substances, such as ethyl carbamate produced by the natural reaction of urea and ethanol during the fermentation step, have been analysed using different electrochemical sensors. Among them, selective immunosensors have been reported based on a cascade reaction involving the target analyte, alkaline phosphatase, 2-phospho-L-ascorbic acid and the final  $Cu^{2+}/Cu^+$  conversion by square wave voltammetry (LOD of 2.28 nM) [139]. The selectivity achieved with the described immunosensors can also be guaranteed using simpler MIP based electrochemical sensors constructed with  $\beta$ -cyclodextrin derivatives functional monomers [140, 141] obtaining even a better LOD value ( $5.86 \mu g L^{-1}$ ) [140]. Electrochemical impedance spectroscopy has also been selected as an analytical sensitive technique for the analysis of ethyl carbamate in rice wine using a working electrode based on a new carbon allotrope, called GUITAR, modified with Mn(II)O. The developed sensor led to the analysis of the carcinogenic agent jointly its precursors citrulline, urea and arginine obtained in all cases LOD values lower than  $2 ng L^{-1}$  [142].

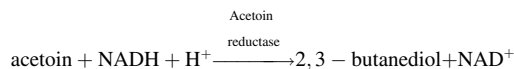
During storage of wine, a varied of contaminants may be incorporated, including plasticizers such as bisphenol A and dibutyl phthalate. These compounds have been classified as hazardous substances, being therefore necessary its sensitive detection. Recently, a GCE based sensor has been developed by means of the deposition of a corncob biochar film by drop casting. This pre-treated electrode was subsequently modified with a MIP using dibutyl phthalate as the template molecule and chitosan as the functional monomer, being the analytical signal registered the intensity of oxidation of the redox probe ferricyanide. The decrease observed in this signal in the presence of analyte by means of differential pulse voltammetry was finally employed for the analysis of rice wine samples with a high selectivity and even a good sensitivity ( $E_{pOx}$  at +0.45 V in phosphate buffer solution pH 7.0 containing 5 mM  $K_3[Fe(CN)_6]$ , LOD of 2.6 nM) [143]. Like this, an ITO electrode has been used for the analysis of bisphenol A in white wine samples by differential pulse voltammetry, as well. The working electrode was covered with an ultrathin polydimethylsiloxane film containing cetyltrimethylammonium bromide micelles, which conferred stability to the electrode preventing it from the characteristic ethanolic environment of wine samples. The sensor also resulted highly sensitive with a LOD of  $0.23 \mu M$  in a phosphate pH 8.0 supporting electrolyte solution [144].

The presence of iron in wine is related to the appearance of turbidity and colour changes due to the ability of this metal to form different compounds with an extensive variety of substances usually present in wine samples. Thus, its analysis in wine is often performed mainly using spectroscopic techniques, but also electrochemical devices including SPCEs modified with deferoxamine. This molecule is able to form very stable complex with iron ions resulting in a very sensitive sensors for the analysis of iron in wine by cyclic voltammetry (LOD of  $0.87 mg L^{-1}$ ), avoiding the pretreatment steps needed by the often used spectroscopic techniques [40].

The tripeptide glutathione is also analysed in wine since, even at low concentration levels, it is able to trap quinones preserving the fruity aroma. Recently, an electrochemical sensor based on the modification of a CPE with N,N'-2-octyloxy-1-methyl-2-oxoethyl)-(-2,4-thiolbutyloxy)-1-methyl-2-oxoethyl)-3,4:9,10-perylene-tetracarboxyldiimide has been described for the analysis of this compound in red wine samples by differential pulse voltammetry with acceptable recovery values. The modification performed improved the conductivity and also allowed the accumulation of the analyte on the electrode surface

increasing the current value of its oxidation peak 4.9 folds ( $E_{pOx}$  at +0.6 V in 50 mM phosphate buffer solution pH 7.5, LOD of  $17 \mu M$ ) [145].

Wine flavour can also be affected by the presence of acetoin which produces a butter-like aroma. This compound is generated in wine as a product of the fermentative process, being also a good indicator of the maturation state of the product. The analysis of acetoin in red wine samples has been performed using a field-effect biosensor based on the immobilization of the enzyme acetoin reductase on the  $Ta_2O_5$  transducer, which detects the changes of the pH value by potentiometry when the enzymatic reaction takes place [146].



### 3. CONCLUSIONS

This review provides a complete overview of the latest developed electrochemical sensors for the analysis of a great number of interesting analytes in wine. Their rapid and early diagnostic has been established as necessary due to, in some cases, their significant effect in the quality of a wine and, in other cases, due to their toxic and harmful health effects. Electrochemical sensors have been shown as an interesting alternative to the more complex and time-consuming techniques, such as chromatography, for this purpose. Different working electrodes have been used in these developments, including 25% approx. of disposable devices, which are undoubtedly orientated towards point-of-care analysis due to their low cost, reduced dimensions and ease of use. The selectivity and sensitivity of the analyses have been achieved by means of different modifications of the working electrode. In this sense, 23% of the developed sensors have been based on the incorporation of bioreceptors highly selective to the analyte of interest, including enzymes, antibodies and aptamers. In fact, very high sensitivities, with LOD values of pM levels, have been achieved when using aptamers together with different nanomaterials for electrode modifications. The remaining 77% of developed sensors have been based on the modification of different electrodes, mostly with nanomaterials, polymers or mixtures of both, with the aim of reaching adequate selectivity and sensitivity values for the analysis of different compounds in a matrix as complex as wine. These non-enzymatic alternatives present advantages related to easier fabrication procedures and a higher stability, avoiding the enzyme degradation limits. In addition, an interesting measurement procedure based on the use of gas sensors sounds lately to improve selectivity. The development of this type of sensors opens new interesting perspectives in wine analysis, improving the selectivity and avoiding direct contact between the sensor and the wine sample, which highlights their potential use in all the stages of wine production. Therefore, an interesting commercial alternative to the more complex and expensive classical analytical methods is offered for *in situ* and on-line applications in wineries.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

### Data availability

No data was used for the research described in the article.

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